Russian Chemical Reviews **79** (11) 945 – 979 (2010) © 2010 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2010v079n11ABEH004114

Modification of carbon nanotubes and synthesis of polymeric composites involving the nanotubes

E R Badamshina, M P Gafurova, Ya I Estrin

Contents

I.	Introduction	945
II.	Modification of carbon nanotubes by low-molecular compounds	946
III.	Modification of carbon nanotubes by polymers. First-group polymeric nanocomposites	957
IV.	Modification of polymers by carbon nanotubes. Polymeric nanocomposites of the second group	963
V.	Conclusion	972

Abstract. The results of studies, mainly published in recent years, on modification of carbon nanotubes and design of composites with these nanotubes for the manufacture of new-generation materials are generalized and analyzed. The methods of modification of the nanotubes by low- and high-molecular compounds and methods of polymer modification by carbon nanotubes are considered. Data on the properties of modified nanotubes are presented. The current and potential applications of materials based on the nanotubes are indicated. The bibliography includes 347 references.

I. Introduction

Among unusual structural forms of carbon discovered in the 1980s and 1990s, which exhibit basically new properties and, as it is now obvious, have an enormous potential for the development of technology, and, hence, the economy, a special place is occupied by carbon nanotubes (CNT) — hollow structures, most often, cylindrical, with a large aspect ratios.

The unique combination of properties such as small size, very large specific surface area, chemical and thermal stability and simultaneously the ability to undergo diverse chemical transformations, high strength, good emission characteristics of the semiconductor CNT and high electrical conductivity of CNT with metallic type conduction is of fundamental interest. This opens up new prospects for their use in technology and engineering in many innovative fields of science and industry.[1] The hope for effective use of CNT in electronics and nanoelectronics, instrument making, and chemical engineering appeared more than a decade ago.[2] As the results of theoretical and experimental studies of CNT accumulated, the optimistic predictions find support,[3–7] and the scope of possible CNT applications is extending to optics,[8–10] micro- and nanomechanics, electromechanics,[11,12] biology, medicine and materials science.[11–19]

The extensive range of CNT properties is a result of the diversity of their types differing in the number of walls, geometric size and chirality, which is determined by the angle of orientation of the graphene lattice relative to the tube axis.[20,21] The orientation affects the electric properties of CNT, which either possess metallic conduction or are semiconductors. Single-walled CNT are graphene sheets rolled to cylinders; multi-walled nanotubes are such cylinders (walls) inserted into one another. Carbon nanotubes can vary in diameter from <0.7 nm to several tens of nanometres and vary in length from hundreds of nanometres to centimetres, and multi-walled CNT may vary also in the number of walls.

As a rule, the nanotube ends are closed by hemispherical 'caps'. Their structure is similar to the fullerene structure (a combination of six- and five-membered rings). During isolation and purification of CNT, the caps are usually destroyed and the ends become open and contain functional groups, most often, carboxyl groups.

Each type of CNT has its own advantages and disadvantages and, correspondingly, applications. Lately, a special group of thin tubes with two to eight layers and 5 – 10 nm in diameter (t-multi-walled CNT) have been distinguished among the multi-walled CNT family. In the authors' opinion, these tubes are superior to both single-walled and multi-walled CNT with larger number of walls as regards the properties and application prospects.[22–24]

The increasing researchers' interest in CNT is reflected in the increasing information flow on this topic. Whereas in 1993 in Russia, this flow consisted of a single (!) publication, there were 205 publications in 2004, and the number of papers published from 1993 to 2004 was 616 (Ref. 25). Even more impressive is the world statistics. In particular, according to the Scirus search, the number of publications

E R Badamshina, M P Gafurova, Ya I Estrin Institute of Problems of Chemical Physics, Russian Academy of Sciences, prosp. Akad. Semenova 1, 142432 Chernogolovka, Moscow Region, Russian Federation.
Fax (7-496) 522 35 07, tel. (7-496) 522 19 16,
e-mail: badamsh@icp.ac.ru (E R Badamshina, M P Gafurova),
tel. (7-496) 522 70 59, e-mail: estriny@icp.ac.ru (Ya I Estrin)

Received 9 October 2009
Uspekhi Khimii **79** (11) 1027 – 1064 (2010); translated by S P Svitanko

in scientific journals with CNT as the key words increased in the following way:

Year	2005	2006	2007	2008	2009
Number of publications	1898	2186	2371	2397	2839

Among the above-mentioned studies, description of the methods of synthesis, studies of the structure, properties and the possible applications of CNT are the subjects of a number of reviews (see, for example Refs 21, 26–32) and monographs.[33–39] Currently, it is beyond doubt that one of the most important areas of nanotube application is the design of functional materials of new generation based on polymers and CNT.

A necessary condition for successful combination of nanotubes and polymers is that the distribution of filler particles in the matrix was as uniform as possible. However, the tendency of CNT to aggregation caused by high surface energy and large aspect ratio prevents the formation of stable CNT dispersions in water and in organic media including polymers. Therefore, intensive search for effective modification methods that would facilitate deaggregation (up to separation into single nanotubes) is in progress. These methods include chemical modification of CNT by low-molecular compounds and polymers to give covalent bonds between the molecules of the modifying agent and the nanotube and non-covalent modification by low- or high-molecular surfactants. The modification reduces the surface energy of CNT, decreases the van der Waals interaction between the tubes, thus favouring deaggregation, which makes the lateral surface of the nanotube more accessible for reagents and the dispersion medium, in particular, polymeric one. Irrespective of the method of CNT modification and the nature of the modifying agent, experiments with nanotubes involve most often sonication of the reaction mixture, which intensifies deaggregation processes of nanotubes and give rise to defects on their surface. This, in turn, increases the chemical reactivity of the tube.

Numerous publications are devoted to CNT modification; they have been largely surveyed in the papers and monographs; some of these are noted above.

This review reflects the achievements mainly made in closely related areas — investigation of the ways of CNT modification by compounds of various nature, in particular, polymers, and development of polymeric nanocomposites using modified tubes. These composites can be divided conventionally into two large groups. The first group includes the composites where the key components are nanotubes, while the polymer modifies their properties (electric, optical, magnetic, *etc*.). Materials of this group are mainly used in instrument making, chemical engineering, biology and medicine. The second group includes composites in which polymers are the main components, while nanotubes are the modifying agents that improve, first of all, particular service characteristics of the polymers. These composites can be considered in the material science, in particular, as structural materials. The background that underlies the preparation of polymeric nanocomposites, the key methods for CNT incorporation into polymers, and the properties and application areas of the modified nanotubes and polymeric composites incorporating them are discussed.

It should be noted that a unified terminology describing the ways of CNT treatment has not been established. Indeed, here the term 'functionalization' is used only to denote chemical modification, *i.e*., covalent grafting of low- and high-molecular compounds to nanotubes, whereas in the literature this term is often applied also to modification through non-covalent interactions, which does not seem quite correct. With true dissolution of CNT in water or organic media being impossible, the terms dissolution and solution are often used in the literature, although the term 'solubilization' borrowed from colloid chemistry and meaning the formation of more or less stable suspensions of tube aggregates would be more pertinent. The word 'dispersion' is often used as a synonym for the last term, although this rather means a decrease in the aggregate size down to disintegration to single CNT (and/or their rupture into small fragments). In principle, solubilization can be accompanied by dispersion but simultaneous occurrence of these two processes can be correctly considered only when independent data on the variation of the characteristic aggregate size (for example, data from scanning electron microscopy) are available. Nevertheless, in this review, we adhere to the terms used by the authors of original publications.

II. Modification of carbon nanotubes by low-molecular compounds

This Section deals with the studies on CNT modification with their intended or actual applications in polymeric nanocomposites and also studies where modified nanotubes are meant for other purposes. It is noteworthy that the latter modification procedures may also be of interest for the development of polymeric composite materials.

1. Functionalization with low-molecular compounds

The ability of CNT to add functional groups upon reactions with various compounds is due to higher reactivity of nanotubes compared to graphene, as the distortion of bond angles between the C–C bonds upon rolling of the graphene sheet to a cylinder results in increase in the total surface energy and possible concentration of excess energy caused by lattice defects. The defects are formed not only during CNT synthesis; they can also appear upon tube deformation (bending, twisting) caused by external action and become sites of higher reactivity. After the treatment has been terminated, the initial CNT structure may be restored.[40] The end caps of nanotubes have enhanced reactivity. In other words, irrespective of their origin, distortions of the graphene lattice may give rise to defects and are responsible for the enhanced chemical reactivity of CNT.

Srivastava *et al*.[40] concluded, based on calculations, that the degree of curvature of the tube lateral surface serves as a measure of reactivity: the smaller the tube diameter and, hence, the greater the curvature, the higher the reactivity. For this reason, the reactivity of the end cups should be even higher. These conclusions are both consistent with experimental results. However, increase in the surface energy is expected to increase the van der Waals interactions of small-diameter tubes with one another and thus lead to the formation of more stable aggregates. In addition, in the aggregates consisting of 'thin' CNT, the number of intertube contacts per unit lateral surface area is higher than that in the aggregates of 'thick' tubes. Therefore, the access of reagents to the lateral surface of the aggregated 'thin' CNT is considerably hampered and, hence, the reactivity should decrease.[41]

Functionalized CNT are able to form stable colloid type suspensions in water or in organic solvents, which is widely used for their purification and fractionation. By attaching

reactive groups by covalent bonds (covalent addition), one can alter the properties of CNT, in particular, improve solubilization, facilitate dispersion, and, as a consequence, extend the range of reactions that nanotubes can undergo and thus extend the scope of their practical use in materials. Furthermore, chemical modification of CNT changes their common electronic system; this can be used to optimize many unique properties of nanotubes and/or impart unusual properties to them.

Functionalization of CNT by low-molecular compounds is performed using oxidation, amidation, cycloaddition, halogenation and other reactions.[14, 28, 42] The type of introduced functional groups depends on the intended application area of CNT. For example, linking of nanotubes to biomolecules in order to prepare compositions meant as vaccination or immunization agents, pharmaceuticals, diagnostic or other biomedical agents requires first of all amino or carboxy groups.[14, 43, 44]

The results of successful use of diverse chemical reactions for covalent modification of CNT published over approximately 10 years were summarized in a review.[45]

a. Oxidation

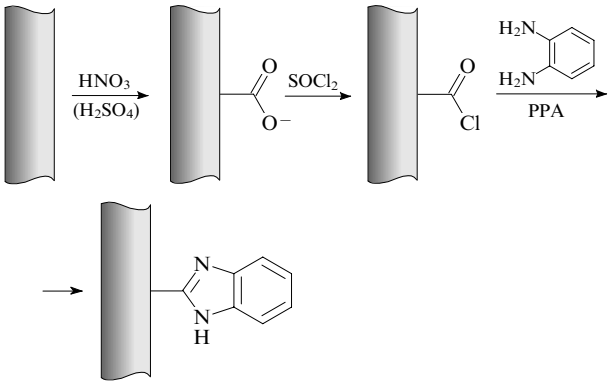
Treatment of CNT with strong oxidants is used most widely for functionalization. This results in tube purification from the remainder of the metal catalyst, opening of the end caps, which are replaced by a 'crown' formed mainly by carboxy and also hydroxy and carbonyl groups (selective oxidation of the ends), and grafting of these groups to the tube lateral surfaces either directly or through linkers.

Treatment of CNT with concentrated acids is the best studied and most widely used oxidation method. An example of this type of study[46] considers the effect of methods of acid treatment of multi-walled CNT on the degree of functionalization and the ability to form stable aqueous dispersions. Note that all operations were carried out at room temperature. The degree of modification can reach $\sim$10% (data of thermogravimetric analysis). Treatment with a nitric and sulfuric acid mixture followed by addition of hydrochloric acid to the reaction mixture was shown to be most efficient. Aqueous dispersions of these nanotubes are stable for 20 days. In the absence of hydrochloric acid, the dispersions formed are somewhat less stable, while without sulfuric acid they are much less stable. In all cases, the initial CNT structure is retained; however, the degree of their defectiveness increases upon functionalization (Raman spectroscopy data).

It was shown[47] that sonication accompanying treatment of CNT with acids substantially increases the concentration of functional groups compared with their concentration attained without ultrasound.

The efficiency of CNT oxidation is characterized by the degree of functionalization of the tubes. For single-walled CNT where all the carbon atoms and grafted groups are located on the tube surface, the degree of functionalization is calculated as the percentage ratio of atomic (molar) concentrations of functional groups to the number of carbon atoms or as the number of carbon atoms per functional group. In the case of multi-walled CNT where the grafted groups can be located, in the opinion of Kirikova *et al.*,[48] both on the outer surface and in the interwall space, the use of weight percent or the number of moles of functional groups per CNT unit weight appears more appropriate. The degree of functionalization of particular tubes can vary due to both surface nonuniformity of real CNT and different accessibility of tube surfaces located outside and inside the aggregates. Therefore, most often the mean value is used, although, as shown below, methods of CNT fractionation according to functionalization degree are being developed. This parameter has been determined using a set of physicochemical methods (thermogravimetric analysis combined with mass spectrometry, titrimetry and fluorometry after fluorescence labelling, Scheme 1) and the conclusion was drawn that multi-walled CNT contain carboxy groups both on the external surface and in the inner layers.[48] This conclusion is based on the fact that titration and (especially) fluorometry give lower degrees of functionalization (2.4% and 1.9%, respectively) than ^{13}C NMR spectroscopy or thermogravimetric analysis (4.9% and 4.8%, respectively). It is stated that only the COOH groups situated on the external surface are accessible for the titration agent and the fluorescence labelling, whereas heat-induced decarboxylation and NMR data refer to the total number of these groups.

Scheme 1



PPA is polyphosphoric acid.

Since the possibility of functionalization of the internal walls of multi-walled CNT is a crucial issue but we did not find any other studies where this possibility was either demonstrated or assumed, it is pertinent to consider the reasoning presented by Kirikova *et al.*[48] in more detail. The mere possibility for the reagent to penetrate a 0.34-nm wide slit between the graphene sheets seems doubtful; so does the result of thermogravimetric analysis based on the weight loss of carboxylated multi-walled CNT referred to the arbitrarily chosen temperature of $\sim$500 °C, although the rate of weight loss increases on further heating. As regards the data from ^{13}C NMR spectroscopy, the intensity of the narrow carbon signal for the carboxy group is $\sim$4 times greater that the noise level of the broad signal from the nanotube carbon atoms, and the accuracy of determination of its fraction was not indicated. The concentrations of the fluorescent groups can be considerably underestimated as a result of both incompletion of the two-step formation of benzimidazole groups (see Scheme 1) and fluorescence quenching by nanotubes.[49] In addition, the oxidation of CNT with nitric acid is known to give C=O and C–O–C or C–O–H groups apart from carboxy groups;[50, 51] *i.e.*, the results of titration and, the more so, imidation do not necessarily cover all of the oxygenated fragments of the oxidized CNT. It is evident that elucidation of this point requires additional studies by various methods.

Other reagents are also used for CNT oxidation. The kinetics of reaction of multi-walled CNT with ozone accompanied by evolution of CO and CO_2 has been studied in detail.[52] The author found several types of ketone groups to be present on the surface of ozonized tubes together with

carboxyls. The microwave-assisted oxidation of multi-walled CNT with nitric acid or sodium hypochlorite occurs over a shorter period.[42]

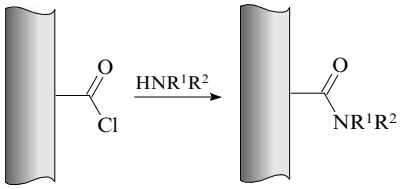
Apart from the above-described methods, oxidation of CNT with a sulfuric acid and hydrogen peroxide mixture [53] and with potassium permanganate [54] was also reported.

Despite the apparent simplicity of the reaction of CNT with strong oxidants, the reaction mechanism is still debated. It was not until recently that it was shown by density functional theory (DFT) that the acidity of carboxy groups formed on the single-walled CNT surface upon the treatment depends on the tube length, diameter and architecture (the carboxy groups on the surface of zigzag-like CNT are more acidic than those of the 'chair-like' tubes) and on the solvent nature.[55]

b. Amidation reactions

The carboxy groups bound to the CNT cage by covalent bonds can serve as 'anchors' for grafting of a diversity of functional fragments, for example, biologically active,[14] fluorescence [48] or biopolymeric ones.[56] A typical sequence of successive CNT functionalization includes grafting of carboxy groups using oxidants, treatment of these groups with thionyl chloride ($SOCl_2$) or oxalyl chloride ($(COCl)_2$) for converting them to acyl chloride groups [C(O)Cl], which then react with amines to afford amide groups.[14, 42, 50, 57]

Scheme 2

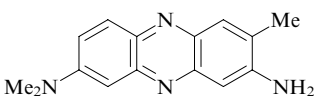


R^1 = H, Alk, Ar; R^2 = Alk, Ar.

The functionalization of t-multi-walled CNT according to Schemes 1 and 2 was first studied in detail by Rakov and co-workers.[50] By IR and X-ray photoelectron spectroscopy, it was found that after treatment with a mixture of sulfuric and nitric acids, t-multi-walled CNT contained C(O)OH (13 at.% relative to carbon), C═O (11 at.%) and C–O (4 at.%) groups. The tubes thus obtained were amidated by the reaction of the acyl chloride form with bisdodecylamine ($R^1 = R^2 = n\text{-}C_{12}H_{23}$). The solubility of carboxylated tubes in water was 3.13 g litre^{-1}, and the amidated tubes dissolved in chloroform up to a concentration of 1.3 g litre^{-1}. It was thus concluded that the behaviour of t-multi-walled CNT in these reactions differs little from the behaviour of single-walled or multi-walled CNT and the degree of functionalization is determined by the reaction conditions. However, one can follow quite a reasonable trend: under comparable conditions, the degree of functionalization (apparently, this means the percentage of functional groups) decreases on going from single-walled to t-multi-walled CNT and then to multi-walled CNT.

According to Scheme 2, the multi-walled CNT oxidized by a reported procedure [42] were amidated with n-octadecylamine.

The amidation of carboxylated multi-walled CNT by the reaction with Neutral Red



in the presence of carbodiimide was described, and electrochemical characteristics of the functionalized tubes were studied.[58] It was shown that they can be efficiently used as active elements in amperometric biosensors.

The exceptionally high water solubility (10 mg ml^{-1}) in the pH range of 5–14 was attained upon amidation with lysine of multi-walled CNT, which were first carboxylated and then converted to acyl chloride form.[59]

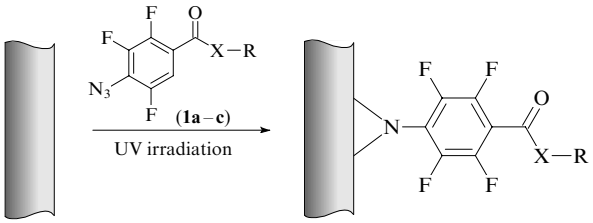
The amidation of the carboxy groups with long-chain alkylamines affords CNT that form stable dispersions in non-polar solvents.[54]

c. Cycloaddition

Some applications, in particular, the manufacture of materials for medical instruments, waterproof coatings, lubricants and working clothes and the use in biotechnology,[53, 60] require superhydrophobic materials, in particular those based on CNT. The superhydrophobicity is imparted to nanotubes using, in particular, cycloaddition reactions involving azides and azomethine ylides.

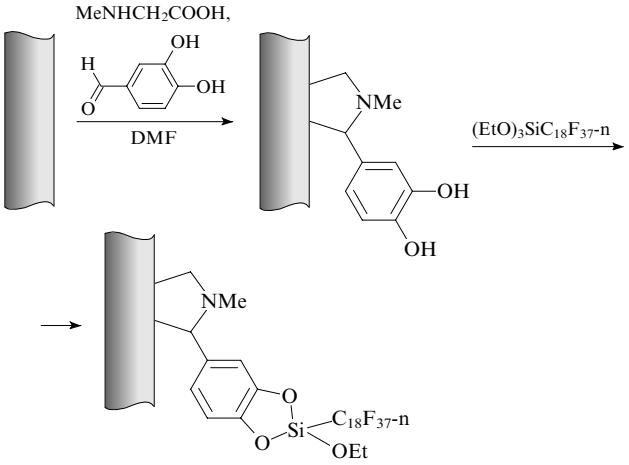
For example, treatment of highly oriented single tubes on a hydrophobic substrate with perfluoroazidobenzoic acid *N*-perfluoroalkylamide (compound **1b** in Scheme 3) under UV irradiation resulted in superhydrophobic CNT (wetting angle >150°), while treatment with compound **1a** gave rise to a superhydrophilic surface.[61]

Scheme 3



X–R = $NH(CH_2)_3OH$ (**a**), $NH(CH_2)_3(CF_2)_7CF_3$ (**b**), $O(CH_2)_2OC(O)CBrMe_2$ (**c**).

A similar result was achieved by 1,3-cycloaddition of azomethine ylide *in situ* to the oxidized multi-walled CNT containing COOH and OH groups followed by treatment of the polyhydroxylated derivatives with perfluorooctadecyltriethoxysilane.[53]

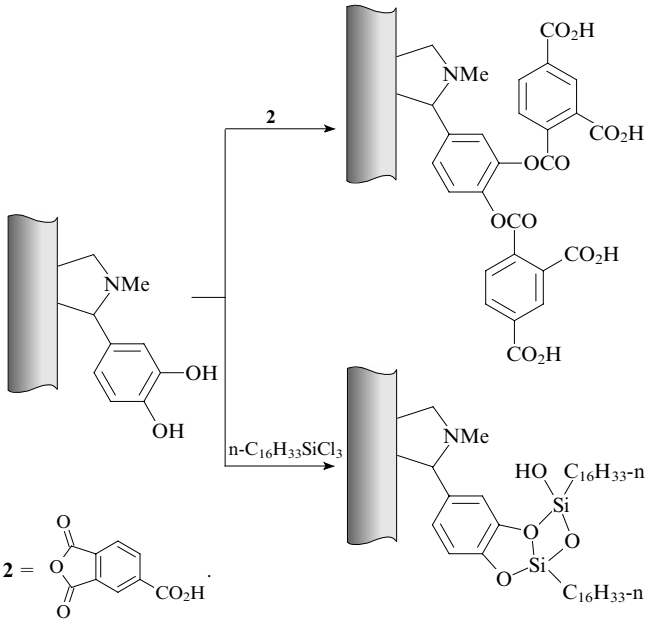


Treatment of a cotton cloth with a solution of poly(methyl methacrylate) (PMMA), to which a suspension of thus modified multi-walled CNT in hexafluoroisopropyl

alcohol has been added, followed by drying make the cloth superhydrophobic.

Nanotubes that contain dihydroxyphenyl group form stable dispersions in a number of polar solvents, readily undergo esterification, react with trimellitic anhydride (**2**) and with alkylchlorosilanes, in particular, with hexadecyltrichlorosilane to give hydrophilic and hydrophobic products, respectively (Scheme 4).[62]

Scheme 4



By addition of azomethine ylide, phenolic groups were introduced into single-walled CNT.[63] This promoted the dispersibility of the tubes in water or acetone.

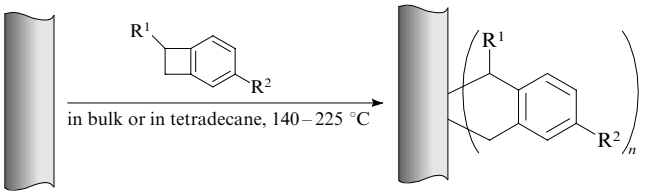
The *in situ* covalent addition of azomethine ylides with pyrene groups to semiconductor tubes, which are then selectively solubilized in the presence of lignoceric acid, was used to separate single-walled CNT with semiconductor and metallic types of conduction.[64]

An unusual usage of dipolar 1,3-cycloaddition involving azide and acetylene groups to give 1,2,3-triazole rings (click-chemistry reaction) was reported.[65] First, 4-azidobutylamide groups were attached to carboxylated single-walled CNT (through the acyl chloride step), and then hexynethiol-coated gold nanocrystals were attached to these groups. This gave nanotubes densely decorated by gold nanoparticles.

The introduction of indolizine fragments on the surface of single-walled CNT annealed at 900 °C was accomplished in two steps, the first one being 1,3-cycloaddition of ylidopyridinium to give a pyrrolidine ring and the second one being the cycloaddition of the same ylide to the product of the first reaction.[66] The process was carried out with usual heating and under microwave radiation; in the latter case, the reaction time was reduced from 5 days to 1 h. Carbon natotubes with metallic conduction were found to be more reactive than semiconducting ones; among the latter, the nanotubes with longer diameters were found to be more reactive, which contradicts the data of the earlier publication.[40] Indolizine derivatives are of interest for their pharmacological, antioxidant, and fluorescence properties used in sensor devices.

The functionalization of single-walled CNT by the reaction with azomethine ylide based on *N*-BOC †-aminoethylglycine followed by transformation of these groups to trifluoroacetate groups was studied.[67] This modification makes it possible to solubilize individual single-walled CNT and study their behaviour in magnetic fields.

The lateral surface of multi-walled CNT behaves as a dienophile. This fact was used for functionalization through [4 + 2]-cycloaddition (the Diels – Alder reaction) of a number of substituted benzocyclobutenes, which can thermally isomerize to *o*-quinodimethanes.[68]



$R^1 = R^2 = H$, $n = 28$ mass %; $R^1 = Br$, $R^2 = H$, $n = 35$ mass %;
$R^1 = H$, $R^2 = Br$, $n = 30$ mass %;
$R^1 = H$, $R^2 = CH_2CH_2OH$, $n = 47$ mass %;
$R^1 = H$, $R^2 = CH{=}PhCH$, $n = 54$ mass %.

An important feature of the proposed method is that the reaction is carried out either without a solvent or in a rather concentrated solution (100 mg of multi-walled CNT in 5 ml of tetradecane);‡ the degree of functionalization can be easily controlled by reaction temperature and time. In the case of unsubstituted benzocyclobutene, up to 28 mass % of the modifying agent can be added, while for 2-hydroxyethyl derivative, this is 37 mass %, and for the 1-phenylethylene (styryl) derivative, this is 54 mass %. Depending on the nature of the substituents in benzocyclobutene, either halogen or hydroxyl derivatives and styryl groups can be attached to the multi-walled CNT surface. It was shown [69] that multi-walled CNT functionalized by benzocyclobutene initiate living anionic polymerization of ethylene oxide and ε-caprolactone.

d. Reactions with arenediazonium salts

The effective functionalization of single-walled CNT is attained by treating their aqueous dispersions obtained in the presence of sodium dodecylbenzenesulfonate (SDBS) with 4-chlorobenzene- and 4-nitrobenzenediazonium salts to give 4-chlorophenyl- and 4-nitrophenyl groups, respectively, covalently bonded to the CNT.[70] Study of the Raman spectra of single-walled CNT showed that this functionalization changes the optical properties, chlorophenyl groups inducing the shift of absorption bands to higher frequencies and nitrophenyl groups inducing low-frequency shifts of the bands. It was also found that the nitrophenyl functionalization is more efficient for metallic-conductive tubes, while the chlorophenyl modification is sensitive to the tube diameter, and this can be used to fractionate single-walled

† Boc is *tert*-butyloxycarbonyl group used for amino group protection (in particular, in the peptide synthesis); it is formed upon treatment of amines with bis(*tert*-butyl) dicarbonate and removed by acid or alkaline hydrolysis.

