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Thermotropic rod-like mesogens as stabilizers for polyolefins and polyvinyl chloride

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The main approaches to stabilization of polymers and requirements to anti-ageing agents are discussed. Considerable attention is paid to the progress in the studies of the stabilizing activity of various substances in polyolefin- and polyvinyl chloride-based compositions. Particular demand for environmentally benign organic heat stabilizers and antioxidants is noted. The so-called mesogenic structures serving as effective light and heat stabilizers for polymer composites are presented. The effects of mesogens on the supramolecular structure of polyethylene, deformation and relaxation properties and thermal parameters as well as melt flow index, tribological properties and other properties of polymer materials are discussed. The bibliography includes 112 references.

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I. Introduction

The vigorous development of the manufacture and the wide use of polymer composites are able to provide both fast innovative development of country economy and a top position in the world for some areas of country science and technology.[1] Apart from easy processability and high physicomechanical and performance characteristics, long-term application of final products requires durability of the materials involved.[2] Therefore, stabilization of polymers is a highly important subject in the industry of polymeric materials.

In the early 1950s, studies into the polymer ageing and stabilization were started at the Institute of Chemical Physics of the USSR Academy of Sciences under the supervision of Academician N M Emanuel; these studies provided the grounds for understanding the mechanisms of thermal and thermal oxidative degradation of polyolefins and carbon-chain polymers.[3–6] Some time later, Neiman, Kovarskaya and other scientists[7–9] proved the necessity of stabilization of thermally stable polymers, and these studies were recognized as a separate trend in the science of polymer degradation and stability. Noteworthy are the works of Russian scientists Zaikov and Minsker[10–12] and foreign scientists Grassi, Scott and Voigt[13,14] published in the 1970s – 1980s, which were also devoted to degradation and stabilization of polymer materials.

Data on degradation mechanisms made it possible to state the key requirements to stabilizers.[15] While selecting a stabilizer, a number of other properties apart from the efficiency should be considered; usually they are subdivided into three groups: chemical, physical and toxic properties.

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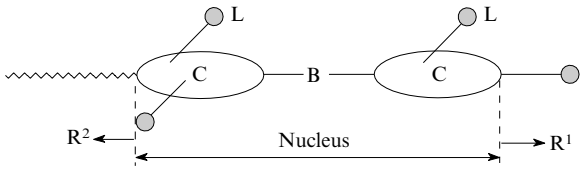
The chemical properties of antioxidants include thermal and hydrolytic stability under plastics processing conditions. The physical properties include solubility, emulsifying properties, volatility, extractability, compatibility and physical state (solid or liquid), which dictates the shape of the finished product. Furthermore, additives should not colour the polymer, although in some cases, colouring additives are used to attain higher thermal stability. An example of this approach is polyamide stabilization by Cu^{2+}/I^- complexes,[16] resulting from mixing of copper salts (chloride, acetate) with inorganic (KI, NaI) or organic iodides (Bu^n_4NI, morpholinium iodide, *etc.*) and the use of amine antioxidants. The polymeric materials used for articles in contact with foodstuff, for utility and drinking water supply pipes and for medical goods and toys should not contain toxic additives.[17]

To date, there is a fairly broad range of chemical additives for special purposes — antioxidants and light stabilizers of various classes.[18] However, the development of new stabilizers still remains a rather vigorously developing area, the relevant research and development works being in progress in many universities and industrial laboratories. During the last 15–20 years, quite a number of new chemical compounds were designed and tested for the stabilizing action in various polymers. The modern stabilizing systems consisting of several components imply, as a rule, virtually complete polymer protection — from the synthesis and processing stage to long-term service of the material under particular operation conditions.

However, despite the achieved progress, the works of Russian and foreign researchers dealing with the creation of new effective multifunctional stabilizers of polymers not only did not stop but, conversely, became more intensive during the last 7–10 years. The development of non-toxic metal-free organic stabilizers is a highly topical and demanded trend of these studies.

Apart from polymers, among organic compounds, a considerable molecular anisotropy is inherent in so-called mesogens — compounds that can form a liquid-crystalline phase under certain conditions. One of the numerous classes of mesomorphic compounds is the class of thermotropic rod