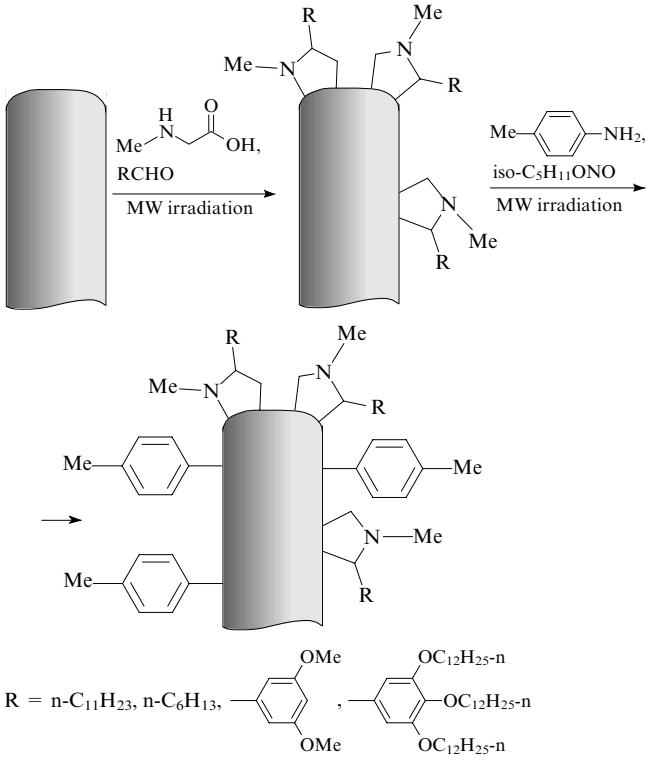
‡ Usually, functionalization of CNT is carried out at an order of magnitude lower concentrations (up to 2 mg ml^{-1}).

CNT according to these parameters. The addition of 4-chlorophenyl groups to single-walled CNT upon their treatment with 4-chloroaniline and isopentyl nitrite in *o*-dichlorobenzene with subsequent replacement of chlorine by a thio group has been reported.[71]

In order to separate the single-walled nanotubes with metallic and semiconductor types of conduction, they were functionalized by treatment with *p*-hydroxybenzenediazonium salt, which reacts at 45 °C mainly with metallic-conductive tubes.[72] These functionalized tubes acquire negative charge in the alkaline medium and thus they can be separated from non-functionalized semiconductor type tubes by electrophoresis.

The successive reaction of non-oxidized single-walled CNT with arenediazonium salts (radical addition of arenes) followed by microwave-assisted dipolar 1,3-cycloaddition to azomethine ylides afforded readily solubilized CNT.[73] Note that the number of active sites on the surface of single-walled CNT capable of dipolar 1,3-cycloaddition is much smaller than in the radical addition of arenes. When performed under microwave radiation, these reactions proceed up to high degrees of conversion over periods of tens of minutes instead of tens of hours needed in the case of conventional heat treatment of the reaction mixture. By changing the order in which the reactions are performed, one can vary the contents of each type of functional groups (Scheme 5).

Scheme 5



The authors' conclusion that the CNT surface has a limited number of sites capable of reacting with chemicals appears significant. This may imply either that the surface of real CNT, unlike the CNT with ideal structure, contains a certain fraction of defective sites possessing enhanced reactivity (variant A), or that the reactivity decreases following increase in the degree of covalent functionalization (variant B). Since the nature of defects and the defectiveness of the CNT surface depend evidently on the method of their preparation and isolation (purification), variant A would imply a considerable dependence of the functionalization behaviour of CNT on these factors (all other factors being the same), while variant B means that this dependence is not so pronounced. Unfortunately, we did dot find any publications presenting systematic research on this issue.

The reactions of initial and purified single-walled CNT with 4-substituted benzenediazonium tetrafluoroborates in aqueous dispersions obtained using surfactants of various nature and at various pH values were studied by near-infrared emission spectroscopy and Raman spectroscopy.[74] The authors concluded that the rates of reactions are different for metallic-conductive and semiconductive CNT, and this can be used to separate them *via* selective reaction routes. It was shown that a change in the diameter of single-walled CNT from 0.7–0.8 to 1.0–1.1 nm reduces their reactivity more than fivefold; this is also supported by the results of earlier theoretical calculations.[40] Higher reactivity of single-walled CNT with smaller diameter was also demonstrated in another study[75] upon introduction of butyl groups. High selectivity of the reaction with respect to metallic-conductive nanotubes and the possibility of easy control of the degree of functionalization of single-walled CNT (both those with metallic and semiconductor types of conduction) were found for grafting of phenyl groups under electrochemical decomposition of benzenediazonium.[76]

The functionalization of single-walled CNT by reactions with diazonium salts based on *p*-aminobenzoic acid (*N*-Boc-8-amino-3,6-dioxaoctylamide) has been studied.[67]

Water-soluble t-multi-walled CNT were prepared in the reaction with the diazonium salt generated *in situ* that contained a protected (Boc) amino group.[77] After deprotection by acid hydrolysis, positively charged ammonium ions are formed on the CNT surface and thus ensure the water-solubility of the material.

Multi-walled CNT with COOH groups grafted using diazotization (treatment with 4-aminobenzoic acid and isopentyl nitrite in acetonitrile) can retain on their surface highly dispersed nanoparticles of crystalline palladium. The material thus formed shows much higher electrocatalytic activity in the methanol oxidation in alkaline medium as compared with the standard Pd catalyst, and has higher stability under cyclic load; hence, in the authors' opinion, it is fairly promising for fuel cell use.[78]

Ellison and Gasda[79] carried out diazotization-mediated functionalization of single-walled CNT *in situ* using 1,4-diaminobenzene. According to IR and Raman spectroscopy and absorption in the UV and visible region, 4-aminophenyl groups capable of subsequent transformations were grafted to the tubes in this reaction. In particular, the reaction with succinimidyl 4-(*N*-maleidomethyl)cyclohexane-1-carboxylate affords 4-(*N*-maleidomethyl)cyclohexane-1-carboxyanilide groups.

e. Radical addition

Functionalization of CNT by addition of free radicals *in situ*, like dipolar 1,3-cycloaddition, is an efficient method for enhancing the reactivity of nanotubes.

The isobutyronitrile radicals resulting from thermal decomposition of azobisisobutyronitrile (AIBN) add to single-walled CNT up to a degree of functionalization of 1 : 23 (1 group per 23 carbon atoms).[80] Effective functionalization of these tubes by attaching free 4-methoxyphenyl radicals obtained by oxidation of 4-methoxyphenylhydrazine hydrochloride has been considered.[81]

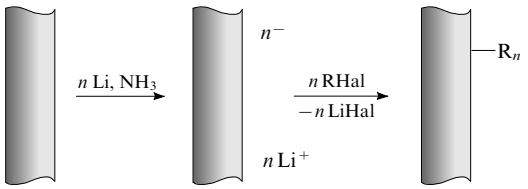
Microwave irradiation sharply accelerates (from several days to several minutes) modification of single-walled CNT by thermally and oxidatively initiated addition of 4-methoxyphenylhydrazine hydrochloride-derived radicals.[82] It was shown that the degree of functionalization as a function of the treatment time passes through a maximum.

Modification of CNT by photoinitiated addition of hydrazine and 1,3,4-oxadiazole has been described.[83] The tubes functionalized in this way form dispersions in nonpolar organic solvents; they are stable for two months and possess high thermal stability (up to 300 °C).

The photoreduction of benzophenone with diphenylmethanol in benzene gives rise to benzhydrol derivatives of single-walled CNT containing one grafted benzhydrol group per 52 carbon atoms.[84] The reduction of benzophenone with metalic potassium occurring as single-electron transfer gives the diphenylmethyl radical, which is directly attached to the nanotube;[85] in the case of two-electron transfer, the addition of diphenylmethyl anion is described by a more complicated mechanism; however, the final outcome is the same. The degree of functionalization is 14% for anionic reaction mechanism or 10% for radical mechanism.

f. Alkylation and acylation

The functionalization of single-walled CNT with solutions of alkali metals in liquid ammonia or in THF with subsequent treatment with alkyl halides (reductive alkylation — the Billups reaction[86]) has been reported.[87]



Performing this reaction in liquid ammonia is inconvenient because it requires low temperatures and removal of ammonia and, furthermore, the process is difficult to scale. Therefore, it is recommended to carry out such reactions in alkylamines or diamines.[88]

A high degree of alkylation (arylation) of single-walled CNT is attained upon the reaction with a solution of lithium in ethylenediamine and subsequent treatment with n-$C_{16}H_{33}I$, Bu^nBr and PhI.[89] This modification procedure is quite applicable for introduction of various functional groups or direct grafting of polymers or oligomers to nanotubes.

The kinetics of reductive alkylation of single-walled CNT was found to be sensitive to the tube diameter (tubes of smaller diameters are more reactive) and structure (tubes with metallic conduction are alkylated much faster than semiconductor tubes).[90] However, the authors noted that in the preparation of hydrogenated products by reactions of single-walled CNT–Na complexes with proton donors (water, alcohols), unlike the reactions with alkyl iodides, no selectivity with respect to the diameter or the type of conduction is observed and the degree of modification is much lower than in the case of alkylation.

The functionalization of single-walled CNT by the Bingel reaction, that is, the reaction with dialkyl iodomalonates in the presence of basic catalysts[91] is accelerated ~50-fold on exposure to microwave radiation as compared with the conventional conditions. For degrees of functionalization of 70 to 300 carbon atoms per functional group, no significant change in the electronic characteristics of single-walled CNT was noted, as opposed to most other covalent functionalization methods. No difference in the reactivity between metallic-conductive and semiconducting CNT was noted in the Bingel reaction either.

Treatment of single-walled CNT with superacids [trifluoroperoxyacetic, *m*-chloroperoxybenzoic and 2-bromo-2-methylperoxypropionic (BMPP) acids] under sonication leads to surface functionalization by acyl groups through the ester bonds.[92] In the case of BMPP, functionalized single-walled CNT were used for the subsequent grafting of PMMA to them by atom transfer radical polymerization.

The Friedel–Crafts acylation of multi-walled CNT with 4-substituted benzoic acids in the presence of a PPA–P_2O_5 mixture has been studied in detail. The degree of functionalization increased upon increase in the reactivity of benzoic acids, and the electronic structure of the tube is retained almost completely.[93] The aggregation of multi-walled CNT to give bundles of 30 to 70 nm diameters is also retained.

Attempted acylation of crude single-walled CNT by treatment with a PPA–P_2O_5 mixture or PPA alone under inert atmosphere at 130–190 °C in the presence of 4-aminobenzoic acid without sonication afforded the addition product of 4-aminobenzoyl groups to nanotubes.[94] This original method of treatment was suitable for simultaneous purification of single-walled CNT from metallic catalysts and amorphous carbon under mild conditions without oxidation and their modification giving covalent bonds.

g. Halogenation and amination

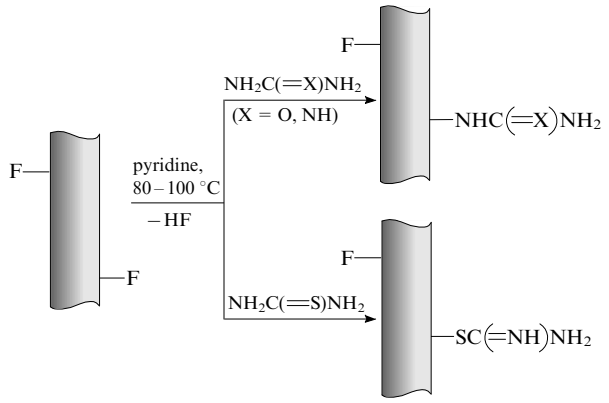
Historically, fluorination was the first method used to functionalize the single-walled CNT surface to form covalent bonds.[95] Complete removal of fluorine atoms by treatment with hydrazine restores the initial state of the tube. Krestinin *et al.*[96] found that under the optimal conditions (temperature not higher than 190 °C, fluorine pressure of 0.8 bar and reaction time of 5 h), fluorine atoms can be incorporated into single-walled CNT up to the ratio C : F = 0.43 virtually without destruction. At higher temperature, noticeable carbon gasification (as CF_4) takes place together with pronounced destruction of the tube.

Apart from fluorine, other halogens can also add to CNT. Modified Hunsdiecker iodination of carboxylated single-walled CNT using elemental iodine and iodosobenzene diacetate was reported.[97] The structure of iodinated single-walled CNT was confirmed by various methods. A substantial change in the electronic characteristics of modified tubes as compared with the initial tubes was noted but no data on the dispersion behaviour and subsequent reactivity was presented.

The fluorinated single-walled CNT can undergo new chemical transformations. In particular, they are successfully functionalized by urea, thiourea and guanidine (Scheme 6).[98] This gives CNT containing amide or heteroamide groups and a considerable number (~20% to 70%) of remaining fluorine atoms. All of the products form stable dispersions in water and DMF, which opens up prospects for their use in biomedical studies and in technology. New types of functionalized CNT possess enhanced mechanical and electrical characteristics and can be used as building blocks in the copolymerization and polycondensation with various polymers (epoxide, polyurea, urea–formaldehyde resins, polyamides, *etc.*), in the production of nanocomposites with enhanced mechanical properties and for the

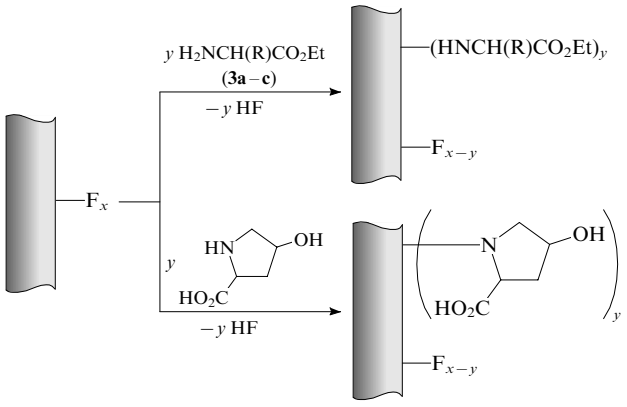
design of new types of field-effect transistors and gas sensors.

Scheme 6



By treatment of fluorinated single-walled CNT ($C:F \approx 2$) with natural α-amino acids with both free and protected (esterified) carboxy groups, nanotubes with covalently linked amino acid fragments were obtained (Scheme 7).[99] The reactions were carried out in *o*-dichlorobenzene in the presence of catalytic amounts of pyridine at temperatures of 80–150 °C. The degree of amino acid functionalization depends on the reaction conditions and the reagent nature and varies from 32 to 8 carbon atoms per functional group. The COOH groups on the lateral walls of such tubes can be used for the formation of covalent bonds with polymeric matrices in the development of composites, fibres and ceramics, for the production of implant materials to be used in dentistry and orthopedics. The functional groups and activated unsaturated C=C bonds on the CNT surface are able to function as free radical acceptors; therefore, it was proposed[99] to employ such tubes as oxidants to fight age-related diseases.

Scheme 7



R = H (**a**), CH_2OH (**b**), CH_2SH (**c**).

Amino groups were introduced into multi-walled CNT by one-pot[§] deprotonation–carbometalation reactions followed by electrophilic substitution reaction with (bromoethyl)diethylamine.[100] The aminated multi-walled CNT meet the requirements imposed on heterogeneous catalysts for biomass decomposition, unlike the catalysts used currently.

Among the methods of introduction of amino groups into CNT, note the simple synthesis of single-walled CNT 'soluble' in organic solvents (especially in THF) with covalently linked propylamine groups through nucleophilic addition of lithium n-propylamide at CNT : amine molar ratios of 1 : 1 to 1 : 50 and subsequent oxidation of the $(Pr^nNH)_n-$(single-walled CNT)$^{n-}-n\,Li^+$ intermediates with atmospheric oxygen.[101] The reaction was carried out in THF. According to thermogravimetric analysis, the weight fraction of propylamine groups in the reaction products reaches 30%. Aminated single-walled CNT form stable dispersions in organic solvents.

h. Miscellaneous functionalization reactions

A highly efficient method was developed for functionalization of single-walled and multi-walled CNT and fullerenes to give zwitterionic intermediates involved in the subsequent addition reactions.[102] The 'capture' of the intermediates by nucleophiles allows one to mount functional groups under mild conditions (60 °C, without addition of strong acids or bases or high pressure). Aqueous dispersions of multi-walled CNT obtained by this method, which are stable over several months, were successfully used to produce CNT–poly(ethylene oxide) (PEO) composites.

Swager and co-workers[103] performed the zwitterionic functionalization of multi-walled CNT with cobalt porphyrin by S_{N_2}-addition reaction. The functionalization product mixed with Nafion[¶] was used as a catalyst in the electrocatalytic reduction of oxygen. This increased the reaction rate compared to the use of non-modified cobalt porphyrin. This new catalytic system is a potential substitute of cathodic materials containing metals (in particular, platinum) for proton-conducting fuel cells.

After functionalization of single-walled CNT by ruthenium porphyrin and ferrocene, visible light absorption by CNT–Si films increases. Electrodes with these films can be used in molecular data storage devices.[104]

Carboxylated multi-walled CNT modified additionally by semiconductor compounds, in particular, by nanostructured ionic zinc complexes $Zn(NH_3)_4^{2+}$ linked through the C–N bond possess strong luminescence.[105]

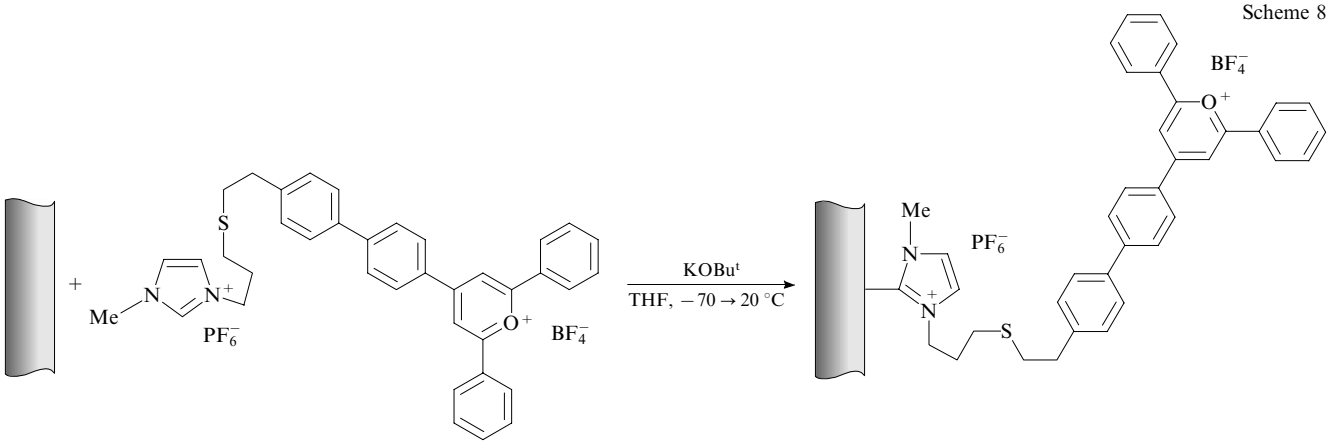
Wang *et al.*[106] hydroxylated multi-walled CNT by the method proposed earlier for single-walled CNT,[107] *i.e.*, by mechanochemical treatment with solid KOH in a ball mill. Aqueous dispersions of multi-walled CNT with OH groups on the surface playing an important role in the non-linear light-scattering proved much more efficient as ophthalmic filters compared with C_{60} and $C_{60}(OH)_n$ dispersions or non-modified or carboxylated multi-walled CNT. The results obtained by the authors allowed them to recommend hydroxylated tubes for the use in optical protective devices.

Nanotubes containing up to 6.8 mass % of pyrylium chromophoric groups were obtained by the reaction of the imidazolium derivative of 2,4,6-triphenylpyrylium tetrafluoroborate with the single-walled CNT surface pretreated by potassium *tert*-butoxide (Scheme 8).[108] The individual single-walled CNT functionalized in this way were studied with atomic force microscopy and thermogravimetry, and their solutions in D_2O (2.6 μg ml^{-1}) were studied by a set of optical and spectroscopic methods; fluorescence and near-IR emission spectra were studied.

§ Performing a complex chemical process in one stage and in the same reactor without isolation of intermediate products.

¶ Tetrafluoroethylene copolymer with perfluorinated vinyl ether of sulfoethoxyoligopropylene oxide.

Scheme 8



After covalent addition of SO_2OH groups (up to 20%) to single-walled CNT on treatment with sulfuric acid at 300 °C, they became soluble in water, ethanol and DMF.[109] In view of the high acidity of the surface functional groups, new material was recommended as a solid acid catalyst. In addition, sulfonated single-walled CNT have high conductivity and behave as superparamagnets.

For functionalization of CNT and metal oxide nanofibres, organotin and -silicon reagents, *viz*., hexadecyltrimethoxysilane, dibutyldimethoxytin and trioctyltin chloride, proved to be effective.[110] Nanomaterials, including multiwalled CNT, treated with these compounds form stable dispersions in CCl_4 and in toluene.

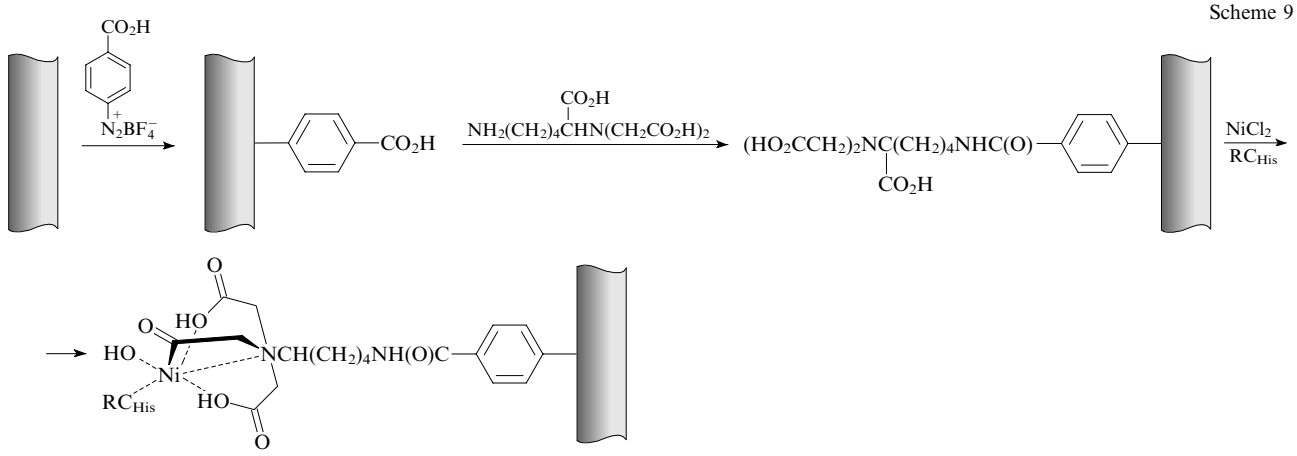
It was noted above that functional groups can be either directly linked to the CNT surface or attached through a linker, as a rule, a hydrocarbon chain or an aromatic structure. The former case is exemplified by functionalization of single-walled CNT by the antitumour agent cisplatin (*cis*-diaminodichloroplatinum).[111] Presumably, modification of this product could increase the efficiency and reduce the toxicity of the drug.

In some cases, only the second option is suitable, for example, for reversible binding of a protein to the surface of individual single-walled CNT without the loss of activity aimed at development of new photovoltaic biocomplexes needed for biological investigations.[56] Thus single-walled CNT that have been carboxylated by the reaction with 4-carboxybenzenediazonium tetrafluoroborate and then amidated with a tricarboxylic amino acid, N_α,N_α-bis(carboxymethyl)-L-lysine hydrate, are capable, in the presence of nickel chloride, to reversibly bind polyhistidine-tagged reaction sites of the protein isolated from *Rhodobacter sphaeroides* with retention of the protein activity (Scheme 9). The single-walled CNT containing carboxy groups directly linked to the surface cannot do this. An immobilized enzyme was obtained in this way.

Successful modification is attained when a suspension of single-walled CNT in liquid ammonia in the presence of lithium amide reacts with bisdodecyl and diphenyl sulfides or with dibenzyl disulfide.[112] The authors believe that upon electron transfer from lithium amide to single-walled CNT, the tubes acquire rather high negative charge, and the Coulomb repulsion results in their complete deaggregation. The subsequent reaction with sulfides binds the hydrocarbon substituents to CNT, while in the reaction with dibenzyl disulfide, the benzyl groups are linked to the CNT through a sulfur atom.

A new strategy of reversible chemical functionalization of single-walled CNT using high-boiling amines (diethylenetriamine, triethylenetetramine, tetraethylenepentamine and pentaethylenehexamine) was proposed.[113] The reaction was carried out in an autoclave at 500 °C in the presence of finely dispersed cobalt as the catalyst. Using *ab initio* and DFT calculations, the authors established the possibility of chemical sorption of hydrogen on the single-walled CNT surface, the character of bonds thus formed and their predominant geometry at different degrees of hydrogenation. The effect of hydrogen on the distance between the

Scheme 9



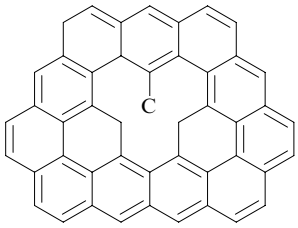
RC_{His} is the histidine-labelled protein.

tubes and the energy of their interaction with one another were estimated quantitatively. The van der Waals interaction in the hydrogenated tubes considerably decreases; on sonication, they form stable dispersions in methanol, ethanol, chloroform or benzene. After annealing at 800 °C, the structure of these tubes is restored (the mass loss is ~8%) but the tube bundles become looser than the bunches of the initial single-walled CNT.

2. Comments to Section II.1

Getting acquainted with the works on chemical transformations of CNT brings about questions, in some cases, that are scarcely considered in the literature. The mechanism of the most popular reaction, the oxidation to give carboxy groups directly linked to the CNT lateral surface, appears obscure. The point is where the carbon atom of this carboxy group comes from. If this atom belonged originally to a defect-free CNT site, the formation of the carboxy group requires cleavage of two C–C bonds, the arising biradical can be closed to give a five-membered ring, and a large 'hole', *i.e.*, a ten-membered ring, is formed nearby. Such a defect in the tube wall would induce a pronounced distortion of its cylindrical shape. The reactivity of the CNT surface should substantially increase at this site; in the presence of a strong oxidant, this would inevitably lead to further spreading of the defect at a higher rate compared to oxidation of the intact surface area. (This might be the mechanism of 'unzipping' of multi-walled CNT to graphene ribbons under the action of a mixture of sulfuric acid with potassium permanganate at room temperature.[114])

If the formation of carboxy groups during oxidation occurs at the existing structural defects, no information is presented concerning the nature of these defects except for one publication,[14] which assumes an incredible defect as a free dangling carbon atom linked to only one lattice carbon atom and a large 'hole' as a 12-membered ring in the tube wall.



Some types of defects resulting in surface distortion and giving rise to kinks were studied theoretically.[40] These defects are observed extremely rarely in electron microscopy images of both native and oxidized CNT. It cannot be ruled out that the intermediate reactive species formed upon oxidation of either amorphous carbon present as an impurity in the CNT or defective CNT serve as one of the sources of carbon atoms for the formation of carboxy groups. (The final oxidation products, CO and CO_2, were found upon ozonolysis of CNT.[52])

The conclusions drawn by Salzman *et al.*[115] appear most reasonable. As a result of thorough fractionation and study of the oxidation products of single-walled CNT with concentrated nitric acid at 100 °C, it was found that amorphous carbon species always present in CNT immediately after the synthesis are the first to be oxidized. This gives carboxylated carbon fragments capable of effective non-covalent interaction with the CNT surface. These fragments can be separated from virtually intact single-walled CNT, and upon mixing of their dispersions, the structure of 'carboxylated single-walled CNT' is restored. Considering this, it would be more reasonable to assign oxidation processes to non-covalent modification of CNT and consider them in the next Section.

Also, the chemistry of CNT acylation in the presence of a PPA–P_2O_5 mixture remains unknown.[93, 94] Usually, reactions of this type refer to substitution reactions and proceed along the following path:

$$RC(O)-X + ArH \longrightarrow RC(O)-Ar + HX,$$

X is halogen, most often Cl, or OH group.

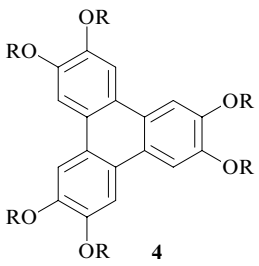
However, the CNT structure contains no hydrogen atoms and substitution along this path is impossible. If reactive cationic species [*e.g.*, $RC(O)^+$] able to add to CNT are involved as intermediate species, then apart from the ketone groups RC(O), the functionalized tubes should contain an equivalent amount of other groups, most likely, hydroxyls.

3. Non-covalent modification by surfactants

Apart from chemical modification, stable dispersions of CNT can be obtained (*i.e.*, CNT can be solubilized) using the ability of many low-molecular compounds of efficient sorption on the CNT surface through non-covalent interactions. Lemek *et al.*[116] measured the equilibrium constants for the sorption of aromatic compounds including fused ones (naphthalene, anthracene, phenanthrene, pyrene) and substituted benzenes (nitrobenzene, di- and trinitrobenzene, chlorobenzene, *N*,*N*-dimethylaniline) and also pyridine, quinoline and isoquinoline on the multi-walled CNT surface. The equilibrium constants were correlated with the results of calculations of the interaction energies of the above-listed compounds with single-walled CNT, although the trend for linear dependence was vague. Electron-deficient aromatic systems formed stronger complexes than electron-enriched systems. As shown below, the ability to sorb compounds containing particular groups (most often, aromatic) is the feature utilized for non-covalent modification of CNT not only by low-molecular compounds but also by polymers.

Surfactants and sonication either before or during the treatment are used most often to make CNT readily dispersible in water and in polar solvents. Neutral [Triton X-100 — octylphenol ethoxylate 4-n-$C_8H_{17}C_6H_4$.$(OCH_2CH_2)_nOH$, $n \approx 9.5$],[24, 117, 118] anionic (sodium dodecyl sulfate,[24, 119–121] sodium dodecylbenzenesulfonate [119]) and cationic surfactants (cetyltrimethylammonium bromide) [122, 123] are widely used for this purpose.

Recently, new amphiphilic surfactants **4** based on triphenylene were proposed for solubilization of single-walled CNT [124, 125]

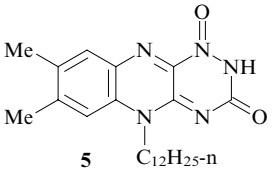


4

R = $(CH_2)_nCO_2H$:
n = 6 [C(6)], 8 [(C(8)], 10 [C(10)].

This structure was chosen in view of the fact that owing to its aromatic nature and geometric parameters, it is capable of strong π−π-interaction with the nanotube surface. Single-walled CNT are effectively dispersed in D_2O with C(10) sodium salt. It was noted that equally efficient destruction of the aggregates of such tubes under the action of the last-mentioned surfactant and SDBS is attained through portionwise addition of reagents in combination with long-term moderate-intensity sonication of the aqueous dispersion. The authors believe that under these conditions, a dispersion of individual tubes is formed because rather intense photoluminescence of solutions is observed even without centrifugation used to precipitate CNT aggregates. However, the dispersions obtained in the presence of C(10), unlike those obtained with SDBS, remain stable upon the addition of methanol up to its content of 70% and are stable against concentrating and freeze-drying. Photoluminescence measurements also showed that C(10) and C(8) solubilize mainly CNT of larger diameter than C(6). In the authors' opinion, new surfactants are retained more firmly on the CNT surface due to simultaneous π−π-interaction and hydrophobic interaction of the aliphatic chains.

The capacity of conjugated fused polycyclic structures for strong interaction with the CNT surface was used in a study by Ju *et al.*[126] Tight encapsulation of single-walled CNT into the shell of 7,8-dimethyl-10-dodecylisoalloxazine [**5**, flavine F(12)]



5

not only promotes dispersion of nanotubes in toluene but also displaces the sorbed oxygen from the surface. This can be used to markedly improve the optoelectronic characteristics of single-walled CNT.

Hydroxylated multi-walled CNT adsorb biogenic aromatic amines from aqueous solutions due to electrostatic interaction and the interaction of the π-systems of CNT and amines.[127] This feature of nanotubes can be used for increasing the sensitivity of electrochemical sensors.

The behaviour of CNT in liquid media is determined by the surfactant nature and concentration, the ionic strength of the solution and morphology of the tube.

The dependences of the photoemission efficiency of aqueous 'solutions' of single-walled CNT on the type and concentrations of dispersion agents and on the nanotube concentration (c_{CNT}) were analyzed in the publication.[128] The following surfactants were employed: dodecyl sulfate, SDBS and sodium cholate, and also some oligomers.

The effects of ionic strength of the solution and tube morphology have barely received attention until recently. The geometric parameter distribution of CNT in the dispersion and in the precipitate was not studied either. Only Anoshkin *et al.*,[118] who studied for the first time Triton X-100-stabilized aqueous dispersions of multi-walled CNT, demonstrated convincingly that the length and diameter distributions of the tubes that passed to the dispersion differ noticeably from these distributions of the tubes that remained in the precipitate. For the CNT present in dispersions, a functional relationship was found between the diameter and the aspect ratio. An electron microscopic examination of the 'soluble' product showed that each multi-walled CNT is enclosed into a rather thick micellar shell. On the basis of their results, the authors concluded that all the solubility values for CNT reported in the literature refer only to a particular set of tubes and have no clear meaning without length and diameter distributions of the tubes being indicated, and for multi-walled tubes, the distribution among the layer numbers is also required.

A pronounced dependence of the properties of dispersions of single-walled CNT on the external conditions, in particular, on the medium composition and pH, was also noted;[119] however, the authors were able to stabilize characteristics of the dispersions (namely, luminescence parameters) over a broad ranges of pH values using a combination of two surfactants: SDBS and polyvinylpyrrolidone (PVP).

The dispersing effect of surfactants and, especially, the stability of the resulting dispersion are determined by the surfactant nature, in particular, the adsorbability on the CNT surface.[129] The higher this ability, the more stable the dispersion even at very low surfactant concentrations. The influence of a number of factors on the CNT–adsorbate interaction, in particular, the nature of the adsorbate and the functional groups in its molecules and on the single-walled CNT surface was investigated in comparison with the interaction of the same compounds with graphite surface.[130] The sorption ability of 1,3-dichlorobenzene, 2,4-dichlorophenol and naphthalene (per unit surface) depend slightly on the type of sorbent, whereas sorption of 2-naphthol and, especially, 1-naphthylamine sharply increases on passing from graphite to single-walled CNT. In addition, 1-naphthylamine is much better sorbed on the surface of oxidized than non-oxidized tubes.

The electronic structure of CNT can be considerably rearranged under the action of surfactants or solvents, which is observed, in particular, in the presence of effective dispersion agents such as sodium dodecyl sulfate.[131] The rearrangement is caused by groups present in the dispersion agent or solvent molecules that give rise to permanent (or induced) dipole moment, which promotes charge transfer between the adsorbate and the CNT changing the electronic structure of the tubes. This issue has received little attention so far. Yoon *et al.*[132] were the first to perform experimental and theoretical (*ab initio* methods in the DFT–LDA approximation) studies of the adsorption behaviour of dispersion agents, partial charge transfer and the electronic properties of the tubes in the single-walled CNT–chlorine oxoanion system with chlorine atoms in various oxidation states. The authors attempted to rearrange the electronic structure of the CNT by means of the adsorbate. The results indicate that such rearrangement is possible. It was shown that single-walled CNT with metallic conduction dispersed in *N*-methylpyrrolidone (NMP) are oxidized with sodium perchlorate even when it is present in low concentrations, whereas semiconductor tubes are markedly oxidized only by high concentrations of the salt, minor physical sorption of the salt being also observed. The sorption of salts containing a chlorine atom in low oxidation state (in particular, sodium hypochlorite) occurs, conversely, as chemisorption, the tube being doped by electrons. The rearrangement of the electronic structure of the tubes affects their conductivity and is manifested as intensity changes and shifts of Raman bands.

Also, the possibility of rearranging the electronic system of single-walled CNT in the desired direction by selecting the core of the solvent molecule and electron-withdrawing or electron-donating groups in it (aromatic compounds:

aniline, benzene, nitrobenzene, or aliphatic compounds: butylamine, hexane, nitromethane, *etc.*) was demonstrated experimentally for the first time.[133] Since with the use of dispersing agents, the effect of the solvent nature is often debated, the solvent effect was determined in the absence of surfactants. Aromatic solvents have much greater influence on the electronic structure of the tube than aliphatic solvents. Electron-withdrawing groups readily withdraw electrons of the metallic-conducting tubes and only slightly withdraw them from the semiconductor single-walled CNT. The change in the electronic structure of the tube under the action of surfactants may result (and actually results) in a considerable increase in the tube conductivity. This approach markedly increases the efficiency of adsorbates by selecting an appropriate solvent.

Due to the exceptional sensitivity of the conductivity to the operation conditions of CNT, the dependences of the conductivity on the temperature, UV irradiation or treatment with oxygen have been studied.[134] Research into the transporting properties of CNT is not only due to the hope for future applications; even today single-walled CNT operate better than the traditional IR-transparent conducting materials.[135]

For successful use of electronic properties of CNT, tubes of some particular type of conduction are needed; however, most of synthetic procedures afford mixtures of CNT with different types of conduction. One method of separating tubes according to their type of conduction is dispersing them by a chloroform solution of tetramethylenesulfone and nitronium tetrafluoroborate. The latter reagent dissociates to BF_4^- and NO_2^+ ions. In a study of adsorption of the resulting anions and cations on the surface of CNT of both conduction types, Cabria *et al.*[136] elucidated some subtle details of the adsorption mechanism of separation and interpreted the experimental results obtained previously.

Selective interaction of single-walled CNT suspended in NMP with covalently modified silica surface was also used for separation.[137] Semiconductor tubes are sorbed on the surface with amino groups, while metallic-conducting tubes are sorbed on the surface with phenyl groups.

In some publications, it was stated that effective dispersion of single-walled CNT is possible without using surfactants: a 'solution' of individual tubes (c_{CNT} of up to 30 μg ml^{-1}) was obtained only by sonication of a suspension in NMP.[137]

Solubilization of CNT without the use of traditional surfactants has been reported.[138] It was shown that in the presence of dibenzo-18-crown-6 and under the action of Na amalgam, single-walled CNT form complexes $[Na(dibenzo\text{-}18\text{-}crown\text{-}6)]_n$–CNT, which are readily soluble in CH_2Cl_2 and DMF and noticeably soluble in hexane, toluene and alcohols.

As an alternative to organic dispersing agents, mixtures of multi-walled CNT with layered silicates have been proposed.[139] These mixtures obtained by grinding the components have a micellar structure and are readily soluble in water, DMF and ethanol. The researchers postulated and indirectly confirmed the possible mechanism of improvement of the dispersibility in the presence of silicates. The considered mixtures (c_{CNT} = 0.5 mass % – 2.0 mass %) inhibit the combustion of polymeric films made of polystyrene (PS), PMMA and PS–PMMA composite more efficiently than traditional fire retardant additives without impairing the mechanical properties of polymers.[140]

The distribution pattern of the surfactant molecules on the CNT surface is not entirely clear until now. Using the sodium dodecyl sulfate–single-walled CNT system as an example, small-angle neutron scattering data were obtained[141] that refute the views on the formation of cylindrical surfactant micelles with CNT being located along their axis. The formation of hemispherical micelles is also unlikely. In the authors' opinion, a random distribution of surfactant molecules on the tube surface is most probable.

In the case of non-covalent interactions, the nature of bonds between CNT and low-molecular agents, including surfactants, is not always clear. Therefore, any study that would clarify this issue is of interest. Leon *et al.*[142] theoretically studied binding of various amino acids, their salts and amides to single-walled CNT . Considering the calculations (*ab initio*, BLYP/DND–DFT) of electron densities, bond lengths and bond angles in the structures formed, the authors concluded that the components experience long-range dispersion interaction. It was shown that arginine, cysteine, alanine and asparagine form the most stable complexes with 'chair-like' single-walled CNT. However, the interaction energy with 'zigzag-like' tubes is rather low. Calculations of this type are useful for the understanding of the mechanism of formation of clusters of CNT and protein molecules.

It follows from the publications considered above that modification of CNT by surfactants not only destroys the aggregates and imparts 'solubility' but also changes the electronic structure and, hence, electroconductive, optical and luminescence properties of the tubes, thus extending the scope of their applicability. In addition, using surfactants, it is possible to separate CNT according to the type of conduction.

Nevertheless, when choosing the modification technique, one should bear in mind that each method has its advantages and drawbacks. Thus in many cases, surfactants efficiently mitigate the intertube interaction but cannot get into bundles. A possible alternative is chemical functionalization. However, some researchers think that functionalization methods such as treatment with strong acids (or arenediazonium salts) are too drastic. Strong oxidants not only destroy the end caps but also shorten the tubes, thus decreasing the aspect ratio. The more drastic the modification method, the greater the changes, more precisely violations, of the electronic structure of CNT up to destruction of the chain of conjugation.

Meanwhile, surfactant-induced dispersion of CNT results in some of their properties becoming rather sensitive to characteristics of the dispersion medium, and this may restrict the scope of applicability of such dispersions. In particular, this refers to photoluminescence of semiconductor single-walled CNT, which depends on the surfactant concentration, pH and contents of salts in buffer solutions.[119] Sonication can also result in CNT shortening and destruction, moreover, undesirable reactions between the tubes and the medium are possible.[143]

Selection of the CNT solubilization method depends on what properties are to be imparted or improved in each particular case. Thus treatment with surfactants is inadmissible when CNT-containing materials are used to produce optoelectronic devices by conventional technology. Urbina *et al.*[144] refused the use of surfactants and preferred esterification of single-walled CNT carboxylated at the ends by successive reactions with thionyl chloride and n-pentyl alcohol. This allowed them to obtain stable dispersions in toluene with tube concentrations of up to 3.6 mg ml^{-1}. Interesting results were obtained upon comparison of the

dispersibilities and conductivities of multi-walled CNT in a silicone elastomer after treatment of the tubes with surfactants (hexadecyltrimethylammonium bromide) and after chemical grafting of γ-aminopropyltriethoxysilane (APTES).[122] Both treatment procedures produce stable dispersions but the CNT–surfactant and CNT–APTES pairs exhibit different transport properties and unequal sensitivities of the conductivity to temperature and pressure. By combining these two dispersions in different ratios, it is possible to control the electric properties of the composite.

Highly luminescent suspensions of individual single-walled CNT stable at pH from 1 to 11 and in buffers with high salt concentrations were prepared by combining CNT pre-suspended by traditional surfactants with polyvinylpyrrolidone, which can be obtained by *in situ* polymerization of the monomeric vinylpyrrolidone on the surface of single-walled CNT–surfactant micelles.[119]

An original, according to researchers' opinion, method of using surfactants for the preparation of homogeneous stable suspensions of individual single-walled CNT in polar solvents was proposed.[145] The process consists of three stages: (i) dispersing of CNT in water containing cetyltrimethylammonium 4-vinylbenzoate (cationic surfactant) with a polymerizable counter-ion; (ii) fixing a surfactant monolayer on the CNT surface by *in situ* free-radical polymerization of the counter-ions without covalent bonding between the surfactant and the tube surface; (iii) freeze-drying of the dispersion to give a treated single-walled CNT powder. After completion of the second stage, the tubes are readily dispersed in water and lower alcohols (up to n-butyl alcohol); the powder obtained after the third stage is also readily dispersed in the same solvents without formation of aggregates and networks. However, note that this procedure resembles the procedure for the preparation of single-walled CNT–polyvinylpyrrolidone composition published previously,[119] which was not accompanied by covalent binding of the modifying agent either.

III. Modification of carbon nanotubes by polymers. First-group polymeric nanocomposites

As noted in the Introduction, modification of CNT by polymers is the way for preparing first-group nanocomposites in which nanotubes are the major component and the polymer serves as the modifying agent affecting their characteristics. These nanocomposites can be formed both through covalent and non-covalent bonding of macromolecules to the CNT; they are meant for the use in medicine, biology, instrument making, chemical engineering, and for the manufacture of second-group composites.

1. Functionalization by polymers

Covalent binding of CNT to macromolecules is often performed using nanotubes functionalized by low-molecular compounds.

a. Water-soluble polyesters

The poly(ethylene glycol) (PEG) macromolecules with different molecular masses were [146] attached by covalent bonds to multi-walled CNT having OH groups on the surface (toluylene diisocyanate as the coupling agent). Nanocomposites were employed to prepare inclusion complexes with α-cyclodextrin, which are of interest for biomedical applications.

The addition of amines to CNT described above was used for functionalization of single-walled CNT by PEG oligomers with terminal amino groups.[41] It was found that the kinetics of this reaction is sensitive to the tube diameter. This allowed fractionation of tubes according to their diameters by repeated treatment of the initial mixture with oligomers with separation of the soluble and insoluble components in each stage. The nature of single-walled CNT (metallic or semiconductor type conduction) does not affect the fractionation.

It was shown[147] that water-soluble single-walled CNT with grafted PEG can bind compounds containing π-conjugated aromatic structures, in particular the antitumour drug doxorubicine, and fluorescein. The amount of the bound reagent can be controlled by varying pH. However, the strength of π-complexes depends on the tube diameter, which allows one to control the reagent release rate by selecting the appropriate fraction of the tubes. This can also be used for so-called fractionation by functionalization.

A simple method of covalent modification comprising esterification of carboxylated multi-walled CNT by the reaction with PEG in the presence of dicyclohexylcarbodiimide has been proposed.[148] The tubes obtained in this way were used as the base for highly sensitive selective gas sensors.

Among the studies on modification of multi-walled CNT containing carboxyl or acyl chloride groups by functional polymers or oligomers, noteworthy is their treatment with poly(ethylene oxide) (PEO) with one terminal amino group.[149] The composites thus formed contain up to 40% PEO and are readily dispersible in polar solvents, in particular, in water, methanol and DMF, their characteristics depending only slightly on the molecular mass of PEO (from 1000 to 2000) and on the nature of the initial functional groups [C(O)OH or C(O)Cl].

Yu *et al.*[150] grafted various heterochain aliphatic polymers with terminal hydroxyl groups containing carbonate groups in the backbone to chloroacylated multi-walled CNT. Of the four different polycarbonates, only one copolymer, poly(propylene oxide)(carbon dioxide)(ε-caprolactone) proved to be suitable for the preparation of a water-soluble composite with multi-walled CNT. It is planned to investigate the resulting nanocomposites as regards their possible use for the development of water-soluble pharmaceuticals.

b. Biopolymers

As a sorbent for affinity chromatography of proteins, in particular, for purification of immunoglobulin G, multi-walled CNT functionalized in the following way were proposed. After purification, the tubes were treated with APTES and then the amino groups were amidated with succinic anhydride, being converted to carboxyl groups to which protein A capable of reversible binding of antibodies was attached either directly or through additional linkers.[151]

Direct covalent bonding of the enzyme to the multi-walled CNT surface has been considered [152] in relation to the self-catalyzed esterification of the carboxylated tubes by lipase. The resulting biocomposite is readily soluble in common organic solvents (tetrahydrofuran, dimethylformamide, chloroform); it may be useful in biocatalysis and for the design of biosensors.

A composite based on multi-walled CNT bearing a covalently attached bis(diphosphine)nickel-containing active site that models the hydrogenase active site has been reported.[153] This composite exhibited high catalytic activity being used as the cathodic material in proton-exchange

membranes both in the reduction of hydrogen ions in dilute sulfuric acid and in hydrogen oxidation, ensuring current densities similar to those observed for materials based on hydrogenase.

c. Dendrimers

The reaction of amino-group-containing single-walled and multi-walled CNT with second-generation dendrimers based on carboxyl-containing cyanodiphenyl gave covalent CNT–dendrimer nanocomposites capable of further modification through transformations of numerous terminal nitrile groups (Scheme 10).[154] Amino groups on the nanotube surface were formed by 1,3-dipolar cycloaddition of azomethine ylides obtained *in situ* by condensation of α-amino acid containing a protected amino group with formaldehyde and subsequent deprotection. The authors state that this way of modification disturbs the electronic system of CNT to the least extent. The degree of dendrimer grafting on the multi-walled CNT was much higher than on single-walled CNT.

Modification of carboxylated CNT by grafting a polyamidoamine dendrimer increases the solubility of CNT, especially in water, due to numerous terminal amino groups.[155] The tubes modified in this way were used for the design of highly sensitive two-enzyme biosensors for detecting microconcentrations of glucose.

The synthesis and properties of multi-walled CNT–polycationic dendrimer nanohybrids suitable for complexing with pharmaceutical agents were described.[156] These complexes can serve for drug delivery to the cells.

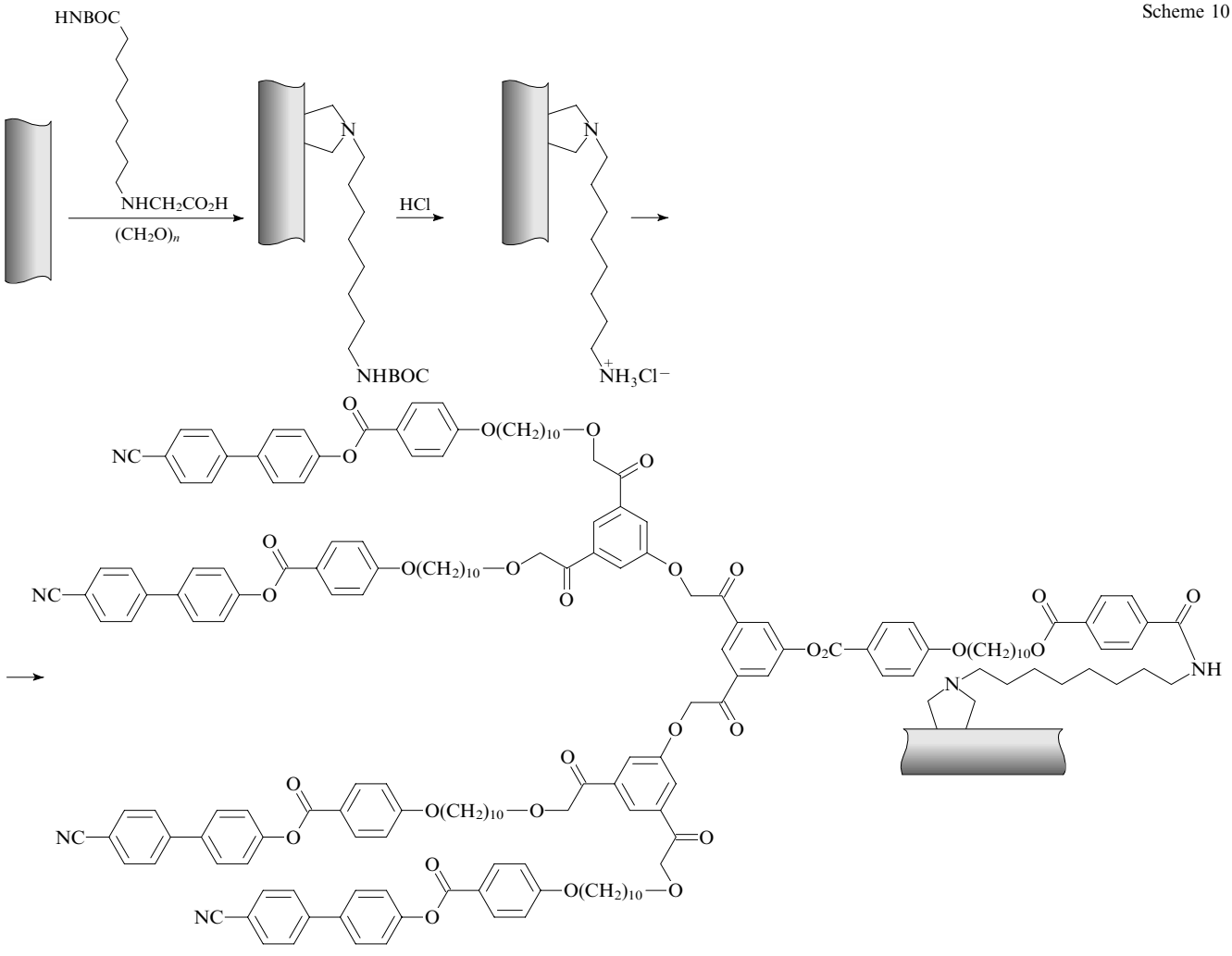
d. Miscellaneous polymers

Effective modification of carboxylated multi-walled CNT is attained by their amidation with hexamethylenediamine followed by the reaction with sulfonated poly(ether-ether-ketone).[157] It was shown by spectroscopy and transmission electron microscopy that after treatment, multi-walled CNT are coated by a polymer layer linked by covalent bonds.

To prepare multi-walled CNT networks suitable for the use in electronic circuits, the carboxy groups of oxidized tubes were converted to acyl chloride groups and then treated with polyamines obtained by the reaction of 1,2-diaminopropane with alternating polyketones.[158] Up to 40% of polyamine can be grafted onto multi-walled CNT in this way. Being cross-linked, the products are poorly soluble in water and organic solvents, unlike the products of treatment with low-molecular diamines.

Effective Pt-based catalysts supported on the surface of multi-walled CNT functionalized by thermally initiated free radical polymerization of 3-ethyl-1-vinylimidazolium tetrafluoroborate were recommended for electrocatalytic oxidation of methanol.[159] The ionic polymer introduces a large number of positively charged evenly distributed functional groups on the tube surface. They prevent CNT from aggregation, promote the formation of their stable dispersions in water and homogeneous distribution, stabilization and binding of platinum nanoparticles to the tubes.

Scheme 10



Carbon nanotubes can be not only the objects of modification by polymers or oligomers; they can also function as the active component of the reaction mixture. For example, Liu and co-workers[160] demonstrated that single-walled and multi-walled CNT can serve as templates for regioselective oxidative polymerization of phenol in water in the presence of peroxidase. This affords oligomers with $M_n \approx 2000$ and polydispersity index of 1.3–1.6 containing ~90% of thermally stable poly(phenylene) structures (POP). The oligomer yield increases upon increase in the CNT concentration and enhancement of their ability to be solvated by phenol, in particular, on passing from non-functionalized multi-walled CNT to hydroxylated or carboxylated tubes. In addition, the yield of oligomers is higher for single-walled CNT than for multi-walled ones. In the same publication, hydroxyphenyl derivatives were obtained by the reaction of carboxylated multi-walled CNT with hydroquinone; the resulting tubes participated in the oxidative polymerization of phenol to give tubes with grafted oligophenol chains. It was found that nanotubes markedly affect the thermal stability of POP: the most intense destruction of POP-linked tubes during thermogravimetric analysis took place at ~640 °C, while in the case of free POP this occurs at 594 °C.

Apart from experimental studies, the covalent bonding of polymers to CNT was simulated theoretically. In particular, the interaction of three-walled CNT with a 'vinyl ester epoxy polymer' was investigated by molecular mechanics techniques. The mechanical properties of the composite were calculated, and it was found that covalent bonding of the polymer induces substantial redistribution of the load applied to the matrix, especially if the load is applied in the direction normal to the tube axis.[161]

It was shown by molecular dynamic simulation that an increase in the number of chemical bonds between the vertical positioned nanotubes and the silicon substrate as well as a decrease in the chain lengths of functional groups entail an increase in the interfacial adhesion and an increase in the interfacial heat conductivity.[162] Using the same method, Byrne *et al.*[163] found that multi-walled CNT are preferred over single-walled CNT for nanocomposite reinforcement because their properties are less sensitive to the size of wall defects and for the same defect sizes, they have higher strength.

2. Non-covalent modification

a. Water-soluble polymers

Aqueous suspensions of isolated semiconducting single-walled CNT obtained by dispersion in the presence of SDBS were stabilized by adding either PVP or the polymer obtained by polymerization of vinylpyrrolidone on CNT–surfactant micelles without formation of polymer–CNT covalent bonds.[119] The individual character of single-walled CNT in their stable dispersions, which show high-intensity luminescence over a broad pH range, was established using luminescence spectra, atomic force microscopy and transmission electron microscopy.

Dispersions in alcohols of isolated single-walled CNT coated by a polymeric shell without formation of covalent bonds were prepared[145] from dispersions of CNT in water in the presence of cetyltrimethylammonium 4-vinylbenzoate followed by free-radical polymerization. The solubility was due to hydrogen bonds between the solvent and the polymeric monolayer on the nanotube surface. The absence of covalent bonds between the polymer and the CNT surface is supported by invariability of the near-IR absorption spectra.

A water-soluble PEG oligomer (molecular mass ~2000) was used to impart hydrophilicity to single-walled CNT as a result of non-covalent bonding.[164] First, terminal hydroxyl groups of the oligomer were replaced by amino groups in several steps. One amino group was used to attach pyrenecarbaldehyde. The resulting α-amino-ω-pyreno-oligoethylene oxide efficiently solubilizes single-walled CNT by interaction of π-electron systems of the pyrene group and the tube. The energy of this interaction was estimated (9.7 kcal mol^{-1}). However, the equilibrium constant calculated on the basis of this value (1×10^7 litre mol^{-1}) is obviously overestimated, as the entropy constituent of the free energy was neglected. The terminal amino groups of the oligomer sorbed on single-walled CNT were used for covalent bonding to the modified protein envelope of the tobacco mosaic virus; this gave CNT–biopolymer hybrids capable of forming self-assembling structures arranged in parallel. The light-harvesting capsids of the virus attached to single-walled CNT are meant for the use as bridging electrodes in the hybrid photovoltaic materials.

The multi-walled CNT treated, after oxidative carboxylation, with a water-soluble polymer, poly(2-ethyloxazoline), in ethanol solution and then sonicated are distinguished by good dispersibility in water, ethanol and DMF.[165] The composite contains up to 15% of the polymer. According to a transmission electron microscopy examination, the diameter of the tubes after enveloping by the polymer increases by 10 nm.

Pluronic type block terpolymers, PEO–poly(propylene oxide) (PPO)–PEO, having a lower critical temperature of water solubility show a peculiar behaviour in the presence of CNT.[166] Hydrophobic PPO blocks of the terpolymer can be selectively sorbed on the CNT surface. The self-association of block terpolymers that takes place when the solution temperature is raised above the lower critical temperature results, in the presence of single-walled CNT of diameter ~1 nm, in enveloping of individual nanotubes by a polymer coat giving rise to micelle-like structures. Meanwhile, multi-walled CNT of diameter ~20 nm are unable to form hybrid structures of this type (as found by differential scanning calorimetry).

Polymer molecules adsorbed on the tube surface can function as bridges between CNT and inorganic materials. Thus PVP and PS–PVP block copolymers connect single-walled CNT (or C_{60} fullerene) to SiO_2 and TiO_2 to give ternary organic-inorganic hybrid nanocomposites obtained *in situ* by sol–gel polycondensation of tetraethoxysilane and tetraethoxytitanium, respectively.[167] These composites are of interest as solid catalysts.

b. Conductive polymers

Polythiophenes are very good dispersion agents for single-walled CNT. In particular, polythiophene containing hexafluoro(hydroxy)isopropyl substituents in position 3 of the thiophene ring (HFIP-PT) was used to create the HFIP-PT–CNT hybrid system. The conductivity of the films formed from this system sharply decreases in the presence of dimethyl methylphosphonate (DMMP) vapour, which simulated the chemical war gas sarin, and is little sensitive to the presence of vapours of 'usual' organic compounds.[168] This system was proposed for the design of highly sensitive, inexpensive selective chemiresistive sensors for the detection of some chemical warfare agents.

The morphology, electrochemistry and electrochromism of thin films of the multi-walled CNT–polythiophene nanocomposites where the polymer was obtained *in situ* by

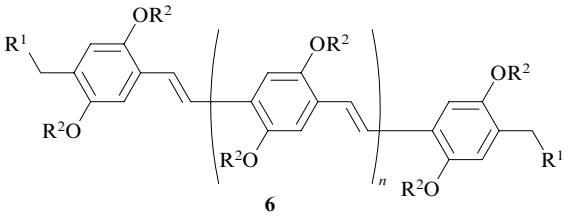
oxidative electropolymerization of 3,4-ethylenedioxythiophene were studied.[169] Due to the strong electrostatic interaction of the porous film framework and the CNT, the polymer macromolecules coat the tubes. In the filled films, the rate of electropolymerization increases and higher electrical conductivity, higher rate constants for redox reactions and enhanced optical properties are observed.

Poly(3-octylthiophene) effectively solubilizes single-walled CNT carboxylated at the ends.[170] The tubes modified in this way are selectively sorbed on the In–Sn oxide surface under conditions of electrophoresis to give structured films having high field emission characteristics.

For the development of effective and readily available photovoltaic devices, a composite was proposed based on poly(3-hexylthiophene) (PHT) and a complex of carboxylated and sulfonated single-walled CNT with C_{60} fullerene.[171] Fullerene proved to be an efficient reagent that forms a layer adsorbed on the tube surface upon microwave irradiation of a CNT suspension. The formed single-walled CNT–C_{60}–PHT composite has a higher conductivity than the C_{60}–PHT composite.

The ability to disperse single-walled CNT in water much exceeding this feature of standard surfactants was shown by amphiphilic oligothiophene-terminated PEG.[172]

The interaction of the π-electron systems of conductive oligomers, oligovinylenephenylenes (**6**, OVP)



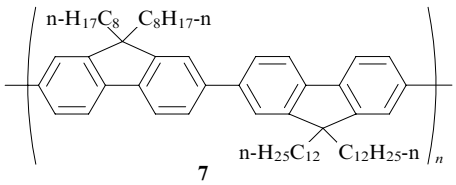
6

R^1 = OH, OC(O)Me, OMe; R^2 = n-$C_{16}H_{33}$.

with CNT gives rise to OVP–CNT composites solubilized in toluene.[173] A solution of OVP in toluene (~10 mg ml^{-1}) forms thixotropic mechanically unstable gels at temperatures below 55 °C; as the concentration decreases by an order of magnitude, the critical gelation temperature decreases by 10 °C. The introduction of single-walled or multi-walled CNT into a solution of OVP in toluene facilitates the self-association of the oligomer, which is manifested as an increase in the critical gelation temperature. Stable hybrid gels appear as a result of formation of a common π-electronic system of individually dispersed CNT, OVP and solvent. The formation of composites was confirmed by spectroscopy. The tubes homogeneously distributed in the gel promote the formation of supramolecular 'ribbons' of OVP and CNT. High aspect ratio and electronic properties of CNT are retained. The stable oligomeric gel is supposed to be used in optoelectronic systems.

The same expedient — the use of strong π-electron interaction between CNT and OVP containing hydrocarbon tails C_8, C_{12} and C_{16} — was utilized to produce a superhydrophobic self-cleaning composite coating. The composite is readily dispersed in organic solvents and can serve to impart hydrophobicity (the wetting angle reaches 162–164°) to glass, metal and mica surfaces.[174]

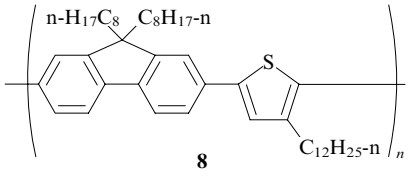
One of the most interesting electroactive conjugated polymers is poly(9,9-dialkylfluorene) (**7**, PF), which has good transport properties, solubility, stability, intense blue fluorescence and simple preparation.



7

M_n = 9000.

It is used as a component in thin-film transistors, light emitting diodes, photovoltaic devices. Poly(9,9-dioctylfluorene-*co*-3-dodecylthiophene (**8**, FTC) containing electron-excessive thiophene and relatively electron-deficient fluorene units in the backbone is also of interest for its conductivity.



8

M_n = 15 000.

Both PF and FTC have rather efficient systems of conjugation needed for strong supramolecular bonding to the CNT surface.[175] The resulting discrete complexes of single-walled CNT with these polymers have excellent solubility in organic solvents in the presence of excess free polymer (c_{CNT} = 0.5 mg ml^{-1} at a polymer concentration of 1.5 mg ml^{-1}); after removal of excess polymer, the solutions are stable for a month. Presumably, macromolecules destroy the CNT aggregates to individual tubes and uniformly coat their surface. Thin films cast from these solutions have high conductivity, which is indicative of rather strong interaction between single-walled CNT and the polymer. They were recommended for the use in electronic recording devices.

A series of new block copolymers including poly[4-(9,9-dihexylfluoren-2-yl)styrene-*block*-poly(2-vinylpyridine)] and poly[4-bi(9,9-dihexylfluoren-2-yl)styrene-*block*-poly(2-vinylpyridine)] with variable molecular mass and fluorene chain length were proposed as dispersing agents for carboxylated single-walled CNT. Their morphology and self-assembly ability were studied.[176]

Hydroxylated ('anionic') single-walled CNT are sorbed from an aqueous dispersion on the poly(ethylene terephthalate) surface bearing the cationic polymer, poly(2-acryloyloxyethyltrimethylammonium chloride), pre-grafted by photopolymerization.[177] As a result of anion–cation interaction, single-walled CNT, being arranged parallel to the surface, form a thin transparent film, and the surface conductivity increases by almost two orders of magnitude. Non-covalent nature of bonding of single-walled CNT with the polymer surface was demonstrated by transmission electron microscopy, atomic-force microscopy and Raman spectroscopy.

A CNT network formed upon electrophoresis with adsorbed polypyrrole was recommended as a detector for a micro-gas chromatograph based on a microelectromechanical system.[178] The detector sensitivity proved to be sufficient for detecting 150 ppm of DMMP.

c. Polyelectrolytes

Nanohybrids readily 'soluble' in water (316 mg litre^{-1}) and miscible with other materials[179] were prepared by mere mixing of multi-walled CNT with polyelectrolytes, which

envelope CNT as a result of $\pi-\pi$ interaction. Polyelectrolytes were obtained by treatment of neutral polymers of highly polar phenylacetylene derivatives (ethynylaniline, ethynylbenzoic acid, *etc.*) with acid or base. These composites can be used as 'platforms' in the manufacture of multi-walled films for immobilization of biomolecules on CNT and preparation of nanotubes decorated by various nanoparticles, in particular metals and metal oxides.

Multi-walled CNT coated by a polyelectrolyte, poly(diallyldimethylammonium chloride) (PDDA), are effectively dispersed in aqueous solutions of salts (owing to Coulombic repulsion of the ammonium cations located on the surface); such dispersions can be used for the formation of platinum nanoparticles of diameter $\sim$1.8 nm on the tube surface.[180] Non-covalent functionalization of tubes with PDDA markedly increased the catalytic activity of platinum applied thereon toward electrooxidation of methanol in fuel cells as compared with the catalysts based on usual oxidized multi-walled tubes.

A simple method of preparation of composite nanofibres by self-assembly from the complexes of single-walled (or multi-walled) CNT and polyelectrolytes such as polystyrene sulfonate, PDDA, and biopolymers — chitosan, poly(L-glutamic acid) — was described for the first time.[181] The nanotubes are dispersed in polyelectrolytes as a result of non-covalent enveloping by polymers. Owing to the CNT network incorporated inside the fibres, they acquire interesting mechanical, chemical and electric properties; these fibres were recommended for the use in flexible electronics, biosensors, chemical electrodes.

d. Biopolymers

A CNT surface can adsorb diverse polymers, including biopolymers. Considerable interest in the interaction of the latter with CNT is related to investigations of the effect of nanotube-containing materials on biosystems, in particular, on the human organism.

An effective dispersing agent for individual single-walled CNT in water is DNA.[182–184] Stable aqueous dispersions in which separate tubes wrapped around by single-stranded [182] or double-stranded [183] DNA incapable of aggregation were prepared by sonication of CNT in the presence of DNA. The authors specially noted that in the DNA–CNT complexes (various oligonucleotides with 30 to 60 units were used), the electronic structure of the tubes (and, hence, their electronic characteristics) considerably change as compared with the CNT structure in dispersions in the presence of SDBS.[182] The new nanosystem can be used to improve the characteristics of field-effect transistors and chemical sensors and to produce a material with tunable fluorescence parameters. Wrapping by single-stranded helical DNA is promising for fractionation of tubes according to length and diameter.

D'yachkov *et al.*[185] investigated in detail the dependence of complexation of single-stranded DNA with CNT on the nucleotide composition of DNA and the tube diameter (molecular docking).

It was shown [186] that near-IR absorption and photoluminescence spectra of individual single-walled CNT dispersed in an aqueous solution of double-stranded DNA change crucially upon slight changes in the solution pH.

The ability of DNA to envelope CNT and thus to efficiently solubilize them was interpreted in the literature.[187, 188] The authors showed that nucleic bases (guanine, adenosine, thymine, cytosine and uracil) are sorbed on the surface of single-walled CNT; this is accompanied by pronounced shifts of the G-mode in the Raman spectra to lower frequency by 0.7–1.3 cm^{-1} for metallic-conducting nanotubes and by 2.1–3.2 cm^{-1} for semiconductor nanotubes. Using quantum chemical calculations (MP2 and DFT), the interaction energy between the base molecules and the single-walled CNT surface was estimated as tens of kilojoules per mole. Presumably, the interaction of nucleic base fragments incorporated in DNA strands with the CNT surface cannot be as efficient as that of free molecules, due to steric hindrance, but cooperative effects that accompany sorption of relatively long macromolecules should counterbalance this loss. In addition, in some cases, the secondary structure of DNA may be retained after attachment to the CNT surface. Gong *et al.*[189] used thionine as the mediator for attaching DNA. The nanocomposite thus formed was used in the design of highly sensitive and stable electrochemical biosensors.

An unusual feature of DNA–single-walled CNT suspensions was discovered, in particular, a 4500-fold acceleration of oxidative polymerization of 3-aminophenylboronic acid hydrogensulfate to give ternary nanocomposite *in situ*.[190]

Deoxyribonucleic acid was used to purify single-walled CNT by solubilization and for the subsequent formation of oriented layers of tubes on solid substrates, in particular, on gold.[191]

Interesting results were obtained in a comparison of the behaviour of aqueous 'solutions' of single-walled CNT obtained by means of DNA (double helix containing 30 alternating guanine and thymine pairs) and THF 'solutions' of single-walled CNT with covalently grafted n-butyl- and n-octadecylamine (ODA) derivatives (size exclusion chromatography with refractometric and viscometric detectors, small-angle neutron scattering and atomic force microscopy).[192] It was found that sonication during dispersion results in crushing of a large portion of CNT into short fragments, so that the lengths of single-walled CNT that have passed through a chromatographic column range from tens to thousand nm. From analysis of the dependences of viscosity on the molecular mass and parameters of atomic-force microscopy, it follows that single-walled CNT–DNA structures can be classified, in view of their characteristics, as flexible rods, whereas the single-walled CNT–butylamine derivative pair forms branched structures, and the single-walled CNT–ODA system forms structures that resemble tight spheres.

A review [193] dealing with covalent and non-covalent modification of nanotubes with DNA considers the properties of modified CNT and unique characteristics of biosensors manufactured using these CNT.

A brief review [194] gives experimental and calculated data on non-covalent interaction of DNA and proteins with non-functionalized CNT over the years from 2000 to 2005 as well as the authors' results of studies of conformational changes of a number of biopolymers, including DNA, upon the reaction with single-walled CNT. The observed structural rearrangements in proteins indicate that they are bonded to the tubes through hydrophobic interactions and overlap of π-systems (π-stacking interactions).

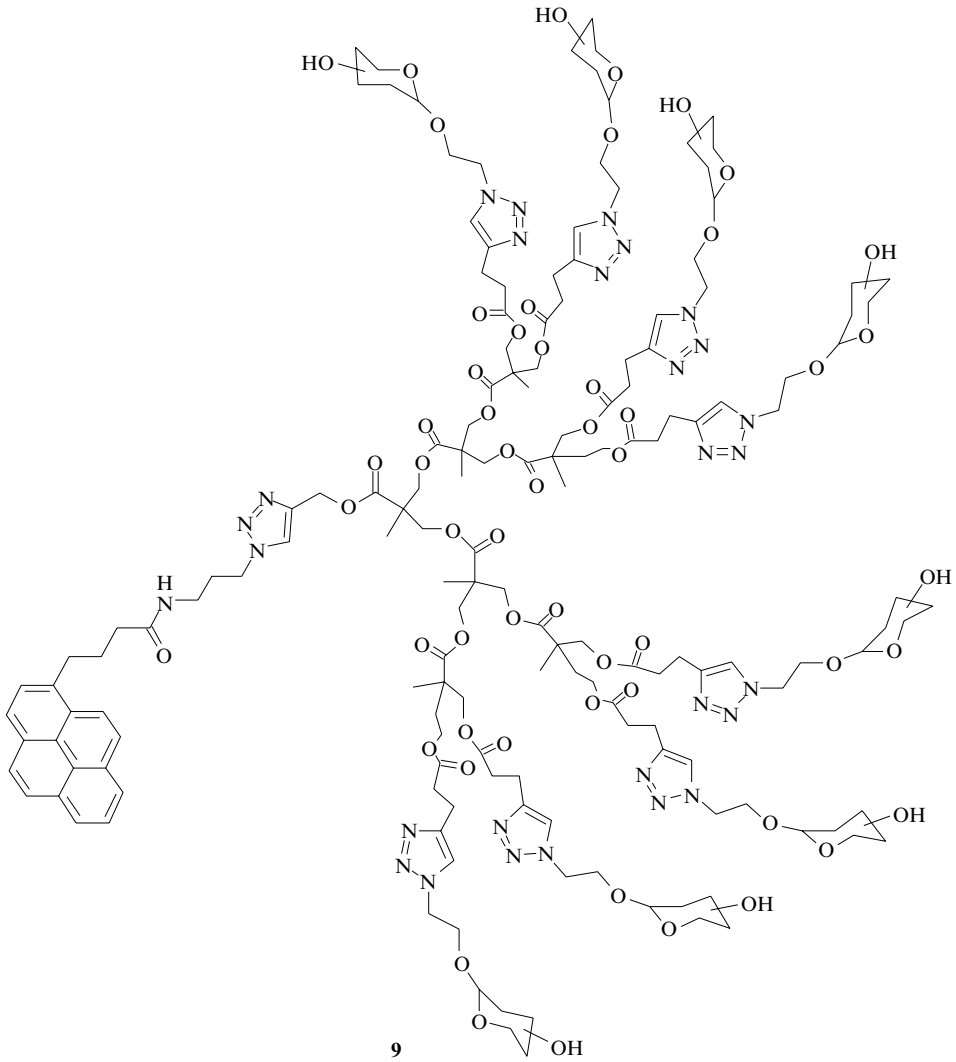
Not only DNA but also other biopolymers, in particular, chitosan,[195] dextrans, can form complexes with CNT.[196, 197] The results of spectral, calorimetric and rheological studies of such systems attest to the formation of single-walled CNT–polysaccharide clathrate complexes. Unlike DNA molecules, which are wrapped around CNT, polysaccharides form a cylindrical clathrate lattice by

means of intra- and intermolecular hydrogen bonds of the hydrophilic part of the macromolecule; the inner hydrophobic cavity of this lattice serves as the host for hydrophobic nanotubes. These observations were confirmed by molecular mechanics calculations for the dextran–single-walled CNT system. The mentioned complexes are formed upon stirring of aqueous solutions of polysaccharides with single-walled CNT either without or with sonication of the mixture over a period of only 30 min.[196, 197] This confirms the crucial role of thermodynamic factors for the non-covalent solubilization of CNT and the equilibrium nature of these processes.

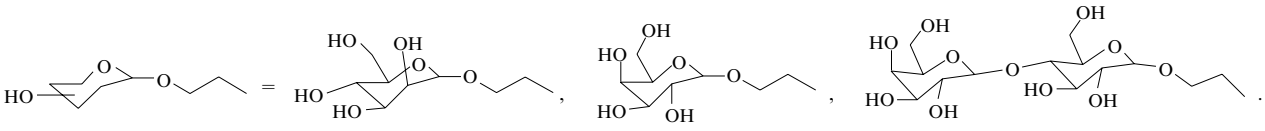
Peptides were proposed as non-covalent modification agents that are suitable for dispersing single-walled CNT to the state of individual tubes.[198] These oligomers with specially selected amino acid sequences can show selectivity with respect to solubilization of tubes with different diameters. Upon this treatment, the electronic properties of single-walled CNT are not changed. By using peptides containing cysteine residues, it is possible to prepare suspensions (their stability does not depend on the peptide concentration) through cross-linking of neighbouring peptide molecules upon oxidation of the thiol groups to disulfide groups and formation of high-molecular polymeric shell on the CNT surface.

Sodium lignosulfonate (SLS), a biopolymer obtained in the manufacture of cellulose, was proposed for non-covalent functionalization of multi-walled CNT.[199] The multi-walled CNT–SLC composite prepared by grinding is water soluble up to a concentration of 1.5 mg ml^{-1} in relation to multi-walled CNT; the suspensions are stable for three months. It is assumed that the polymer envelopes the tubes through $\pi-\pi$-stacking and hydrophobic interactions, and the anionic nature of the polymer leads to electrostatic repulsion of likely charged particles. On the surface of these composites in aqueous medium, it is possible to form *in situ* uniformly distributed 4–6 nm SnO_2 and CdS quantum dots. The results on the modification of CNT by various biopolymers were summarized in a review.[200]

In order to use single-walled CNT for medico-biological purposes, it is necessary to reduce their cytotoxicity. For solving this problem, a homogeneous bioactive coating of glycodendrimers containing a pyrene group in the tail unit (**9**) was proposed. Second- and third-generation glycodendrimers with terminal groups based on galactose, lactose and mannose are adsorbed on the surface of single-walled tubes under sonication of an aqueous solution of CNT.



9



Adsorption is due to the interaction of the π-systems of the pyrene tails and the tubes.[201]

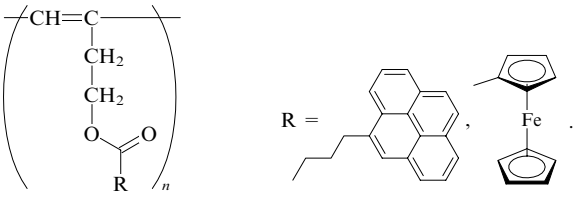
Dispersions of the tubes coated by a thin uniform dendrimer layer are stable for several months. The growth rate of the human embryonic kidney 293 cells is sharply decelerated in the presence of non-modified tubes as compared with that in the absence of tubes. Meanwhile, glycodendrimer complexes with single-walled CNT have almost no effect on the cell growth rate.

A publication [202] is devoted to the study of adsorption of natural organic matter on the surface of multi-walled CNT. The adhesion and formation of a stable dispersion of multi-walled CNT in water are determined by the nature, the molecular mass and concentration of the material, water quality and concentration of the tubes.

A review by Zhao and Stoddart [203] considers non-covalent modification of single-walled CNT by biomacromolecules, conductive polymers, dendrimers and low-molecular aromatic compounds and gives a brief account of the achievements (up to 2008) in the preparation, determination of characteristics and applications of new hybrid materials.

e. Miscellaneous polymers

Poly(alk-1-ynes) with pyrene and ferrocene pendants are excellent solvating agents, which make single-walled CNT 'soluble' in common organic solvents.[204]



The following mechanism of solubilization was conceived:[204] owing to the electronic interaction between the polyaromatic pendants and the CNT surface, the polymer chains are successively attracted to, stick to and wrap around the tube. Then the first macromolecules that have got on the CNT surface attract the next molecules due to the interaction between their aromatic fragments. Finally, this gives a thick coating. Deaggregation of CNT by polymers is much more efficient than by the corresponding monomers. Obviously, a considerable role is played by the cooperative nature of interactions of polymer macromolecules with the CNT surface.

Stable dispersions of oxidized multi-walled CNT in methyl methacrylate were obtained using oligomeric and branched polymethacrylates as stabilizing agents.[205] Di- and triblock copolymers such as PMMA – poly(n-butyl acrylate) (PnBA) and PMMA – PnBA – PMMA in a 2-ethylhexan-1-ol solution form micelle-like aggregates around single-walled CNT, which facilitates the formation of stable CNT dispersions.[206] A considerable part of single-walled CNT was dispersed to individual tubes. Dispersions stable at room temperature for several months lose stability at temperature of >40 °C; however, these changes are reversible.

Chang *et al.*[207] were the first to prepare triple nanohybrids by non-covalent assembly of the CNT – block copolymer [PS – *block*-poly(2-vinylpyridine)] system with subsequent immobilization of gold nanoparticles obtained by growth *in situ* on the walls and inside the nanotube.

Non-covalent *in situ* enveloping of multi-walled CNT by a polymer is attained during the synthesis of polyimides (PI) in a DMF solution.[208] The presence of π – π-stacking between the PI imide groups and benzene rings with the 'graphene' lateral walls of the CNT was demonstrated.

3. Characteristic features of non-covalent modification of carbon nanotubes by polymers

Analysis of the publications dealing with non-covalent modification of CNT by polymers considered in this Section confirms the conclusions of earlier studies (approximately from 2000) about the diversity of the CNT – polymer systems. This may be single- or multi-walled coatings of polymers whose adhesion to the tube surface is due to hydrogen and ionic bonds, π – π interactions, which are preferred over the forces that join the tubes to agglomerates. Note that non-covalent modification of CNT by low-molecular compounds is performed by means of the above-indicated bonds. However, in the case of modification by polymers, there are some specific features that were considered in a publication.[209] The authors used their own data, generalized the known results on the nature of forces that act between the components upon non-covalent modification of CNT by polymers, analyzed the results obtained by various molecular modelling techniques and different approaches to this problem and thus arrived to interesting conclusions. First, in dilute solutions of high-molecular compounds, a universal phenomenon of uniform adsorption and enveloping of CNT by polymer molecules of different flexibility was observed. Second, polymers solubilize tubes with larger diameter more easily, as opposed to low-molecular compounds, which form stronger non-covalent bonds with tubes of smaller diameter.

The adsorption of macromolecules, according to the data of Gurevich and Srebnik,[209] occurs successively. Having attached to one point on the surface, the polymer chain loses abruptly the ability to diffuse in the direction perpendicular to the tube axis but is still able to diffuse in parallel to the tube axis. Therefore, the macromolecule can move along the tube, being gradually twisted. The conformation change of the adsorbed site of the macromolecule depends on the chain rigidity and the tubes diameter, ranging from random conformations of flexible chains to fully helical conformations of rigid chains. In the authors' opinion, the views they developed could be useful for interpreting the experimentally observed features of enwrapping (enveloping) of tubes by polymers; they also pointed to the possibility to control this process.

An obvious feature of non-covalent modification of CNT by polymers containing numerous sorbable groups along the chain is the cooperative nature of this interaction; as a result, the polymer chain can be firmly held on the tube surface by the bonds that are much weaker than it is necessary for strong adsorption of non-covalently bonded compounds with few sorbable groups.

IV. Modification of polymers by carbon nanotubes. Polymeric nanocomposites of the second group

A promising recent line of research in the polymer and materials science is the design of polymeric nanocomposites with specified properties.[210, 211] There are two basically different ways for the preparation of polymeric composites containing nanoparticles:

— formation of nanoparticles inside the polymeric matrix (in block copolymers, dendrimers, nanoporous polymers, *etc.*) functioning as nanoreactors;[212]

— introduction of pre-formed nanoparticles into the polymeric matrix.

It is obvious that composites involving CNT can be formed only by the second route, the formation of covalent bonds between CNT and the polymeric matrix and physical binding of the tubes with the macromolecules being both possible.

1. Premises for the preparation of polymeric nanocomposites

The primary prerequisite for the preparation of polymeric nanocomposites is uniform distribution of CNT in the matrix. In the preceding Sections, we analyzed the ways of treatment of CNT that provide their dispersion and thus promote the formation of compositions with as uniform distribution of the tubes as possible. Knowing the factors that determine the distribution function and optimizing these factors, it is possible to produce most efficient composites. For example, for the single-walled CNT – urethane-acrylate copolymer system, by combining optical and electron microscopy, dielectric spectroscopy and Raman spectroscopy, and also computation methods, it was possible to determine the form of the CNT distribution function and to study the effect of 10 Hz and 1 kHz electric fields on this function.[213] The authors concluded that higher-frequency field facilitates a better distribution of CNT in the polymer. To evaluate the quality of distribution, the authors proposed measuring the electrical conductivity of nanocomposites, as this parameter is highly sensitive not only to the CNT preparation method and morphology, to the type of polymer and to the method of composite formation, but also, all other factors being the same, to the quality of dispersion in the polymeric matrix.

It was shown that the dependences of the conductivity of PS-based nanocomposites on the concentration of CNT of different origin are considerably different.[214] The limiting conductivity of the composites and the percolation threshold also vary as functions of the dispersion technique (with polyphenylenevinylene as a surfactant or by oxidation) and the tube diameter and aspect ratio. The conductivity of composites based on polyamide (PA) mixtures with the ABS rubber (acrylonitrile, butadiene and styrene copolymer) and with multi-walled CNT obtained by melt mixing was studied over a broad range of electric field frequencies (from 10^{-2} to 10^{6} Hz);[215] the frequency dependences of the conductivity were substantially different for the composites containing native and NH_2-functionalized CNT.

The second condition needed for full implementation of the CNT potential in a polymeric nanocomposite is interfacial interaction ensuring effective transfer of mechanical strain from the polymer to the tubes. In order to obtain composites with definite functional properties, it is necessary to know the CNT characteristics that affect the character of the adhesion interaction between the components. Earlier publications are mainly devoted to interactions of tubes of various lengths with polymers of various types, while the effect of chirality on this interaction barely received attention. Probably, Zheng *et al.*[216] were the first to demonstrate the relationship between adhesion of single-walled CNT to a PMMA-based matrix and the tube chirality. It was found that CNT with similar geometric parameters but a greater angle of chirality have higher bonding energies, while 'chair-like' CNT are the best type of tubes for mechanical reinforcement of PMMA. Since a number of properties (in particular, strength, conductivity, magnetic properties) of CNT and, hence, of the composites involving them depend on the chirality, the variation of this characteristics during the tube growth was studied in order to gain the possibility to control this parameter and to prevent its undesirable changes during the synthesis.[217]

Studies of the magnetic properties of single-walled CNT in a polymeric matrix as a function of their morphology, concentration in the composite, temperature and magnetic field characteristics provide a new tool for the researchers to gain insight into the interfacial interactions in polymeric nanocomposites. Thus it was found[218] that magnetization of the composites based on polyimide and single-walled CNT per CNT unit weight decreases with an increase in the tube concentration. This phenomenon is attributable to the fact that interfacial interaction of the polymeric matrix with the tube surface induces diamagnetic response from the CNT, thus decreasing the overall magnetization.

Due to the experimental difficulty of investigating the relationships between the phases in nanosystems, complexity of the stress transfer mechanism and destruction of nanocomposites upon the transfer of deforming stress,[219] computation methods came at the forefront. The role of oriented polymer layers near the filler surface in the formation of the mechanical properties of filled polymers has long been debated in the literature, but many aspects of this problem are still unclear. The interaction mechanisms of macromolecules with the filler are studied using computational methods of molecular mechanics and molecular dynamics.[216] Wall *et al.*[220] used the model of harmonic interaction of chains with a rigid periodic potential (extension of the so-called Frenkel – Kontorova model), and Svistkov *et al.*[221] substantiated the possibility of using simpler models (namely, probabilistic and continual models) for estimating the degree of orientation of the polymer chains *versus* their distance from the filler surface in an analytical form. It was shown that if biaxially oriented macromolecules in the near-surface layer can transmit the orienting influence to the neighbouring areas of the polymer, the formation of a rather extended layer with specific mechanical properties near the filler surface is possible.

The formation of up to 225 nm thick polymer layers with a structure other than the structure of the whole matrix was observed experimentally[222] in the composites based on cross-linked polydicyclopentadiene and multi-walled CNT linked to the matrix by covalent bonds. It was shown that physicomechanical characteristics of the composite (especially relative elongation at rupture and impact strength) are substantially improved following an increase in the nanotube concentration.

The molecular dynamics of polymers and orientation of the molecules of composite components determine to a large extent the properties of polymeric nanocomposites. Furthermore, for developing the manufacture processes for the composites, it is necessary to understand the mechanism of the orientation response of the components to the force fields that act during the manufacture processes (*e.g.* moulding, extrusion). Finally, it is known that CNT act in polymers as nucleating agents affecting the nucleation and growth rates of the polymer crystals and orient the crystals at right angle to their longitudinal axis.[223] This hampers the monitoring and, the more so, targeted orientation of the macromolecules in the presence of CNT. Meanwhile, the force loads can affect the density of the originating crystal-

lization centre and orientation of the filler network in the matrix.

Studies of the effect of CNT on the molecular dynamics of polymers and studies of the orientation of components in nanocomposites have not received adequate attention as yet; therefore, the works along this line are of particular interest. Thus it was found that multi-walled CNT linked to a polymer by covalent bonds serve as crystallization centres of PEO and poly-ε-caprolactone; in such systems, the degree of supercooling during crystallization decreases and the melting temperature and crystallization rate of the polymers increase.[69] By simultaneous action of shear deformation and temperature gradient, it is possible to form and detect diverse crystalline structures [*e.g.*, single-walled CNT – poly(butylene terephthalate)].[223]

The considerable effect of single-walled CNT forming no covalent bonds on the structure of non-crystallizable polymer (PS) is manifested as an increase in the glass transition temperature and a decrease in the change in the composite heat capacity upon devitrification.[224] The authors believe that these effects are due to the restriction of mobility of a considerable part of the polymer, the most pronounced changes in the parameters occur when the nanotube concentration is only ~0.5 mass %.

Using the uncured epoxy resin – multi-walled CNT pair, it was demonstrated[225] that the degree of aggregation – deaggregation of CNT (determined by the shear deformation rate) is responsible to higher extent for their stable orientation and, hence, for the preparation of stable systems.

Many works on the synthesis of polymeric nanocomposites involving CNT give examples of considerably improved principal performance properties (first of all, physicomechanical characteristics) of composites compared to the properties of the initial polymers. However, it should be noted that not all of the researchers are optimistic for the prospects of this trend in the polymeric material science. When studying composites based on various types of polymers with nanofillers of various nature (silica gels, carbon nanotubes, layered aluminosilicates) by ultrasmall-angle X-ray scattering, light scattering and electron microscopy, Schaefer and Justice[226] concluded that these fillers result in large-scale disordering of the polymer structure and, hence, considerable deterioration of their mechanical characteristics, first of all, the elastic modulus, compared to the characteristics predicted by idealized models.

2. Methods of nanotube introduction into the polymers. Characteristics and application of nanocomposites

In the preparation of polymeric nanocomposites, the following methods are used to introduce CNT into the polymeric matrix: displacement of the components in the melt, mixing of tube dispersions and polymer solutions followed by removal of the solvent, polymerization *in situ*, latex process, electrodeposition of polymers on CNT, mixing of powdered components in a mill and some other,[21,227] and combinations of several methods. The three first-mentioned methods are used most often.

a. Melt and solution mixing

Melt mixing involves a simple procedure but has a number of drawbacks such as poor quality of the dispersions and the risk of filler destruction during mixing.[228] Nevertheless, this method was used to prepare, for example, the composites CNT – isotactic polypropylene (PP),[229] single-walled CNT – PMMA,[216] multi-walled CNT – PA.[215] The quality of mixing of poly(ether-imide) with multi-walled CNT can be appreciably improved by simultaneous mixing in an extruder and sonication of the melt at the die outlet.[230] Sonication considerably improves the rheological characteristics of the composite, slightly changes the mechanical properties, while the percolation threshold and electrical conductivity remain almost invariable.

A new two-stage method for the preparation of the multi-walled CNT – polymer composite with enhanced mechanical characteristics has been proposed,[231] consisting in mixing of pre-powdered polymer with thoroughly dispersed tubes followed by extrusion of the mixture melt. The resulting multi-walled CNT – isotactic PP composite containing ~1 mass % of the tubes showed a 1.5-fold increase in Young's modulus compared to the unfilled polymer. This is accompanied by noticeable increase in the temperature of the onset of decomposition (from 407 to 446 °C) and the yield point (from 33.1 to 40.8 MPa). However, the elongation at rupture and the strength change slightly. Better results were obtained with smaller-diameter CNT. Higher crystallization rate of the polymer was found in the composites as compared with the unfilled polymer.

For the successful synthesis of nanocomposites by this method, it is necessary to understand the features of rheological behaviour of the systems in the melt. The rheology is closely connected with the process conditions, the polymer molecular mass and morphology, the CNT aspect ratio and concentration and the quality of dispersion in the polymeric matrix. In the above-mentioned works,[215,216] the effect of a number of listed factors on the rheology of nanocomposites was studied. It was shown that the dependence of the rheological characteristics on the degree of uniformity of tube distribution can be used for quantitative determination of the state of CNT dispersions in the polymer.

The solution method† provides more uniform distribution of CNT in a low-viscosity medium and, hence, more homogeneous mixing with the polymer. This method was used, in particular, to prepare nanocomposites of multi-walled CNT with poly(vinyl alcohol) (PVAl),[232] poly-ε-caprolactone,[233] PA,[234] polyvinylcarbazole (PVC),[235,236] and composites of single-walled CNT with PI, PVC,[235–238] poly(ether-urethane-urea).[239] In the last-mentioned case, a considerable increase in the initial elastic modulus of the elastomer and the rupture strength was achieved even at a CNT content of about 0.002 mass %; on further increase in their concentration, the physicomechanical properties of the composites are deteriorated.

The solution method was also employed to prepare composites of native and hydroxylated single-walled CNT (0.1 mass % – 2.6 mass %) with poly(tetramethylene oxide) polyurethane thermoplastic elastomers with high contents of rigid non-aromatic segments based on hexylene 1,6-diisocyanate, butane-1,4-diol and bis(4,4′-diisocyanatocyclohexyl)methane, which proved to be beneficial for dispersing nanotubes.[240] It was found that the extent to which the physicomechanical characteristics of the composites increase with respect to the characteristics of unfilled polymers (elastic modulus and rupture strength, ~1.5-fold) depends only slightly on the tube functionalization.

† Note that the solution method is the key one for the production of first-group polymeric nanocomposites.

In the case of hydroxylated tubes, the conductivity of the composites changes slightly after the percolation threshold has been attained; meanwhile, in the case of native tubes, the conductivity may increase by 8 orders of magnitude.

Upon the synthesis of segmented polyurethane block copolymers from methylene-4,4′-bis(phenyl isocyanate), poly-(ε-caprolactone)diol and tri(hydroxymethyl)propane in the presence of carboxylated multi-walled CNT (1 mass % – 5 mass %%), the thermal stability of the polymer substantially increases, the rupture strength increases almost twofold and Young's modulus increases almost threefold, while the melting temperature somewhat decreases compared with non-modified copolymers.[241]

Many researchers believe that for significant enhancement of the physicomechanical characteristics of polymeric materials *via* their modification by nanotubes, functionalization of the nanotubes is required. However, this is not always true. Kim and Jo [242] introduced, into PMMA, multi-walled CNT modified in the non-covalent fashion by the 3-hexylthiophene – PMMA block copolymer. The composition was prepared by the solution method. As compared with the initial PMMA, the resulting material has a twice higher rupture strength and Young's modulus when the CNT content was 0.1 mass %. The elongations at rupture almost did not change. In the absence of a compatibilizing agent, the introduction of multi-walled CNT entails an increase in the composite strength and elastic modulus by ~30% at a CNT concentration of 0.01%. As the nanotube concentration was further increased, the strength decreased to the initial level, while the elastic modulus slightly increased and the elongation at rupture decreased.

These results can be interpreted as follows: for strong bonding of the nanofiller with the polymeric matrix, a significant role is played by not only the nature of the bond between the modifying agent and the nanotube surface (covalent or non-covalent bond) but rather by the real strength of this bond. In the case described above, cooperative non-covalent interaction of the polythiophene block with the multi-walled CNT surface obviously takes place, thus ensuring relative stability of the coat of PMMA blocks around the nanotube.

A similar approach was used in another work.[243] The amine or carboxy terminal groups are formed due to interaction with the defects on the multi-walled CNT surface. The subsequent introduction of these complexes into the PS matrix ensures good adhesion between CNT and the matrix which is manifested as a considerable increase in the strength properties of the material.

By mere mixing of single-walled and multi-walled CNT functionalized by oxyphenyl groups and 'dissolved' in DMF with a solution of polyacrylonitrile (PAN) in DMF and a toluene solution of poly(vinyl acetate) (PVAc), it was possible to prepare homogeneous transparent composite films and gels.[62]

The transparency of films of the composite obtained by introducing a suspension of multi-walled CNT into solution of PS in toluene (CNT concentration 1 mass % – 3 mass %) is markedly improved in the region of 230 – 250 nm in which pure PS fully absorbs.[244] The transmission maximum is attained when the CNT content is 1.5 mass %. The binding between the system components is through the shared electrons of the six-membered carbon rings.

The use of films of the single-walled CNT – water-soluble polymer (carboxymethylcellulose, PVAl) composites as a saturable absorber for pulse laser systems is more attractive than the use of traditional materials manufactured using complex and expensive processes.[245, 246] The dispersions in D_2O of native, not preliminarily purified, single-walled CNT were prepared in the presence of 1% sodium dodecyl sulfate under long-term sonication (similarly to the procedure described in the study [124]) followed by centrifugation of the solution at 150 000 g (~30 000 rpm). The individual character of single-walled CNT that remained in the solution after precipitation of the impurities and of non-dispersed CNT was confirmed by optical spectra and Raman spectra. The polymers were dissolved in ready dispersions of single-walled CNT.

When the solution method was used to introduce a mixture of multi-walled CNT with soot into the butadiene – styrene copolymer, it was found that the dispersibility of CNT in a hydrocarbon matrix and the strength and transport properties of the ternary composite are substantially better than analogous properties of the composites containing the same fillers separately.[247] Thus the elastic modulus of the composites increases 4-fold, the strength increases ~10-fold, the relative elongation at rupture increases ~1.7-fold, and the conductivity increases by ~12 order of magnitude.

Despite the preference given, as a rule, to the solution method over the melt mixing, it is desirable to select the most appropriate method of nanocomposite synthesis for each particular system. This is indicated by the results of studies of the effect of methods of CNT introduction into the polymer on the quality of dispersions, interfacial interactions and, finally, on the physicomechanical properties of, for example, nanocomposites based on native and oxidized multi-walled CNT and styrene–vinylphenol copolymer at a CNT concentration of ~5 mass %.[248] In this case, melt mixing of a mixture of multi-walled CNT that were precipitated from a DMF 'solution' with the copolymer at 185 °C was better in all respects than either precipitation from solution without the subsequent melt mixing or melt mixing without preliminary dispersion of CNT in a solvent. According to IR-spectroscopy data, in the first-mentioned case, more hydrogen bonds between the tubes and the polymer are formed. It was also demonstrated [249] that the properties of nanocomposite can be optimized by selecting the method for CNT introduction into the polymeric matrix in the single-walled CNT – curable polydimethylsiloxane PSW 2286 system. More homogeneous distribution of filler is attained in this case by grinding of the mixture obtained by concentrating the polymer solution with the CNT dispersion as compared with solvent-free procedures. In both cases, better results were obtained upon introducing the CNT dispersion into the polymer followed by action of shear stress in a highly viscous medium.

Under conditions of high shear stress and elevated temperature, up to 10 mass % of single-walled CNT was introduced into polypropylene in the presence of benzoyl peroxide (BP).[250] The free radicals formed upon BP decomposition create active sites on the CNT surface, which ensure the covalent bonding of the tube to the polymer. As a consequence, the strength characteristics of the PP fibres formed from the resulting composite sharply increase, the increase in the rupture strength reaching 173% and the increase in the elastic modulus reaching 134%.

In order to select a strategy for the production of polymeric composites from PP and multi-walled CNT suitable for large-scale industrial production, Pujari *et al.*[251] compared the properties of dispersions of multi-

walled CNT in polypropylene prepared by conventional melt mixing and by solid-phase mixing of powdered components under the shear stress. It was found that the degrees of dispersions are similar in both cases (in the latter case, it is somewhat higher), however, the performance properties are different. In the second case of mixing, the electrical conductivity is much lower. Probably, the minor difference in the size and distribution of the clusters of multi-walled CNT (none of the mixing variants provides deaggregation down to individual tubes) results in considerable difference in CNT 'networks', and in the case of melt mixing, PP is also affected, in particular, its molecules are destroyed on long-term intensive stirring, which is needed to obtain homogeneous dispersions. The results of studies indicate that complete comparison of the states of dispersions cannot serve as a criterion for the choice of the method of CNT introduction into the polymers. The choice depends on the properties that are related to the particular application of the nanocomposite.

This conclusion was confirmed in another work[252] where the percolation threshold of electrical conductivity was reached at a single-walled CNT content of 0.14 mass % in the composite based on superhigh-molecular polyethylene [$M \approx (3-6) \times 10^6$]. The composite was prepared by the simplest method: dry mixing of the polymer powder with the powder of single-walled CNT – silica gel mixture (7 : 93 ratio) followed by pressing into sheets at 175 °C and at a pressure of 100 kg cm^{-2}. All of the physicomechanical characteristics of the composite (elastic modulus, strength and elongation at rupture) sharply decreased as compared with the initial polymer.

b. Polymerization *in situ*

When CNT are introduced into polymers using *in situ* polymerization of the monomer in which nanotubes have been dispersed, the polymerization active sites (free radicals, functional groups, catalytic complexes, *etc.*) are formed on the nanotube surface and the chain growth starts on these sites (grafting from), or, otherwise, the growing polymer chains are attached to CNT (grafting to). In the latter case, interaction can occur both directly with the tube surface and with the functional groups pre-grafted to the CNT. The introduction of nanotubes into polymers *in situ* may solve simultaneously the problems of polymer synthesis, functionalization of CNT by macromolecules and formation of a composite.

As a rule, polymerization *in situ* results in covalent bonding of CNT to the polymer. In particular, this method has recently been employed to obtain nanocomposites from single-walled CNT with polyepoxides,[253] poly(butylene terephthalate) (PBTP),[254] and multi-walled CNT with polyurethane (PU),[255] poly(ether-ketones)[256] and PMMA.[257] A large review of studies published before 2007 was devoted to composite preparation by covalent grafting of polymers [PS, PMMA, poly(*N*-isopropylacrylamide) and so on] to CNT using living radical polymerization involving nitroxide radicals, atom transfer polymerization, reversible decomposition – addition polymerization, *etc.*[258] The grafting to and grafting from reactions are also considered in this review.

Non-polar polymers. A series of publications[259–263] present a method for the preparation of nanocomposites by *in situ* catalytic polymerization of non-polar monomers, in particular, propylene, in the presence of CNT.

The authors used the principle of close contact between the catalytic sites and the surface of filler particles — this is not a new principle but earlier it had been used only to introduce CNT into polymers by radical polymerization.[219, 220, 249] An experimental technique suitable for industrial application was developed. A specific feature of the technique is that the liquid monomer, propylene, serves as the medium for dispersing CNT. Its subsequent polymerization produces a nanocomposite in high yield with rather high molecular mass of the polymeric matrix. Oxidized multi-walled CNT are dispersed by ultrasound in the presence of a co-catalyst, methylalumoxane (MAO), which is immobilized on the tube surface, partly due to weak ionic interactions and partly due to covalent bonds with hydroxyl and carboxyl groups. After introduction of the metallocene catalyst to the reaction mixture, the active sites of polymerization are formed near the tube surface upon the catalyst interaction with the immobilized MAO. Depending on the nature of the catalyst, this gave crystalline isotactic and syndiotactic PP and amorphous elastomeric stereoblock PP. The use of t-multi-walled CNT of small diameter was due to the fact that they are much less prone to aggregation than single-walled CNT, and therefore, they provide the highest efficiency of polymer modification. The nanocomposite morphology, thermal and electrical properties, and physicomechanical characteristics have been studied in detail, the CNT concentration being varied in the range of 0.1 mass % – 3.5 mass %. It was shown that nanotubes dispersed mainly down to individual tubes stabilize the composite against thermal and thermooxidative destruction. As the filling degree increases, the dielectric constant increases, the elastic modulus changes from 25% to 60%. Below the glass transition temperature (T_g), the reinforcing effect of CNT was 20% – 40%, and above T_g this was up to 50%; furthermore, for considerable increase in the physicomechanical characteristics, the presence of only 0.1 mass % of the tubes is sufficient and the optimal properties are observed when their content is in the range of 0.1 mass % – 0.4 mass %.

The effect of additives of multi-walled CNT containing COOH and OH groups and additionally functionalized by maleic anhydride (c_{CNT} = 0.5 mass % – 2 mass %) on the rupture strength of films made of non-miscible PP and ethylene – co-vinyl acetate elastomer with various component ratios was studied. The reinforcement is governed by the film morphology, which is specified by its composition and CNT concentration.[264]

The composites comprising multi-walled CNT – low-density polyethylene (LDPE) and multi-walled CNT – ethylene copolymers with α-olefins were obtained using MAO-activated double metallocene catalysts (Co – Zr and Co – Ti).[265] The electrostatic interaction of the anions of the co-catalyst fixed on the CNT surface with the cationic centres of metallocenes results in the formation of active sites initiating the growth of polymer chains, which are deposited on CNT, and the CNT aggregates are thus destroyed down to individual tubes, which are coated with polymer macromolecules. The proposed method for the synthesis allows one to efficiently control the microstructure of polyolefins, namely, the type and number of branchings.

Direct *in situ* grafting of PS, PS – PAN copolymer and PAN on the multi-walled CNT surface by atom transfer polymerization or copolymerization of monomers initiated by 2-hydroxyethyl 2-bromoisobutyrate was considered.[266] It was noted that the grafting of polymers affects slightly the

CNT structure but increases considerably the glass transition temperature of the polymers. The modified multi-walled CNT are readily dispersed in organic solvents.

The radical polymerization of styrene in an aqueous emulsion in the presence of non-ionic surfactant and a cationic cross-linking agent, [2-(methacryloyloxy)ethyl]trimethylammonium chloride, was used for *in situ* grafting of PS on the multi-walled CNT.[267] Functionalized CNT are dissolved in toluene; when introduced into the PS–PI–PS block copolymer, they are incorporated in the PS domains.

A method of PS grafting on the multi-walled CNT surface to give a 5-nm thick polymeric layer was considered.[268] First, hydroxylation was carried out by treatment of a dispersion of multi-walled CNT in dichloromethane with an acidified aqueous solution of $KMnO_4$ in the presence of a phase transfer catalyst; this was followed by condensation with methacryloyloxypropyltrimethoxysilane in which groups capable of polymerization were attached to the OH group. The subsequent radical polymerization of styrene gave a product readily dispersible in organic solvents.

An original method of functionalization of multi-walled CNT meant for modification of PS was reported.[269] In the first stage, styrene groups linked to the CNT surface by ester bridges were obtained by treatment of carboxylated tubes in the salt form with 4-vinylbenzyl chloride. The multi-walled CNT modified in this way are introduced in PS. The composite has much higher mechanical characteristics and enhanced thermal stability compared with the composites based on non-functionalized tubes.

By treatment of multi-walled CNT with acyl chloride groups with living (capable of further transformations) polystyryllithium, PS macromolecules were grafted to them.[270] The new composite containing ~40% PS is homogeneously dispersed in common organic solvents and can be used to obtain styrene-based nanomaterials. In another study,[271] it was shown that living PS obtained by anionic polymerization can be directly attached to various types of CNT: single-walled, multi-walled and truncated multi-walled ones.

The papers [270, 271] illustrate well the general approach to the design of polymeric composites involving CNT that is outlined in Ref. 272. It is known that polymers with different structures are most often poorly compatible. The authors believe that to attain the best dispersibility of CNT in the polymeric matrix, CNT should be modified by a polymer whose structure is identical or similar to the structure of the matrix polymer. Partially oxidized CNT are most convenient for this purpose. The carboxyl groups of these CNT can be used either for the formation of polymerization centres of the corresponding monomers or for esterification or amidation by a polymer containing appropriate functional groups (hydroxyl or amino groups).

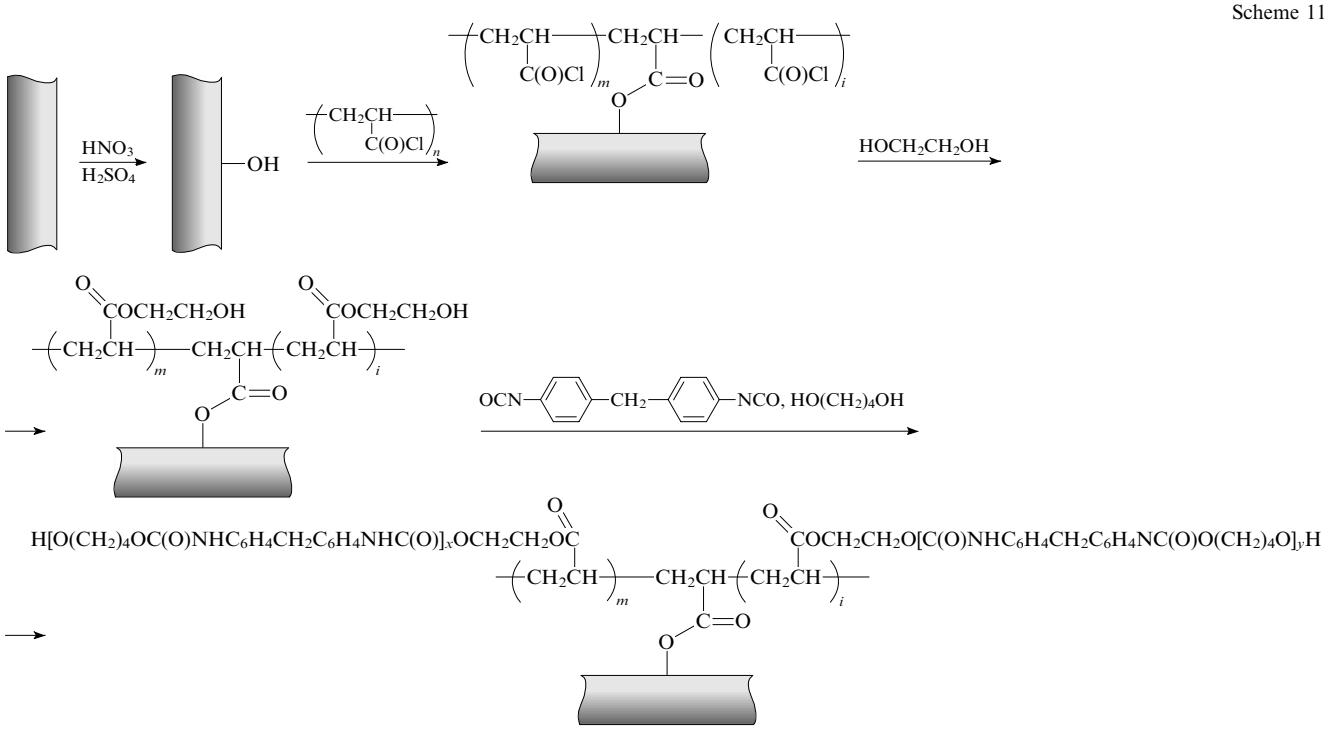
Polar polymers. The composites based on carboxylated single-walled CNT and PBTP [254] were synthesized by polycondensation of dimethyl terephthalate with butane-1,4-diol containing suspended CNT. When the content of single-walled CNT in PBTP is 0.01 mass %–0.2 mass %, the crystallization rate of the polymer after cooling of the melt sharply increases and the crystallite structure is ordered compared to the structure of the neat polymer.

The chemical grafting of the polymer induces strong adhesion between the components; as a consequence, the rupture strength of the polyurethane composite increases by 60.6% with respect to the strength of the unfilled polymer and the elastic modulus increases by 6.3% when the content of hydroxylated multi-walled CNT in the composite is 0.1 mass % (Scheme 11).[255]

The modification method of oxidized CNT by successive treatment with poly(acryloyl chloride) and ethylene glycol can be used for introducing them into other polymers able to react with hydroxyl groups, in particular, into PU.

Note that according to this scheme, the synthesis of composite *in situ* refers only to the last stage. In addition,

Scheme 11



unlike the PU obtained from methylene-4,4′-bis(phenyl isocyanate) and butanediol, the composite obtained in the presence of modified polyfunctional filler should contain a noticeable amount of the gel fraction. Unlike most other methods, hydroxyl rather than carboxyl groups on the surface of oxidized tubes were used [255] for polymer grafting to CNT.

Functionalization of single-walled CNT was carried out in three stages.[273] First, the tubes were treated with a solution of lithium in liquid ammonia and then with ω-bromopentanoic or ω-bromodecanoic acid; the resulting carboxyl groups bound to the CNT surface through aliphatic linkers (C_4 or C_9, respectively) were converted to acyl chloride groups. Then phase transfer polycondensation of hexamethylenediamine with decanedioyl chloride was carried out in the presence of the tubes functionalized in this way. Nylon-6,10 containing up to 1 mass % of functionalized single-walled CNT has 2.5-fold higher elastic modulus and strength than nylon without nanotubes; however, the relative elongation at rupture decreases. The polymer modification by native tubes induces a slight increase in the elastic modulus and the rupture strength and almost twofold decrease of the relative elongation at rupture.

Metallic lithium reduces single-walled CNT in THF in the presence of 4,4′-di-*tert*-butylbiphenyl (DTBP, 10 mol.% with respect to lithium) and electrophiles such as trimethylchlorosilane, methyl methacrylate (MMA), methyl 2-acetamidoacrylate, which react with Li-derivatives of CNT *in situ*.[274] The reaction is carried out at room temperature under sonication. The single-walled CNT obtained under these conditions were covalently functionalized, being either coated by trimethylsilyl groups (up to the ratio Si : C = 2) or embedded into a polymer shell. It was noted that DTBP is much more efficient as electron transfer agent to CNT than naphthalene or hexametapol. The density and the average length of polymer chains attached to the tube walls can be controlled by varying the amounts of the monomer, lithium and the catalyst. Modified CNT are convenient intermediates in the reactions with diverse electrophilic reagents, especially in view of the fact that multiply negatively charged CNT are separated from the aggregates due to the Coulomb repulsion, pass to the solution and react with electrophiles.

Interesting results were obtained in a study of the anionic polymerization of acrylate monomers in the presence of single-walled CNT treated with Bu^sLi.[275] It was found that MMA cannot add to the carbanions formed on the CNT surface, whereas grafting of *tert*-butyl acrylate (BA) is performed successfully, the content of the grafted polymer being ~14 mass %. Successive polymerization of BA and MMA gave single-walled CNT with block copolymer macromolecules grafted to the lateral surface; the content of the grafted polymer was ~47 mass %. The authors concluded that direct addition of MMA to the carbanionic centres of single-walled CNT is impossible due to steric hindrance caused by the presence of the methyl group at the C=C bond. Suspensions of modified nanotubes in THF with concentrations of 1 mg ml^{-1} are stable for a month.

Poly(tetramethylene oxide) was grafted to the surface of carboxylated multi-walled CNT by cationic polymerization of THF.[276] The carboxyl groups were converted to acyl chloride groups; silver perchlorate served as the catalyst.

Velasco-Santos *et al.*[277] introduced carboxylated multi-walled CNT into MMA, which was polymerized in the presence of AIBN. Presumably, grafting of PMMA to the CNT surface occurs as a result of chain transfer to carboxyl groups. Composites based on PMMA containing 1 mass % – 1.5 mass % of carboxylated multi-walled CNT are twice as strong as non-modified polymers and possess high heat-resistance — the elastic modulus at 90 °C increases more than tenfold and is roughly equal to the elastic modulus of neat PMMA at 40 °C. Upon the introduction of non-functionalized multi-walled CNT, characteristics of the polymer (especially heat resistance) were enhanced much less considerably.

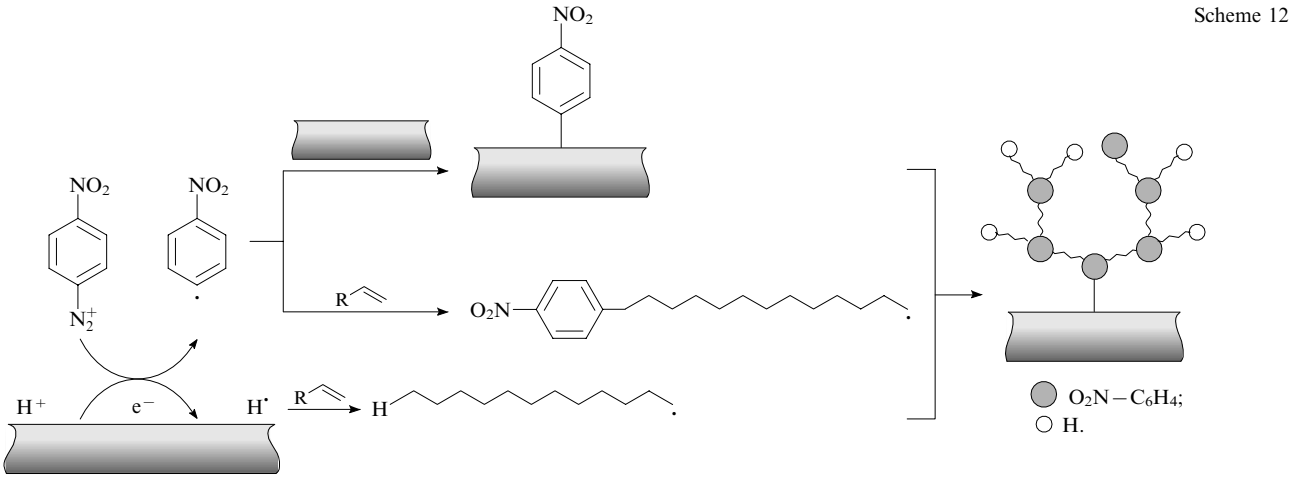
The grafting of PMMA by atom transfer radical polymerization to single-walled CNT containing covalently bonded 2-bromo-2-methylpropionyloxy groups was carried out.[92]

Tang *et al.*[278] carried out *in situ* functionalization of multi-walled CNT by free-radical polymerization of acrylic acid. The surface of covalently modified CNT was decorated by nickel nanoparticles. The ternary composite proved to be an efficient catalyst for hydrogenation of α,β-unsaturated aldehyde, citral. The hydrogenation product, citronellal, which is an important material used in food and perfume industries, is obtained in a yield seven times higher than that obtained using the traditional nickel catalyst.

Among the studies considering the development of polymeric composites with covalently bonded CNT, attention is attracted by the work [279] where the effects of various types of nanotubes on the properties of composites are compared using PVAl as an example. It was found that non-functionalized CNT increase the tensile modulus of the polymer; however, the angular coefficients of the linear dependences between the elastic modulus and the CNT concentration have different values for tubes of different diameter; this angle and the tube diameter follow clearly antiparallel patterns of variation. The dependence of the modulus on the ratio of the overall CNT surface to the composite volume is described satisfactorily by increasing linear function from which single-walled CNT deviate due to their higher tendency to form aggregates. It is of interest that similarly to the elastic modulus, the degree of crystallinity of PVAl grows linearly with increase in the CNT concentration. According to the authors' opinion, this effect is related to crystallization of the polymer near the surface and small-diameter multi-walled CNT are best candidates for polymer reinforcing agents.

A simple one-stage method for functionalization of multi-walled CNT was proposed for polymers, which can be grown on CNT by radical polymerization.[280] This is attained by electroinitiated (with highly oriented, multi-walled CNT grown on a substrate as the cathode) miniemulsion polymerization of 4-vinylpyridine, acrylic acid or butyl methacrylate at room temperature. The authors called the new method surface electroinitiated emulsion polymerization (SEEP). This process makes use of 4-nitrobenzenediazonium tetrafluoroborate, which undergoes cathodic reduction to give atomic hydrogen and nitrophenyl radical, which initiate the polymerization of the vinyl monomer. Simultaneously, aromatic radicals add to the CNT surface and create the primary grafted layer on the surface of multi-

Scheme 12



walled CNT the nitro groups of which are able to react with the macroradicals growing in solutions (Scheme 12). As a result, CNT acquire a thick polymeric coat. In the authors' opinion, the SEEP method is of interest for the preparation of nanocomposites, which would find use in electronics and as selective sensors.

Atom transfer radical polymerization of vinylquinolines was first used for functionalization of single-walled CNT by photoactive polymers (polyhydroxyquinolines) for optimization of electronic and optical properties of polyvinylquinolines.[281] The tubes were first functionalized by introducing 2-chloropropionyl groups as chlorine atom transfer agents. The functionalization was carried out in two ways (amino or hydroxy derivatives) in several stages.

An unusual way of grafting a polymer to the CNT surface was reported.[282] On treatment of multi-walled CNT with atomic nitrogen formed in an argon–nitrogen microwave plasma on the tube surface, nitrogen-containing functional groups, including amino groups, are formed on the tube surface; they initiate the polymerization of ε-caprolactone (triethylaluminium as the cocatalyst). According to transmission electron microscopy, polycaprolactone linked by covalent bond through the amide group forms evenly arranged islets on the multi-walled CNT surface.

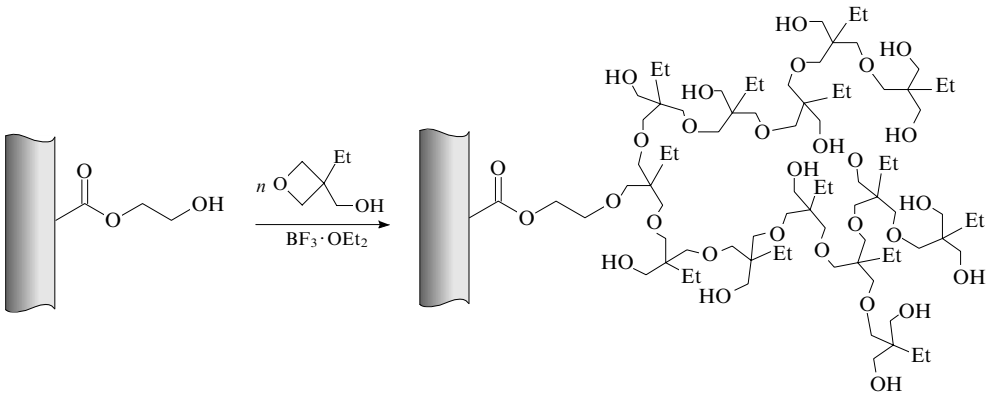
The action of plasma on single-walled CNT was also used in another work.[283] After treatment of thoroughly purified tubes with argon plasma followed by keeping in air, the tubes were placed in 1-vinylimidazole and exposed to UV radiation. This resulted in grafting of ~30 mass % of the polymer to the CNT surface, whereas without plasma treatment the degree of grafting did not exceed 15 mass %. Argon plasma treatment gives rise to defects on the tube surface, which serve as the centres of formation of peroxide, hydroxyl and carboxyl groups.

Hyperbranched polymers. Hyperbranched polymers having unusual topology and differing by a number of unique properties from linear and cross-linked analogues with a similar composition are interesting polymeric objects for functionalization of CNT. In particular, they have enhanced solubility, high sorption capacity, low viscosity of solutions and melts, and contain large numbers of functional groups, which opens up prospects for their subsequent modification in the desired direction.

Xu *et al.*[284] used the strategy of *in situ* ring opening polymerization to grow hyperbranched polymers on the multi-walled CNT surface. The carboxyl groups of CNT were converted to acyl chloride groups by treatment with thionyl chloride, and then hydroxyl groups, which are the active sites of cationic polymerization of 3-ethyl-3-hydroxymethyloxetane, were obtained by esterification with excess glycol. This approach gave rise to the multi-walled CNT–hyperbranched polymer composite, which was rather readily dispersed in methanol, ethanol, DMF, DMSO and was capable of further transformations owing to the presence of numerous OH groups (Scheme 13).

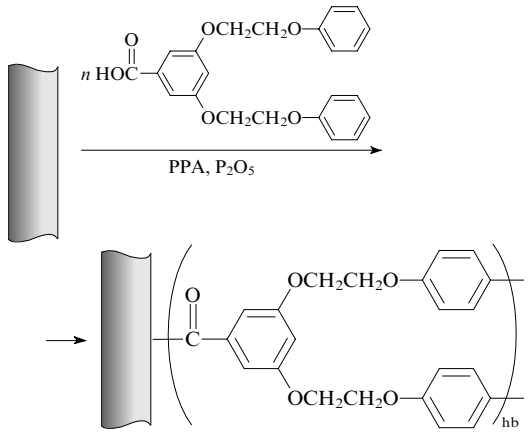
An original method for the synthesis of poly(etherketone) nanocomposites by *in situ* polycondensation was proposed.[256] Three alternatives for conduction of the process based on AB [3- and 4-(2-phenoxyethoxy)benzoic acids] and AB_2 [3,5-bis(2-phenoxyethoxy)benzoic acid] monomers in the presence of non-modified multi-walled CNT in a PPA–phosphorus pentoxide mixture at 110–120 °C were

Scheme 13



discussed. Of particular interest is the third variant (Scheme 14) giving rise to the hyperbranched polymer.

Scheme 14



hb is hyperbranched.

The composites thus obtained, which contain 10 mass % of multi-walled CNT, are readily soluble in phenol, cresol and most strong acids (sulfuric, trifluoroacetic, methanesulfonic); they have high thermooxidative stability and can be used as structuring additives to other polymers.

Conducting polymers. Researchers pay considerable attention to investigation of covalent grafting to CNT of polyconjugated conducting polymers, in particular, polyaniline (PAn), and production of the corresponding nanocomposites. Abalyaeva and Efimov[285] generalized the knowledge on the PAn–CNT compositions accumulated up to 2008 inclusive. It was noted that introduction of CNT, especially by the polymerization filling technique, improves considerably the electrochemical characteristics of PAn, first of all, increases the conductivity. The composite materials have enhanced stability, and owing to the formation of microporous structure of the material, they can adjust themselves to the volume changes following the reversible intercalation–deintercalation of Li^+ ions. Methods for preparing the composites with CNT contents from 0.2 mass. % to 65 mass % were described and numerous examples of their use in electrochemical cells, light emitting diodes, gas sensors, battery cells and so on are considered.

The PAn–multi-walled CNT (0.8 mass %) composites were obtained by *in situ* oxidative polymerization of aniline.[286] Electrodes made of the composite showed better thermal stability, higher conductivity and better capacitance characteristics than electrodes made of the non-modified polymer. Similar results were obtained in another work[28] where ready solubility in *N*-methylpyrrolidone, the ability to form films, coatings and fibres from solutions to be used in optoelectronic devices were noted for the PAn–multi-walled CNT composite in the emeraldine base form (semi-oxidized form of PAn).

The single-walled CNT–PAn composites were also prepared *in situ* in the following way: nanotubes were dispersed in ionic liquid (1-butyl-3-methylimidazolium hexafluorophosphate) containing 1 mol litre^{-1} of trifluoroacetic acid, and in this medium, electrochemical polymerization of aniline was carried out.[288] The resulting 'copolymers' based on a *p*-type conductive polymer and *n*-type conductive single-walled CNT can be applied in photovoltaic devices.

The effects of two methods of CNT functionalization on the properties of the single-walled CNT–PAn composites obtained *in situ* were compared.[289] The composites based on oxidized tubes were found to have higher conductivity than the composites based on single-walled CNT functionalized by covalently bonded dodecylamine; this is at variance with the data obtained by other researchers and cited above.

In order to combine highly stable PAn whose electro-optical characteristics can be controlled with inorganic magnetic nanoparticles (Fe_3O_4), *in situ* oxidative polymerization of aniline in the presence of multi-walled CNT was carried out.[290] On the tube surface, monodisperse Fe_3O_4 nanoparticles of diameter 1.76 nm were pre-formed. These were obtained by successive treatment of carboxylated multi-walled CNT with iron chlorides and aqueous ammonia.[290] The multi-walled CNT–Fe_3O_4–PAn composites combine high electrical conductivity and superparamagnetism. It was shown that the tubes, together with magnetic nanoparticles, are coated with a polymer layer.

Polysulfonylamide (PSA) was grafted on the multi-walled CNT surface through the addition of 2,5-diaminobenzenesulfonic acid and subsequent *in situ* condensation with diphenylamine-4-sulfonic acid (DPASA).[291] The properties of covalently modified multi-walled CNT were compared with the characteristics of the PSA composite obtained by *in situ* condensation of DPASA in the presence of non-functionalized multi-walled CNT. Both composites are readily soluble in water and able to form films. The conductivity of the grafted material is almost twice as high as the conductivity of non-grafted one; however, the conductivity of composites is several orders of magnitude higher than that of neat PSA.

The enhancement of the conductive properties of polymers after the introduction of CNT was attributed in most of the studies cited to the electric properties of the proper nanotubes and the change in the morphology of polymers in the presence of nanotubes irrespective of the introduction method and the type of bonds formed. The joint action of these factors gives rise to more efficient charge-transport paths with respect to those present in the initial systems.

Epoxy resins. A large number of publications are devoted to the use of CNT for modification of epoxy resins that serve as matrices in the structural composite materials.

Wang *et al.*[253] developed an epoxy composite using single-walled CNT pre-treated in two ways: grafting of poly(glycidyl methacrylate) by *in situ* radical polymerization and functionalization with amino groups using an aminodiazonium salt. It was shown that epoxy composites with functionalized single-walled CNT are much more sensitive to temperature variation than composites based on native tubes.

The strength characteristics of a composite material based on carbon fibre are considerably enhanced when the epoxy matrix is modified by single-walled CNT.[292] The authors noted that to gain a noticeable effect, it is necessary first to disperse the CNT, which can be done only using the solution method for reactant mixing. The introduction of up to 0.5 mass % of single-walled CNT carboxylated at the ends (unlike the native ones) increases the shear strength of the carbon fibre-reinforced plastic by 40% with slight decrease in the bending strength. It was assumed that reinforcement is due to stronger bonding of the matrix to the carbon fibre surface.

Usually, CNT are pre-dispersed in epoxy resin with or without a solvent, and then a curing agent is added. However, it was found that pre-dispersion in the curing agent also improves the mechanical,[293,294] conducting[293] and tribological[295] properties of the epoxy composites.

A new method for deliberate modification of CNT for reinforcement of the epoxy matrix was proposed.[293] Maleic anhydride was grafted to plasma-pretreated multi-walled CNT, and then the tubes bearing the anhydride groups were dispersed in an amine curing agent, and the obtained suspension was introduced in the epoxy resin. The functionalized multi-walled CNT were much better dispersed in the cured matrix than untreated tubes. The material thus obtained had enhanced mechanical characteristics, and its conductivity increased from 10^{-12} to $10^{-4}\ \Omega\ m^{-1}$ at a CNT concentration of 0.1 mass % – 1 mass %. The same concentration range of CNT modified by covalently bonded poly(acryloyl chloride)[296] provided a 45% increase in the rupture strength and a 90% increase in the elastic modulus of epoxy composites.

A less pronounced enhancement of the strength characteristics (~19%) and increase in the thermal stability (by 25 – 27 °C) of composites was achieved by introducing 0.5 mass % of multi-walled CNT into the composites;[297] when APTES-modified CNT were used,[298] the effect was more pronounced than for non-modified tubes.

A considerable increase in the strength (by 40%) and Young's modulus (by 60%) was induced by introducing 1 mass % of epoxidized single-walled CNT.[299] A similar outcome was obtained by modification of epoxy resin by multi-walled CNT functionalized by silanes.[300] However, the authors of another study[301] failed to achieve the expected substantial increase in the strength characteristics of the composites by using polyamidoamine dendrimer-functionalized single-walled CNT compared to non-functionalized tubes.

An interesting fact was observed[302] in the modification of epoxy composite. The introduction of 1 mass % of single-walled CNT into the resin resulted in considerable decrease in the thermal expansion coefficient of the cured resin as compared with the intact resin at temperatures below T_g (in the case of functionalized tubes, by a factor of almost two), which was however accompanied by a noticeable increase in this coefficient at temperatures above T_g. A similar finding was observed in another study,[294] the effect being independent of the method of introduction of CNT.

A significant change in the characteristics of epoxy composites upon introduction of multi-walled CNT was reported.[303] The introduction of 0.5 mass % of tubes entails an increase in the resin curing rate accompanied by embrittlement; higher concentrations of multi-walled CNT (up to 1.5%) lead to decrease in the curing rate and deteriorate the mechanical characteristics. The authors concluded that for effective functioning as a modifying agent, CNT need to be appropriately functionalized.

An extensive review[304] is devoted only to the modification of epoxy composites by CNT additives. The authors concluded that modification of epoxy resins by CNT may considerably improve the performance characteristics provided that the tubes covalently bonded to the matrix are evenly distributed in the resin.

However, it was noted[305] that solubilization of CNT by a non-ionic surfactant such as Triton X-100 allows one to attain an even distribution of the tubes in the epoxy matrix due to better wettability of the tube surface by the resin by means of a successful combination of hydrophilic and hydrophobic fragment of the surfactants. Finally, the strength and impact characteristics of the nanocomposite are enhanced. It was emphasized that unlike chemical modification, treatment with surfactants changes little the electrical conductivity of nanocomposites. The benefits of non-covalent modification of CNT were also pointed out in other works. For example, multi-walled CNT modified through sorption of $H_2N(CH_2)_2ONa$ proved to be a much more effective filler for attaining the optimal relationship between the increase in the electrical conductivity and mechanical characteristics of epoxy composites compared with the tubes covalently functionalized by NH_2 groups.[306]

De *et al.*[307] introduced non-oxidized multi-walled CNT non-covalently modified by melamine and t-multi-walled CNT dispersed in ethanol into a thermoset based on bisphenol A glycidyl ether and polycyclic amine (CNT concentration of 0.075 mass %). This induced an increase in T_g by 7 – 8 °C and extension of glass-transition range with respect to that observed with the use of neat CNT, which is indicative of more intense filler – matrix interaction in the composite.

V. Conclusion

The increase in the number of publications on the modification of carbon nanotubes and development of polymeric nanocomposites involving them observed in recent years attests to the increasing interest of researchers in this topic. Certain progress has been achieved in the search for new and optimization of the known methods for CNT modification by low-molecular compounds and polymers of various nature, in the theoretical and experimental studies of the properties of modified tubes and the possibility of forming bonds between them and polymers for the development of new-generation materials and in the studies of the properties of these materials.

The developed methods for CNT modification with low-molecular compounds have considerably extended the range of nanofillers capable of bonding to the polymeric matrix for the development of materials with a broad scope of applicability.[98,99] In addition, new sorts of CNT modified in this way could find use in biological and medical studies,[58,98] in optical safety devices,[106] in data storage devices,[104] as catalysts,[109] for imparting hydrophobicity to materials of various destinations[53,61,62] and for other purposes.

The range of compounds suitable for effective solubilization of CNT,[124,126,138] in particular, for the preparation of stable concentrated aqueous and aqueous methanol dispersions of non-functionalized individual single-walled CNT, has been extended.[182 – 184]

Original methods for separation of CNT with metallic and semiconductor types of conduction based on the difference in their reactivities towards low-molecular-mass compounds,[64,72] and simple separation methods using CNT suspensions[136,137,145] have been proposed. Subtle details of the adsorption mechanism of separation were studied.[136] The possibility of systemic rearrangement of the electronic structure of CNT was theoretically predicted and experimentally confirmed for the first time.[132,133]

Optimization of the known methods of CNT modification under the action of microwave radiation reduced the time of treatment of nanotubes from several days to several minutes,[42, 73, 82] and plasma treatment increased severalfold the degree of grafting of polymers to CNT.[283]

Modification of nanotubes by different polymers produced promising polymeric composites for the design of sensor devices for various purposes having high sensitivity, stability and selectivity;[148, 152, 155, 168, 181, 186, 189, 193, 285] catalytic systems free from the drawbacks of traditional catalysts;[152, 159, 167, 180, 278] pharmaceutical agents,[146, 147, 150] and for the use in optoelectronic,[169, 173] photovoltaic[164] and electronic recording devices.[175]

Polymeric materials with considerably enhanced performance properties as compared with the initial polymers, in particular, strength,[247, 273, 277, 292–294, 298–300, 304] thermal,[231, 241] tribological,[295] electrophysical properties[240, 293] were proposed and the range of their possible applications was described. In some cases, substantial improvement was achieved upon the introduction of CNT in amounts of several hundredths or even thousandths of mass percent.[242, 239, 254] In some cases, methods for the preparation of composites suitable for industrial application were developed.[251, 259, 263] By optimization of the electronic properties of CNT and polymers,[285–291] materials with high electrical conductivity and superparamagnetism were developed.[290]

Researchers made considerable advances in the understanding of the nature of bonds formed upon CNT modification,[116, 126, 127, 142, 209] problems of interfacial adhesion[161, 162, 216, 221] and interfacial conduction[161, 162] in nanocomposites.

A relatively new line of research, the development of nanocomposites CNT–hyperbranched polymer has been further developed.[256, 284] Composites with high thermooxidative stability, structuring additives to polymers were obtained.[256]

Numerous data needed for the understanding of the effect of CNT-containing materials on biosystems were published.[151–153, 182–200]

With the obvious advances made in the development of polymeric composites involving CNT, quite a few fundamental and applied problems remained unsolved. In particular, development of the procedures for controlled functionalization of CNT, elucidation of the features of nanotube behaviour in colloid systems and studies of the diversity of factors that determine the formation of polymeric nanomaterials with optimal properties are still topical tasks. Study of these issues at a quantitative level is complicated by the fact that CNT obtained by different methods have broad size, aspect ratio and morphology distributions. The chemistry of some functionalization reactions of CNT is still unclear (see Section II.2); the nature of structural changes in the polymers upon the introduction of CNT, resulting in crucial changes in the properties of the matrix are far from being always known; the issues concerning the mechanisms of action of ultrasound and microwave radiation on the CNT modification processes are being scarcely studied.

The studies on the combined use of nanofillers of different type in polymeric composites appear promising. For example, synergism was found in the reinforcing action of components in the combinations single-walled CNT–nanodiamond or single-walled CNT–'small-layer' graphene introduced in the concentrations of 0.1 mass % – 1 mass % to polyvinyl alcohol,[308] and synergistic fire-retardant action was found for the components of the multi-walled CNT–layered silicate system.[140]

A number of studies dealing with this subject matter were published during preparation of this review for publication. These include, in particular, a brief review[309] considering new data on CNT–polymer nanocomposites published from the mid-1990s to 2004, a large paper[310] on the chemistry, preparation and mechanical and electric properties of polymeric nanocomposites (covering the results obtained mainly in 2003–2008) and a review[311] on the applications of CNT-containing composites in sensor devices.

Among the publications, a significant place is occupied by works dealing with enhancement of the electrophysical properties of polymers due to the introduction of CNT. Conducting composites were obtained from polythiophene,[312, 313] polystyrenesulfone,[313] PI,[314] various electroactive block copolymers[315] and other polymers.[316–320]

The influence of the number of factors on the electrical characteristics of CNT–polymer composites was studied; these factors include the microstructure of polymers,[321] the length,[322] aspect ratio and orientation of CNT,[323] and the conditions of formation[324] and operation modes[318] of nanocomposites. The formation of conductive networks of multi-walled CNT in polymers was studied.[325, 326]

New nanocomposites for the use in solar batteries,[327] high-voltage power cables,[328] polymeric membranes,[329] photovoltaic[330] and sensor devices,[311, 331–333] and for other purposes[334, 335] were proposed.

Enhancement of electrooptical properties of liquid crystals upon the introduction of nanocomposites was established.[312, 336–338]

A ternary hybrid containing, apart from poly(vinylidene fluoride) and multi-walled CNT, a ceramic component, namely, nanocrystalline barium titanate, has a high dielectric constant,[339] the Ag–CNT–nylon 6 hybrid has antimicrobial properties,[340] and the poly(sodium styrene sulfonate–CNT–Pt) hybrid shows high electrocatalytic activity and is proposed as a fuel cell material.[341]

By using ozone-mediated functionalization of CNT by unreactive polymers, a broad range of composites with high performance characteristics were obtained.[342]

The formation of nanocomposites under the action of plasma was studied.[343] The LIFT (Laser Induced Forward Transfer) technology was used for the precise deposition of pixels based on the polymer–CNT composite on aluminium microelectrodes for the production of chemical sensors and for high-quality printing on glass substrates.[344]

Problems of non-covalent modification of CNT with low-molecular compounds and polymers are the subjects of Refs 341, 345 and 346.

A theoretical work[347] considers structuring and phase behaviour of polymeric nanocomposites containing fillers consisting of non-spherical particles, including CNT.

The authors are grateful to T N Fedotova (Institute of Problems of Chemical Physics of the Russian Academy of Sciences), who helped us to prepare the review for publication.

This work was performed with financial support of the Programme of the Presidium of the Russian Academy of Sciences No. 21.

References

1. A K Geim, P Kim *Scientific American* **298** (4), 68 (2008)
2. A V Eletskii *Usp. Fiz. Nauk* **167** 945 (1997) [*Physics-Uspekhi* **131** 899 (1997)]
3. A V Eletskii *Ros. Nanotekhnol.* (5–6) 6 (2007) [a]
4. F B Anders, D E Logan, M R Galpin, G Finkelstein *Phys. Rev. Lett.* **100** 086809 (2008)
5. A G Kolmakov, M I Alymov *Perspekt. Mater.* (5) 5 (2006) [b]
6. G Magadur, J-S Lauret, V Alain-Rizzo, G Voisin, Ph Roussignal, E Deleporte, J A Delaire *Angew. Chem., Int. Ed.* **47** 5492 (2008)
7. V A Tartakovskii, S M Aldoshin *Vestn. Ross. Akad. Nauk* **79** 229 (2009) [c]
8. M B Belonenko, E V Demushkina, N G Lebedev *Izv. Akad. Nauk, Ser. Fiz.* **72** 28 (2008) [d]
9. M B Belonenko, E V Demushkina, N G Lebedev *Izv. Akad. Nauk, Ser. Fiz.* **72** 711 (2008) [d]
10. N Zhao, G Wang, Y Huang, B Wang, B Yao, Y Wu *Chem. Mater.* **20** 2612 (2008)
11. E M Shpilevskii, A S Zhdanok, in *Nanochastitsy v Kondensirovannykh Sredakh. Sbornik Nauchnykh Statei* (Nanoparticles in Condensed Media. Collection of Scientific Articles) (Ed. P A Vityaz') (Minsk: Belarus State University, 2008) p. 231
12. A G Krivenko, N S Komarova *Usp Khim.* **77** 995 (2008) [*Russ. Chem. Rev.* **77** 927 (2008)]
13. A N Enyashin, A L Ivanovskii *Neorg. Mater.* **42** 1464 (2006) [e]
14. M Prato, K Kostarelas, A Bianco *Acc. Chem. Res.* **41** 60 (2008)
15. V E Bochenkov, G B Sergeev *Usp. Khim.* **76** 1084 (2007) [*Russ. Chem. Rev.* **76** 1013 (2007)]
16. S M Aldoshin, E R Badamshina, E N Kablov, in *Tezisy Dokladov Mezhdunarodnogo Foruma po Nanotekhnologiyam* (Abstracts of Reports of the International Forum on Nanotechnologies, Moscow, 2008) p. 385
17. E R Badamshina, M P Gafurova, Yu A Ol'khov, Ya I Estrin, in *Tezisy Dokladov 8-i Mezhdunarodnoi Konferentsii po Khimii i Fiziko-khimii Oligomerov 'Oligomery-2009'* (Abstracts of Reports of the 8th International Conference on Chemistry and Physicochemistry of Oligomers 'Oligomer-2009') (Ed. M A Vaniev) (Volgograd: Volgograd State Technical University, 2009) p. 230
18. Yu D Tretyakov, E A Gudilin *Usp. Khim.* **79** 867 (2009) [*Russ. Chem. Rev.* **79** 801 (2009)]
19. M A Pal'tsev, V I Kiselev, P G Sveshnikov *Vestn. Russ. Acad. Nauk* **79** 627 (2009) [c]
20. E T Thostenson, R Zhifeng, T-W Chou *Compos. Sci. Technol.* **61** 1899 (2001)
21. M Moniruzzaman, K I Winey *Macromolecules* **39** 5194 (2006)
22. E G Rakov, D A Grishin, Yu V Gavrilov, E V Rakova, A G Nasibulin, Kh Dzhian, E I Kauppinen *Zh. Fiz. Khim.* **78** 2222 (2004) [f]
23. E G Rakov *Usp. Khim.* **76** 3 (2007) [*Russ. Chem. Rev.* **76** 1 (2007)]
24. I V Anoshkin, Author's Abstract of Candidate Thesis in Chemical Sciences, D I Mendeleev Russian Chemical and Technological University, Moscow, 2008
25. Yu N Klimov *Oboronnyi Kompleks — Nauchno-tekhnicheskomu Progressu* (1) 17 (2006)
26. A L Ivanovskii *Usp. Khim.* **68** 119 (1999) [*Russ. Chem. Rev.* **68** 103 (1999)]
27. E G Rakov *Usp. Khim.* **69** 41 (2000) [*Russ. Chem. Rev.* **69** 35 (2000)]
28. B P Tarasov, N F Goldshleger, A P Moravskii *Usp. Khim.* **70** 149 (2001) [*Russ. Chem. Rev.* **70** 131 (2001)]
29. E G Rakov *Usp. Khim.* **70** 934 (2001) [*Russ. Chem. Rev.* **70** 827 (2001)]
30. C Wang, Z-X Guo, S Fu, W Wu, D Zhu *Prog. Polym. Sci.* **29** 1079 (2004)
31. C Lynam, A I Minett, S E Habas, S Gambhir, D L Officer, G G Wallace *Int. J. Nanotechnol.* **5** 331 (2008)
32. S Bal, S S Samal *Bull. Mater. Sci.* **30** 379 (2007)
33. A L Ivanovskii *Kvantovaya Khimiya v Materialovedenii. Nanotubulyarnye Formy Veshchestva (Quantum Chemistry in Materials Science. Nanotubular Forms of Substance)* (Ekaterinburg: Ural Branch of the Russian Academy of Sciences, 1999)
34. *Nanotubes and Nanofibres* (Ed. Yu Gogotsi) (Boca Raton, CA: Taylor and Francis, 2006)
35. *Nanotubes and Nanofibres* (Ed. P J Burke) (New York: World Sci., 2007)
36. E G Rakov *Nanotrubki i Fullereny. Uchebnoe Posobie dlya VUZov* (Nanotubes and Fullerenes. Handbook for Higher School) (Moscow: Universitetskaya Kniga, Logos, 2006)
37. *Issledovanie Ugleroda. Uspekhi i Problemy* (Investigation of Carbon Advances and Problems) (Ed. Yu N Bubnov) (Moscow: Nauka, 2007)
38. P Kharris *Uglerodnye Nanotruby i Rodstvennye Struktury: Novye Materialy XXI v* (Carbon Nanotubes and Related Structures: New Materials of XXI Century) (Moscow: Tekhnosfera, 2003)
39. A T Ponomarenko *Belaya Kniga po Nanotekhnologiyam: Issledovaniya v Oblasti Nanochastits, Nanostruktur i Nanokompozitov v Rossiiskoi Federatsii* (White Book on Nanotechnologies: Investigations in Nanoparticles, Nanostructures and Nanocomposites in the Russian Federation) (Moscow: LKI, 2008)
40. D Srivastava, D W Brenner, J D Schall *J. Phys. Chem. B* **103** 4330 (1999)
41. K A S Fernando, Y Lin, W Wang, L Cao, M J Meziani, X Wang, M L Veca, P Zhang, R A Quinn, L F Allard, Y-P Sun *J. Phys. Chem. C* **111** 10254 (2007)
42. Y Tsukahara, T Yamauchi, T Kavamoto, Y Wada *Bull. Chem. Soc. Jpn.* **81** 387 (2008)
43. S P Gubin, N A Kataeva *Koord. Khim.* **32** 883 (2006) [g]
44. E Nakamura, M Koshino, T Tanaka, Y Niimi, K Harano, Y Nakamura, H Isobe *J. Am. Chem. Soc.* **130** 7808 (2008)
45. D Tasis, N Tagmatarchis, A Bianco, M Prato *Chem. Rev.* **106** 1105 (2006)
46. A G Osorio, I C L Silveira, V L Bueno, C P Bergmann *Appl. Surf. Sci.* **255** 2485 (2008)
47. C Yang, D Wang, X Hu, C Dai, L Zhang *J. Alloys Compd.* **448** 109 (2008)
48. M N Kirikova, A S Ivanov, S V Savilov, V V Lunin *Izv. Akad. Nauk, Ser. Khim.* 291 (2008) [h]
49. G Xu, B Zhu, Y Han, Z Bo *Polymer* **48** 7510 (2007)
50. N T Hung, I V Anoshkin, A P Dement'ev, D V Katorov, E G Rakov *Neorg. Mater.* **44** 270 (2008) [e]
51. A B González-Guerrero, E Mendoza, E Pellicer, F Alsina, C Fernández-Sánchez, L M Lechuga *Chem. Phys. Lett.* **462** 256 (2008)
52. F Cataldo *Fullerenes, Nanotubes Carbon Nanostruct.* **16** 1 (2008)
53. V Georgakilas, A B Bourlinos, R Zboril, C Trapalis *Chem. Mater.* **20** 2884 (2008)
54. T J Aitchison, M Ginic-Markovic, J G Matisons, G P Simon, P M Fredericks *J. Phys. Chem. C* **111** 2440 (2007)
55. T Kar, S Scheiner, A K Roy *Chem. Phys. Lett.* **460** 225 (2008)
56. R A Graff, T M Swanson, M S Strano *Chem. Mater.* **20** 1824 (2008)
57. G-X Chen, H Shimizu *Polymer* **49** 943 (2008)
58. D R S Jeykumari, S S Narayanan *Nanotechnology* **18** 125501 (2007)
59. N Hu, G Dang, H Zhou, J Jing, C Chen *Mater. Lett.* **61** 5285 (2007)
60. L B Boinovich, A M Emel'yanenko *Usp. Khim.* **77** 619 (2008) [*Russ. Chem. Rev.* **77** 583 (2008)]
61. S J Pastine, D Okawa, B Kessler, M Rolandi, M Lorente, A Zettl, J M Frgchet *J. Am. Chem. Soc.* **130** 4238 (2008)
62. V Georgakilas, A B Bourlinos, D Gournis, T Tsoufis, C Trapalis, A Mateo-Alonso, M Prato *J. Am. Chem. Soc.* **130** 8733 (2008)
63. H R Sung, H B Jong, A M Shanmugharaj, H N Woo, S C Won *Appl. Surf. Sci.* **253** 4150 (2007)
64. C Ménard-Moyon, N Izard, E Doris, C Mioskowski *J. Am. Chem. Soc.* **128** 6552 (2006)
65. R Voggu, P Suguna, S Chandrasekaran, C N R Rao *Chem. Phys. Lett.* **443** 118 (2007)
66. M K Bayazit, K S Koleman *J. Am. Chem. Soc.* **131** 10670 (2009)
67. J Tumpane, N Karousis, N Tagmatarchis, B Nordén *Angew. Chem., Int. Ed.* **47** 5148 (2008)

68. G Sakkelariou, J Haining, J W Mays, N Hadjichristidis, D Baskaran *Chem. Mater.* **19** 6370 (2007)
69. D Priftis, G Sakkelariou, N Hadjichristidis, E K Penott, A T Lorenzo, A J Müller *J. Polym. Sci., Part A: Polym. Chem.* **47** 4379 (2009)
70. C Fantini, M L Usrey, M S Strano *J. Phys. Chem. C* **111** 17941 (2007)
71. D J Nelson, H Rhoads, C Brammer *J. Phys. Chem. C* **111** 17872 (2007)
72. K Woo-Jae, M L Usrey, M S Strano *Chem. Mater.* **19** 1571 (2007)
73. F G Brunetti, M A Herrero, J de M Muñoz, A Dìaz-Ortiz, J Alfonsi, M Meneghetti, M Prato, E Várquez *J. Am. Chem. Soc.* **130** 8094 (2008)
74. C D Doyle, J-D R Rocha, R B Weisman, J M Tour *J. Am. Chem. Soc.* **130** 6795 (2008)
75. A Pekker, D Wunderlich, K Kamaras, A Hirsch *Phys. Status Solidi B* **245** 1954 (2008)
76. K Balasubramanian, M Burghard, K Kern *Phys. Chem. Chem. Phys.* **10** 2256 (2008)
77. N Karousis, H Ali-Boucetta, K Kostarelos, N Tagmatarchis *Mater. Sci. Eng. B* **152** 8 (2008)
78. Z Wang, Y-X Li, Z-Z Zu, H-L Li *Chin. J. Chem.* **26** 666 (2008)
79. M D Ellison, P J Gasda *J. Phys. Chem. C* **112** 738 (2008)
80. X Wang, S Li, Y Xu, L Wan, H You, Q Li, S Wang *Appl. Surf. Sci.* **253** 7435 (2007)
81. E McRae, J Liu, M R I Zubiri, M Dossot, B Vigolo, R H Hauge, Y Fort, J-J Ehrhardt *Chem. Phys. Lett.* **430** 93 (2006)
82. E McRae, J Liu, M R I Zubiri, B Vigolo, M Dossot, Y Fort, J-J Ehrhardt *Carbon* **45** 885 (2007)
83. J Li, T Tang, X Zhang, S Li, M Li *Mater. Lett.* **61** 4351 (2007)
84. L Wei, Y Zhang *Nanotechnology* **18** 495703 (2007)
85. L Wei, Z Li, Y Zhang, in *The 2nd IEEE International Nano-electronics Conference (NEC), Shanghai, China, IEEE, US, 2008* p. 276
86. F Liang, A K Sadana, A Peera, J Chattopadhyay, Zh Gu, R H Hauge, W E Billups *Nano Lett.* **4** 1257 (2004)
87. F Borondics, E Jakab, S Pekker *J. Nanosci. Nanotechnol.* **7** 1551 (2007)
88. E M Garst, L J Dolby, S Esfandiari, N A Fedoruk, N C Chamberlain, A A Avey *J. Org. Chem.* **65** 7098 (2000)
89. X Tang, Q Jiao, Y Cao, P Zhang, H Liu, H Wu, M Zhou, X Li, Y Zhao *Chem. Lett.* **38** 220 (2009)
90. D Wunderlich, F Hauke, A Hirsch *J. Mater. Chem.* **18** 1493 (2008)
91. T Umeyama, N Tezuka, M Fujita, Y Matano, N Takeda, K Murakoshi, K Yoshida, S Isoda, H Imahori *J. Phys. Chem. C* **111** 9734 (2007)
92. M Liu; Y Yang, T Zhu, Z Liu *J. Phys. Chem. C* **111** 2379 (2007)
93. H-J Lee, S-W Han, Y-D Kwon, L-S Tan, J-B Baek *Carbon* **46** 1850 (2008)
94. S-W Han, S-J Oh, L-S Tan, J-B Baek *Carbon* **46** 1841 (2008)
95. E T Mickelson, C B Huffman, A G Rinzler, R E Smalley, R H Hauge, J L Margrave *Chem. Phys. Lett.* **296** 188 (1998)
96. A V Krestinin, A P Kharitonov, Yu M Shul'ga, O M Zhigalina, E I Knerel'man, M Dubois, M M Brzhezinskaya, A S Vinogradov, A B Preobrazhenskii, G I Zvereva, M B Kislov, V M Martynenko, I I Korobov, G I Davydova, V G Zhigalina, N A Kiselev *Ros. Nanotekhnol.* (4) 67 (2009) [a]
97. K S Coleman, A K Chakraborty, S R Bailey, J Sloan, M Alexander *Chem. Mater.* **19** 1076 (2007)
98. M X Pullikkathara, V Kuznetsov, V N Khabashesku *Chem. Mater.* **20** 2685 (2008)
99. M Kh Pullikkatara, V N Khabashesku *Izv. Akad. Nauk, Ser. Khim.* 1035 (2008) [h]
100. J-P Tessonnier, A Villa, O Majoulet, D S Su, R Schlögl *Angew. Chem., Int. Ed.* **48** 6543 (2009)
101. Z Syrgiannis, F Hauke, J Röhrl, M Hundhausen, R Graupner, Y Elemes, A Hirsch *Eur. J. Org. Chem.* 2544 (2008)
102. W Zhang, J K Sprafke, M Ma, E Y Tsui, S A Sydlik, G C Rutledge, T M Swager *J. Am. Chem. Soc.* **131** 8446 (2009)
103. W Zhang, A U Shaikh, E Y Tsui, T M Swager *Chem. Mater.* **21** 3234 (2009)
104. J Yu, S Mathew, B S Flavel, M R Johnston, G J Shapter *J. Am. Chem. Soc.* **130** 8788 (2008)
105. X Wang, B Xia, X Zhu, J Chen, S Qui, J Li *J. Solid State Chem.* **181** 822 (2008)
106. Q Wang, Y Qin, Y Zhu, X Huang, Y Tian, P Zhang, Z-X Guo, Y Wang *Chem. Phys. Lett.* **457** 159 (2008)
107. H Pan, L Liu, Z-X Guo, L Dai, F Zhang, D Zhu, R Czerw, D L Carroll *Nano Lett.* **3** 29 (2003)
108. C Aprile, R Martín, M Alvaro, H Garcia, J C Scaiano *Chem. Mater.* **21** 884 (2009)
109. H Yu, Y Jin, Z Li, F Peng, H Wang *J. Solid State Chem.* **181** 432 (2008)
110. A Gomathi, S J Hoseini, C N R Rao *J. Mater. Chem.* **19** 988 (2009)
111. C Tripisciano, E Borowiak-Palen *Phys. Status Solidi B* **245** 1979 (2008)
112. J Chattopadhyay, S Chakraborty, A Mukherjee, R Wang, P S Engel, W E Billups *J. Phys. Chem. C* **111** 17928 (2007)
113. G P Miller, J Kintigh, E Kim, P F Weck, S Berber, D Tománek *J. Am. Chem. Soc.* **130** 2296 (2008)
114. D V Kosynkin, A L Higginbotham, A Sinitskii, J R Lomeda, A Dimiev, B K Price, J M Tour *Nature (London)* **458** 872 (2009)
115. C G Salzman, S A Llewellyn, G Tobias, M A H Ward, Y Hyu, V L H Green *Adv. Mater.* **19** 883 (2007)
116. T Lemek, J Mazurkiewicz, L Stobinski, H M Lin, P Tomasik *J. Nanosci. Nanotechnol.* **7** 3081 (2007)
117. F F Komarov, V B Karpovich, O V Mil'chanin, in *Nanochastitsy v Kondensirovannykh Sredakh. Sbornik Nauchnykh Statei* (Nanoparticles in Condensed Media. Collection of Scientific Works) (Ed. P A Vityaz') (Minsk: Belarus State University, 2008) p. 99
118. I V Anoshkin, O S Bazykina, E V Rakova, E G Rakov *Zh. Fiz. Khim.* **82** 322 (2008) [f]
119. J Duque, L Cognet, A N G Parra-Vasquez, N Nicholas, H K Schmidt, M Pasquali *J. Am. Chem. Soc.* **130** 2626 (2008)
120. A Mdarhri, F Carmona, C Brosseau, P Delhaes *J. Appl. Phys.* **103** 054303 (2008)
121. H Wei, S N Kim, M Zhao, S-Y Ju, B D Huey, H L Marcus, F Papadimitrakopoulos *Chem. Mater.* **20** 2793 (2008)
122. M-J Jiang, Z-M Dang, S-H Yao, J Bai *Chem. Phys. Lett.* **457** 352 (2008)
123. R Jung, H-S Kim, S-M Kwon, S H Lee, H-J Jin *J. Polym. Sci., Part B: Polym. Phys.* **46** 1235 (2008)
124. T Yamamoto, Y Miyauchi, J Motoyanagi, T Fukushima, T Aida, M Kato, S Maruyma *Jpn. J. Appl. Phys.* **47** 2000 (2008)
125. T Yamamoto, J Motoyanagi, Y Murakami, Y Miyauchi, S Maruyama, M Kato *Appl. Phys. Express* **2** 055501 (2009)
126. S-Y Ju, W P Kopcha, F Papadimitrakopoulos *Science* **323** 1319 (2009)
127. I G Sidorenko, O V Markitan, N N Vlasova, G M Zagorovskii, V V Lobanov *Zh. Fiz. Khim.* **83** 1139 (2009) [f]
128. C Fantini, J Cassimiro, V S T Peressinotto, F Plentz, A G Souza Filho, C A Furtado, A P Santos *Chem. Phys. Lett.* **473** 96 (2009)
129. Q Wang, Y Han, Y Wang, Y Qin, Z-X Guo *J. Phys. Chem. B* **112** 7227 (2008)
130. W Chen, L Duan, L Wang, D Zhu *Environ. Sci. Technol.* **42** 6862 (2008)
131. H-Z Geng, K K Kim, K P So, Y S Lee, Y K Chang, Y H Lee *J. Am. Chem. Soc.* **129** 7758 (2007)
132. S-M Yoon, S J Kim, H-J Shin, A Benayad, S-J Choi, K K Kim, S M Kim, Y J Park, G Kim, J-Y Choi, Y H Lee *J. Am. Chem. Soc.* **130** 2610 (2008)
133. H-J Shin, S M Kim, S-M Yoon, A Benayad, K K Kim, S J Kim, H K Park, S-J Choi, Y H Lee *J. Am. Chem. Soc.* **130** 2062 (2008)
134. C Morgan, Z Alemipour, M Baxendale *Phys. Status Solidi A* **205** 1394 (2008)

135. Z Wu, Z Chen, X Du, J M Logan, J Sippell, M Nikolou, K Kamaras, J R Reynolds, D B Tanner, A F Hebard, A G Rinzler *Science* **305** 1273 (2004)
136. I Cabria, M Lopez, J A Alonso *J. Chem. Phys.* **128** 214703 (2008)
137. M C LeMieux, M Roberts, S Barman, Y W Jin, J M Kim, Z Bao *Science* **321** 101 (2008)
138. R E Anderson, A R Barron *J. Nanosci. Nanotechnol.* **7** 3436 (2007)
139. Y-F Lan, J-J Lin *J. Phys. Chem. A* **113** 8654 (2009)
140. S Pack, T Kashiwagi, D Stemp, J Koo, M Si, J C Sokolov, M H Rafailovich *Macromolecules* **42** 6698 (2009)
141. K Yurekli, C A Mitchell, R Krishnamoorti *J. Am. Chem. Soc.* **126** 9902 (2004)
142. A de Leon, A F Jalbout, V A Basiuk *Chem. Phys. Lett.* **457** 185 (2008)
143. N K Tolochko, S A Stanovoi, S A Zhdanok, A V Krauklis *Perspekt. Mater.* (2) 5 (2008) [b]
144. A Urbina, C Miguel, J L Delgado, F Langa, C Díaz-Paniagua, M Jiménez, F Batallán *J. Phys.: Condens. Matter* **20** 104208 (2008)
145. T-H Kim, C Doe, S R Kline, S-M Choi *Macromolecules* **41** 3261 (2008)
146. Y Wang, H Xiong, Y Gao, H Li *J. Mater. Chem.* **43** 5609 (2008)
147. Zh Liu, X Sun, N Nakayama-Ratchford, H Dai *ACS Nano* **1** 50 (2007)
148. N Li, L Yanling, L Zhanqing *Sens. Actuators, B* **126** 361 (2007)
149. J S An, B-U Nam, S H Tan, S C Hong, in *Conference Advanced Polymers for Emerging Technologies, Busan, South Korea, 2006* (Weinheim: Wiley, VCH, 2007) p. 276
150. J-G Yu, S-Q Liu, K-L Huang, J-C Tang *Chin. J. Chem.* **26** 560 (2008)
151. L Yu, C M Li, Q Zhou, Y Gan, Q L Bao *Nanotechnology* **18** 115614 (2007)
152. Q Shi, D Yang, Y Su, J Li, Z Jiang, Y Jiang, W Yuan *J. Nanopart. Res.* **9** 1205 (2007)
153. A Goff, V Artero, B Jousselme, P D Tran, N Guillet, R Métayé, A Fihri, S Palacin, M Fontec *Science* **326** 1384 (2009)
154. A Garcia, M A Herrero, S Frein, R Deschenaux, R Muñoz, I Bustero, F Toma, V Prato *Phys. Status Solidi A* **205** 1402 (2008)
155. Y-L Zeng, J-H Jiang, R-Q Yu, Y-F Huang, X-B Zhang, C-R Tang, G-L Shen *Electrochem. Commun.* **9** 185 (2007)
156. M A Herrero, F M Toma, K T Al-Jamal, K Kostarelos, A Bianco, T Da Ros, F Bano, L Casalis, G Scoles, M Prato *J. Am. Chem. Soc.* **131** 9843 (2009)
157. M-R Babaa, J-L Bantignies, L Alvarez, P Parent, F Le Normand, M Gulas, J Mane Mane, P Poncharal, B P Doyle *J. Nanosci. Nanotechnol.* **7** 3463 (2007)
158. Y Zhang, A A Broekhuis, M C A Stuart, T F Landaluce, D Fausti, P Rudolf, F Picchioni *Macromolecules* **41** 6141 (2008)
159. B Wu, D Hu, Y Kuang, B Liu, X Zhang, J Chen *Angew. Chem., Int. Ed.* **48** 4751 (2009)
160. Y Peng, H Liu, X Zhang, Y Li, S Liu *J. Polym. Sci., Part A: Polym. Chem.* **47** 1627 (2009)
161. M Grujicic, Y-P Sun, K L Koudela *Appl. Surf. Sci.* **253** 3009 (2007)
162. H-B Fan, K Zhang, M M F Yuen *J. Appl. Phys.* **106** 034307 (2009)
163. E M Byrne, M A McCarthy, Z Xia, W A Curtin *Phys. Rev. Lett.* **103** 045502 (2009)
164. P G Holder, M B Francis *Angew. Chem., Int. Ed.* **46** 4370 (2007)
165. S H Tan, J C Goak, N Lee, J-Y Kim, S C Hong, in *Conference Advanced Polymers for Emerging Technologies, Busan, South Korea, 2006* (Weinheim: Wiley, VCH, 2007) p. 270
166. R Shvartzman-Cohen, M Florent, D Goldfarb, I Szleifer, R Yerushalmi-Rozen *Langmuir* **24** 4625 (2008)
167. N Fujita, M Asai, T Yamashita, S Shinkai *J. Mater. Chem.* **14** 2106 (2004)
168. F Wang, H Gu, T M Swager *J. Am. Chem. Soc.* **130** 5392 (2008)
169. S Bhandari, M Deepa, A K Srivastava, A G Joshi, R Kant *J. Phys. Chem. B* **113** 9416 (2009)
170. E Iton, Y Kato, Y Sano, K Miyari *Jpn. J. Appl. Phys.* **47** 2016 (2008)
171. C Li, Y Chen, Y Wang, Z Iqbal, M Chowallab, S Mitra *J. Mater. Chem.* **17** 2406 (2007)
172. H J Won, U L Jea, J Huh, H K Keon, C Park *Carbon* **45** 1051 (2007)
173. S Srinivasan, S S Babu, V K Praveen, A Ajayaghosh *Angew. Chem., Int. Ed.* **47** 5746 (2008)
174. S Srinivasan, V K Praveen, R Phili, A Ajayaghosh *Angew. Chem., Int. Ed.* **47** 5750 (2008)
175. F Cheng, P Imin, C Maunders, G Botton, A Adronov *Macromolecules* **41** 2304 (2008)
176. C Li, J-C Hsu, K Sugiyama, A Hirao, W-C Chen, R Mezzenga *Macromolecules* **42** 5793 (2009)
177. Y Yamaguchi, S Haraguchi, N Nakashima *Chem. Lett.* **37** 546 (2008)
178. C Y Lee, R Sharma, A D Radadia, R Masel, M S Strano *Angew. Chem., Int. Ed.* **47** 5018 (2008)
179. W Z Yuan, L Tang, H Zhao, J K Jin, J Z Sun, A Qin, H P Xu, J Liu, F Yang, Q Zheng, E Chen, B Z Tang *Macromolecules* **42** 52 (2009)
180. S Wang, S P Jiang, X Wang *Nanotechnology* **19** 265601 (2008)
181. S Razdan, P K Patra, S Kar, L Ci, R Vajtai, A Kukovecz, Z Kónya, I Kiricsi, P M Ajayan *Chem. Mater.* **21** 3062 (2009)
182. J F Campbell, I Tassmer, H H Thorp, D A Erie *J. Am. Chem. Soc.* **130** 10648 (2008)
183. Y Noguchi, T Fujigaya, Y Niidome, N Nakashima *Chem. Phys. Lett.* **455** 249 (2008)
184. E A Obraztsova, Author's Abstract of Candidate Thesis in Physical and Mathematic Sciences, Moscow: M V Lomonosov Moscow State University, 2008
185. E P D'yachkov, S P Dolin, P N D'yachkov *Dokl. Akad. Nauk* **423** 202 (2008) [i]
186. Y Noguchi, T Fujigaya, Y Niidome, N Nakashima *Chem. – Eur. J.* **14** 5966 (2008)
187. S G Stepanian, M V Karachevtsev, A Yu Glamazda, V A Karachevtsev, Z L Adamowich *Chem. Phys. Lett.* **459** 153 (2008)
188. S G Stepanian, M V Karachevtsev, A Yu Glamazda, V A Karachevtsev, Z L Adamowich *J. Phys. Chem. A* **113** 3621 (2009)
189. M Gong, T Han, C Cai, T Lu, J Du *J. Electroanal. Chem.* **623** 8 (2008)
190. Y Ma, P L Chiu, A Serrano, S R Ali, A M Chen, H He *J. Am. Chem. Soc.* **130** 7921 (2008)
191. G Sanchez-Pomales, L Santiago-Rodriguez, N E Rivera-Velez, C R Cabrera *Phys. Status Solidi A* **204** 1791 (2007)
192. B J Bauer, M L Becker, V Bajpai, J A Fagan, E K Hobbie, K Migler, C M Guttman, W R Blair *J. Phys. Chem. C* **111** 17914 (2007)
193. K S Rao, S Daniel, T P Rao, S U Rani, G R K Naidu, L Hea-Yeon, T Kawai *Sens. Actuators, B* **122** 672 (2007)
194. G N Dovbeshko, O M Fesenko, E D Obraztsova, K R Allakhverdiev, A E Kaiya *Zh. Strukt. Khim.* **50** 991 (2009) [j]
195. W Zheng, Y Q Chen, Y F Zheng *Appl. Surf. Sci.* **255** 571 (2008)
196. E Polaczek, L Stobiński, J Mazurkiewicz, P Tomasik, H Kolaczek, H-M Lin *Polymer* **52** 34 (2007)
197. L Stobiński, E Polaczek, K Rębilas, J Mazurkiewicz, R Wrzalik, H-M Lin, P Tomasik *Polymer* **53** 571 (2008)
198. L S Witus, J-D R Rocha, V M Yuwono, S E Paramonov, R B Weisman, J D Hartgerink *J. Mater. Chem.* **17** 1909 (2007)
199. Y Liu, L Gao, J Sun *J. Phys. Chem. C* **111** 1223 (2007)
200. D Cui *J. Nanosci. Nanotechnol.* **7** 1298 (2007)
201. P Wu, X Chen, N Hu, U C Tam, O Blixt, A Zettl, C R Bertozzi *Angew. Chem., Int. Ed.* **47** 5022 (2008)
202. H Hyung, J-H Kim *Environ. Sci. Technol.* **42** 4416 (2008)
203. Y-L Zhao, J F Stoddart *Acc. Chem. Res.* **42** 1161 (2009)
204. W Z Yuan, Y Mao, H Zhao, J Z Sun, H P Xu, J K Jin, Q Zheng, B Z Tang *Macromolecules* **41** 701 (2008)

205. E O Perepelitsina, V P Grachev, S V Kurmaz, I S Kochneva, S V Kondrashov, I V Anoshkin, in *Tezisy Lektsii i Dokladov 3-i Mezhdunarodnoi Shkoly po Khimii i Fiziko-khimii Oligomerov* (Abstracts of Lectures and Reports of the Third International School on the Chemical and Physical Chemistry of Oligomers) (Chernogolovka: Institute of Problems of Chemical Physics, Russian Academy of Sciences, 2007) p. 86
206. A B Schoch, R S Kenneth, L C Brinson *Macromolecules* **41** 4340 (2008)
207. S Chang, S Singamaneni, E Kharlampieva, S L Young, V V Tsukruk *Macromolecules* **42** 5781 (2009)
208. Z Yang, X Chen, C Chen, W Li, H Zhang, L Xu, B Yi *Polym. Compos.* **28** 36 (2007)
209. I Gurevitch, S Srebnik *J. Chem. Phys.* **128** 144901 (2008)
210. V F Posokhova, L L Gapochkina, V V Kireev, V P Chuev *Plast. Massy* (9) 10 (2006)
211. F V Kiryukhantsev-Korneev, A N Sheveiko, E A Levashov, D V Shtanskii *Vop. Materialoved.* (2) 187 (2008) [b]
212. L M Bronshtein, S N Sidorov, P M Valetskii *Usp. Khim.* **73** 542 (2004) [*Russ. Chem. Rev.* **73** 501 (2004)]
213. R Pérez, S Banda, Z Ounaies *J. Appl. Phys.* **103** 074302 (2008)
214. M N Tchoul, W T Ford, M L P Ha, I Chavez-Sumarriva, B P Grady, G Lolli, D E Resasco, S Arepalli *Chem. Mater.* **20** 3120 (2008)
215. S Bose, A R Bhattacharyya, A P Bondre, A R Kulkarni, P Pötschke *J. Polym. Sci., Part B: Polym. Phys.* **46** 1619 (2008)
216. Q Zheng, Q Xue, K Yan, X Gao, O Li, L Hao *J. Appl. Phys.* **103** 044302 (2008)
217. W Zhu, A Rosén, K Bolton *J. Chem. Phys.* **128** 124708 (2008)
218. K J Sun, R A Wincheski, C Park *J. Appl. Phys.* **103** 023908 (2008)
219. C-W Lin, L C Huang, C-C M Ma, A C-M Yang, C-J Lin, L-J Lin *Macromolecules* **41** 4978 (2008)
220. A Wall, J N Coleman, M S Ferreira *Phys. Rev. B* **71** 125421 (2005)
221. A L Svistkov, L A Komar, G Heinrich, B Lauke *Vysokomol. Soedin., Ser. A* **50** 903 (2008) [k]
222. W Jeong, M R Kessler *Chem. Mater.* **20** 7060 (2008)
223. J J Hernández, M C Garcia-Gutiérrez, A Nogales, D R Rueda, T A Ezguerra *Macromolecules* **42** 4374 (2009)
224. B P Grady, A Paul, J E Peters, W T Ford *Macromolecules* **42** 6152 (2009)
225. S Pujari, S S Rahatekar, J W Gilman, K K Koriol, A H Windle, W R Burghardt *J. Chem. Phys.* **130** 214903 (2009)
226. D W Schaefer, R S Justice *Macromolecules* **40** 8501 (2007)
227. O Breuer, U Sundararaj *Polym. Compos.* **25** 630 (2004)
228. S-Y Fu, Z-K Chen, S Hong, C C Han *Carbon* **47** 3192 (2009)
229. H E Miltner, N Grossiord, L Kangbo, J Loos, C E Koning, B van Mele *Macromolecules* **41** 5753 (2008)
230. A I Isayev, R Kumar, T M Lewis *Polymer* **50** 250 (2009)
231. J Masuda, J M Tarkelson *Macromolecules* **41** 5974 (2008)
232. A Katsuki, H Yamamoto, Y Fujiwara, M Fujiwara, M Endo, Y Tanimoto *Chem. Lett.* **37** 728 (2008)
233. T-M Wu, E-C Chen *J. Polym. Sci., Part B: Polym. Phys.* **44** 598 (2006)
234. R Song, D Yang, L He *J. Mater. Sci.* **43** 1205 (2008)
235. A D Grishina, L Ya Pereshivko, L Licea-Jiménez, T V Krivenko, V V Savel'ev, R W Rychwalski *Khim. Vys. Energ.* **41** 311 (2007) [l]
236. A D Grishina, L Licea-Jiménez, L Ya Pereshivko, T V Krivenko, V V Savel'ev, R W Rychwalski, A V Vannikov *Vysokomol. Soedin., Ser. A* **50** 1665 (2008) [k]
237. A R Tameev, L Ya Pereshivko, A V Vannikov *Vysokomol. Soedin., Ser. A* **51** 235 (2009) [k]
238. N A Plate, in *Otchet o Deyatel'nosti Rossiiskoi Akademii Nauk v 2006 g* (Report about Activity of Russian Academy of Sciences in 2006) (Moscow: Nauka, 2007) Vol. 2, p. 79
239. E R Badamshina, E G Atovmyan, A A Grishchuk, A V Krestinin, V A Lesnichaya, Yu A Ol'khov, Ya I Estrin, in *Tezisy Dokladov II Mezhdunarodnogo Foruma po Nanotekhnologiyam 'Rosnanotekh'09'* (Abstracts of Reports of the IInd International Forum on Nanotechnology, Rosnanotekh'09', Moscow, 2009) p. 306
240. F Buffa, G A Abraham, B P Grady, D Resasco *J. Polym. Sci., Part B: Polym. Phys.* **45** 490 (2007)
241. N G Sahoo, Y C Jung, H H So, J W Cho *J. Korean Phys. Soc.* **51** 1 (2007)
242. K H Kim, W H Jo *Compos. Sci. Technol.* **68** 2120 (2008)
243. S H Lee, J S Park, B K Lim, S O Kim *J. Appl. Polym. Sci.* **110** 431 (2008)
244. E M Shpilevskii, E V Levshukova, in *Nanochastitsy v Kondensirovannykh Sredakh. Sbornik Nauchnykh Statei* (Nanoparticles in Condensed Media. Collection of Scientific Articles) (Ed. P A Vityaz') (Minsk: Belarus State University, 2008) p. 37
245. A V Tausenev, E D Obraztsova, A S Lobach, V I Konov, A V Konyashchenko, P G Kryukov, E M Dianov *Kvantovaya Elektron.* **37** 847 (2007) [*Quantum Electron.* **37** 847 (2007)]
246. D V Khudyakov, A S Lobach, S M Aldoshin, V A Nadtochenko *Ros. Nanotekhnol.* **3** 129 (2008) [a]
247. L Bokobza, M Rahmani, C Belin, J-L Bruneel, N-E el Bounia *J. Polym. Sci., Part B: Polym. Phys.* **46** 1939 (2008)
248. C Lee, M D Dadmun *J. Polym. Sci., Part B: Polym. Phys.* **46** 1747 (2008)
249. J Xu, K M Razeeb, S Rou *J. Polym. Sci., Part B: Polym. Phys.* **46** 1845 (2008)
250. D McIntosh, V N Khabashesku, E V Barrera *J. Phys. Chem. C* **111** 1592 (2007)
251. S Pujari, T Ramanthan, K Kasimatis, J Masuda, R Andrews, J M Torkelson, L C Brinson, W R Burghardt *J. Polym. Sci., Part B: Polym. Phys.* **47** 1426 (2009)
252. B P Grady, D J Arthur, J Ferguson *Polym. Eng. Sci.* **49** 2440 (2009)
253. S Wang, R Liang, B Wang, C Zhang *Chem. Phys. Lett.* **457** 371 (2008)
254. M C García-Gutiérrez, J J Hernández, A Nogales, P Panine, D R Rueda, T A Ezquerra *Macromolecules* **41** 844 (2008)
255. X Wang, Z Du, C Zhang, C Li, X Yang, H Li *J. Polym. Sci., Part A: Polym. Chem.* **46** 4857 (2008)
256. I-Y Jeon, L-S Tan, J-B Baek *J. Polym. Sci., Part A: Polym. Chem.* **46** 3471 (2008)
257. B Dong, Z Yang, Y Huang, H-L Li, L Liu, F-Y Yan *J. Mater. Sci.* **40** 4379 (2005)
258. C M Homenick, G Lawson, A Adronov *Polym. Rev.* **47** 265 (2007)
259. A A Koval'chuk, A N Shchegolikhin, V G Shevchenko, P M Nedorezova, A N Klyamkina, A M Aladyshev *Macromolecules* **41** 3149 (2008)
260. A A Koval'chuk, A N Shchegolikhin, V G Shevchenko, P M Nedorezova, A N Klyamkina, A M Aladyshev, in *Tezisy Dokladov XIX Simpoziuma 'Sovremennaya Khimicheskaya Fizika'* (Abstracts of Reports of the XIXth Symposium 'Modern Chemical Physics' (Chernogolovka: Institute of Problems of Chemical Physics, Russian Academy of Sciences, 2007) p. 124
261. A A Koval'chuk, A N Shchegolikhin, I L Dubnikova, P M Nedorezova, A N Klyamkina, A M Aladyshev *Plast. Massy* (5) 27 (2008)
262. A A Koval'chuk, V G Shevchenko, A N Shchegolikhin, P M Nedorezova, A N Klyamkina, A M Aladyshev *Macromolecules* **41** 7536 (2008)
263. A A Koval'chuk, Author's Abstract of Candidate Thesis in Chemical Sciences, Institute of Chemical Physics, Russian Academy of Sciences, Moscow, 2008
264. L Liu, Y Wang, J Wu, F Xiang, Z Zhou *J. Polym. Sci., Part B: Polym. Phys.* **47** 1331 (2009)
265. A Toti, G Giambastiani, C Bianchini, A Meli, S Bredeau, Ph Dubois, D Bonduel, M Claes *Chem. Mater.* **20** 3092 (2008)
266. A M Shanmugharaj, J H Bae, R N Rati, H R Sung *J. Polym. Sci., Part A: Polym. Chem.* **45** 460 (2007)
267. I Park, W Lee, J Kim, M Park, H Lee *Sens. Actuators, B* **126** 301 (2007)
268. M Kim, C K Hong, S Choe, S E Shim *J. Polym. Sci., Part A: Polym. Chem.* **45** 4413 (2007)
269. X Chen, F Tao, J Wang, H Yang, J Zou, X Chen, X Feng *Mater. Sci. Eng. A* **499** 469 (2009)

270. H-M Huang, I-C Liu, C-Y Chang, H-C Tsai, C-H Hsu, R C-C Tsiang *J. Polym. Sci., Part A: Polym. Chem.* **42** 5802 (2004)
271. G Mountrichas, S Pispas, N Tagmatarchis *Mater. Sci. Eng. B (Adv. Functional Solid-State Materials)* **152** 40 (2008)
272. Y Lin, M J Meziani, Y-P Sun *J. Mater. Chem.* **17** 1143 (2007)
273. M Moniruzzaman, J Chattopadhyay, W E Billups, K I Winey *Nano Lett.* **7** 1178 (2007)
274. A Garcta-Gallastegui, I Obieta, I Bustero, G Imbuluzqueta, J Arbiol, J I Miranda, J M Aizparua *Chem. Mater.* **20** 4433 (2008)
275. S Chen, D Chen, G Wu *Macromol. Rapid Commun.* **27** 882 (2006)
276. X Wang, H Liu, L Qiu *Mater. Lett.* **61** 2350 (2007)
277. C Velasco-Santos, A L Martìnez-Hernández, F T Fisher, R Ruoff, V M Castañ *Chem. Mater.* **15** 4470 (2003)
278. Y Tang, D Yang, F Qin, J Hu, C Wang, H Xu *J. Solid State Chem.* **182** 2279 (2009)
279. M Cadek, J N Coleman, K P Ryan, V Nicolosi, G Bister, A Fonseca, J B Nagy, K Szostak, F Beguin, W J Blau *Nano Lett.* **4** 353 (2004)
280. L Tessier, J Chancolon, P-J Alet, A Trenggono, M Mayne-L'Hermite, G Deniau, P Jégou, S Palacin *Phys. Status Solidi A* **205** 1412 (2008)
281. C Chochos, A A Stefopoulos, S Campidelli, M Prato, V G Gregoriou, J K Kallitsis *Macromolecules* **41** 1825 (2008)
282. B Ruelle, S Peeterbroeck, R Gouttebaron, T Godfroid, F Monteverde, J-P Dauchot, M Alexandre, M Hecq, P Dubois *J. Mater. Chem.* **17** 157 (2007)
283. Y H Yan, J Cui, M B Chan-Park, X Wang, Q Y Wu *Nanotechnology* **18** 115712 (2007)
284. Y Xu, C Gao, H Kong, D Yan, Y Z Jin, P C P Watts *Macromolecules* **37** 8846 (2004)
285. V V Abalyaeva, O N Efimov, in *Nanostrukturnye Materialy dlya Zapasaniya i Preobrazovaniya Energii* (Nanostructural Materials for Energy Storage and Conversion) (Eds V F Razumova, M V Klyueva) (Ivanovo: Ivanovo State University, 2009) p. 164
286. L-B Kong, J Zhang, J-J An, Y-C Luo, L Kang *J. Mater. Sci.* **43** 3664 (2009)
287. W K Maser, R Sainz, M T Martínez, A M Benito *Contrib. Sci.* **4** 187 (2008)
288. C Kvarnstrom, W Di, T Lindfors, A Ivaska *Electrochem. Commun.* **9** 206 (2007)
289. E Lafuente, M A Callejas, R Sainz, A M Benito, W K Maser, M L Sanjuan, D Saurel, J M de Teresa, M T Martinez *Carbon* **46** 1909 (2008)
290. L Kong, X Lu, W Zhang *J. Solid State Chem.* **181** 628 (2008)
291. K-P Lee, A I Gopalan, K S Kim, P Santhosh *J. Nanosci. Nanotechnol.* **7** 3386 (2007)
292. E Bekyarova, E T Thostenso, A Yu, M E Itkis, D Fakhrutdinov, T-W Chou, R C Haddon *J. Phys. Chem. C* **111** 17865 (2007)
293. C-H Tseng, C-C Wang, C-Y Chen *Chem. Mater.* **19** 308 (2007)
294. C E Pizzutto, J Suave, J Bertholdi, S H Pezzin, L A F Coelho, S C Amico *J. Rein. Plast. Compos.* **29** 524 (2010)
295. H Chena, O Jacobs, W Wua, G Rudigerb, B Schadelb *Polym. Test.* **26** 351 (2007)
296. W Zou, Z Du, Y Liu, X Yang, H Li, C Zhang *Compos. Sci. Technol.* **68** 3259 (2008)
297. J T Kim, H-C Kim, S-K Kim, J Kathi, K-Y Rhee *J. Compos. Mater.*; online first published as doi: 10.1177/0021998309345313 (2009)
298. K John, K Y Rhee *J. Mater. Sci.* **43** 33 (2008)
299. S Wang, R Liang, B Wang, C Zhang *Nanotechnology* **19** 085710 (2008)
300. P C Ma, J-K Kim, B Z Tang *Compos. Sci. Technol.* **67** 2965 (2007)
301. L Sun, G L Warren, J Y O'Reilly, W N Everett, S M Lee, D Davis, D Lagoudas, H-J Sue *Carbon* **46** 320 (2008)
302. S Wang, Z Liang, P Gonnet, Y-H Liao, B Wang, C Zhang *Adv. Funct. Mater.* **17** 87 (2007)
303. A Visco, L Calabrese, C Milone *J. Rein. Plast. Compos.* **28** 937 (2009)
304. S Rana, R Alagirusamy, J Mangala *J. Rein. Plast. Compos.* **28** 461 (2009)
305. Y Geng, M Y Liu, J Li, X M Shi, J K Kim *Composites, Part A: Appl. Sci. Manufact.* **39** 1876 (2008)
306. X Li, S Y Wong, W C Tjiu, B P Lyons, S A Oh, C B He *Carbon* **46** 829 (2008)
307. L A S De A Prado, A De La Vega, J Sumfleth, K Shulte *J. Polym. Sci., Part B: Polym. Phys.* **47** 1860 (2009)
308. K E Prasada, B Das, U Maitra, U Ramamurty, C N R Rao *Proc. Natl. Acad. Sci. USA* **106** 13186 (2009)
309. S K Swain, I Jena *Asian J. Chem.* **22** 1 (2010)
310. Z Spitalsky, D Tasis, K Papagelis, C Galiotis *Prog. Polym. Sci.* **35** 357 (2010)
311. I Tiwari, K P Singh, M Singh *Russ. J. Gen. Chem.* **79** 2685 (2009)
312. S Ghosh, P Nayek, S K Roy, R Gangopadhyay, M R Molla, R Dabrowski *Appl. Phys. Lett.* **96** 073101 (2010)
313. D Kim, Y Kim, K Choi, J C Grunlan, C Yu *ASC Nano* **4** 513 (2010)
314. J H Kang, C Park, J A Scholl, A H Brazin, N M Holloway, J W High, S E Lowther, J S Harrison *J. Polym. Sci., Part B: Polym. Phys.* **47** 1635 (2009)
315. D Izuhara, T M Swager *Macromolecules* **42** 5416 (2009)
316. R D Kroshefsky, J L Price, D Mangaraj *Rubber Chem. Technol.* **82** 340 (2009)
317. A A Bezhenar, V S Kopan', N I Piven' *Nanosist., Nanomater., Nanotekhnol. Zb. Nauk. Prats* **6** 25 (2008)
318. B Li, Y C Zhang, Z M Li, S N Li, X N Zhang *J. Phys. Chem. B* **114** 689 (2010)
319. M Kalbac, L Kavan, L Dunsch *Synth. Met.* **159** 2245 (2009)
320. K Kamarás, B Botka, Á Pekker, S Ben-Valid, A Zeng, L Reiss, S Yitzchaik *Phys. Status Solidi B* **246** 2737 (2009)
321. X X Sun, M Song *Macromol. Theory Simul.* **19** 57 (2010)
322. I Singh, A Verma, I Kaur, L M Bharadwaj, V Bhatia, V K Jain, C S Bhatia, P K Bhatnagar, P C Mathur *J. Polym. Sci., Part B: Polym. Phys.* **48** 89 (2010)
323. R Simoes, J Silva, S Lanceros-Mendez, R Vaia *J. Mater. Sci.* **45** 268 (2010)
324. G O Lim, K T Min, G H Kim *Polym. Eng. Sci.* **50** 290 (2010)
325. M Saphiannikova, I Alig *Phys. Status Solidi B* **246** 2453 (2009)
326. D Lellinger, T Skipa, W Bom, I Alig *Phys. Status Solidi B* **246** 2667 (2009)
327. S H Liao, C C Weng, C Y Yen, M C Hsiao, C C M Ma, M C Tsai, A Su, M Y Yen, Y F Lin, P L Liu *J. Power Sourses* **195** 263 (2010)
328. K U Jeong, J Y Lim, J Y Lee, S L Kang, C Nah *Polym. Int.* **59** 100 (2010)
329. K Lee, S S Lee, J A Lee, K C Lee, S Ji *Appl. Phys. Lett.* **96** 013511 (2010)
330. Z R Li, V Saini, E Dervishi, V P Kunets, J H Zhang, Y Xu, A R Biris, G J Salamo, A S Biris *Appl. Phys. Lett.* **96** 033110 (2010)
331. M D Rubianes, A S Arribas, E Bermejo, M Chicharro, A Zapardiel, G Rivas *Sens. Actuators, B* **144** 274 (2010)
332. N Jha, S Ramaprabhu *J. Nanosci. Nanotechnol.* **10** 2798 (2010)
333. N Hu, Y Karube, M Arai, T Watanabe, C Yan, Y Li , Y L Liu, H Fukunaga *Carbon* **48** 680 (2010)
334. L L Lebel, B Aissa, M A El Khakani, D Therriault *Adv. Mater.* **22** 592 (2010)
335. F P Yu, H Cai, W J He, W M Yang, Z K Me *J. Appl. Polym. Sci.* **115** 2946 (2010)
336. X Xin, H G Li, S A Wieczorek, T Szymborski, E Kalwarczyk, N Ziebacz, E Corecka, D Pociecha, R Holyst *Langmuir* **26** 3562 (2010)
337. L Domov, O Yaroshchuk, M Lebovka *Nanosist., Nanomater., Nanotekhnol. Zb. Nauk. Prats* **6** 625 (2008)
338. N G Sahoo, H K F Cheng, L Li, S H Chan, Z Judeh, J Zhao *Adv. Funct. Mater.* **19** 3962 (2009)
339. L X He, S C Tjong *Curr. Nanosci.* **6** 40 (2010)
340. V K Rangari, G M Mohammad, S Jeelani, A Hundley, K Vig, S R Singh, S Pillai *Nanotechnology* **21** 095102 (2010)
341. W Yang, Y Wang, J Li, X R Yang *Energy Environ. Sci.* **3** 144 (2010)

342. C M Chang, Y L Liu *Carbon* **4** 1289 (2010)
343. I H Chen, C C Wang, C Y Chen *Plasma Proc. Polym.* **7** 59 (2010)
344. C Boutopoulos, C Pandis, K Giannakopoulos, P Pissis, I Zergioti *Appl. Phys. Lett.* **96** 041104 (2010)
345. W Yi, A Malkovskiy, Y Wang, X-Q Xu, A P Sokolov, M Lebron-Colon, M A Meador, Y Pang *Polymer* **51** 475 (2010)
346. K K Reddy, B C Sin, C H Yoo, D Sohn, Y Lee *J. Colloid Sci.* **340** 160 (2009)
347. L M Hall, K S Schweizer *Sof. Matter* **6** 1015 (2010)

[a] — *Nanotechnol. Russ. (Engl. Transl.)*
[b] — *Inorg. Mater., Appl. Res. (Engl. Transl.)*
[c] — *Herald Russ. Acad. Sci. (Engl. Transl.)*
[d] — *Bull. Russ. Acad. Sci., Phys. (Engl. Transl.)*
[e] — *Inorg. Mater. (Engl. Transl.)*
[f] — *Russ. J. Phys. Chem., Ser. A (Engl. Transl.)*
[g] — *Russ. J. Coord. Chem. (Engl. Transl.)*
[h] — *Russ. Chem. Bull., Int. Ed. (Engl. Transl.)*
[i] — *Dokl. Phys. Chem. (Engl. Transl.)*
[j] — *Russ. J. Struct. Chem. (Engl. Transl.)*
[k] — *Polym. Sci. (Engl. Transl.)*
[l] — *High Energy Chem. (Engl. Transl.)*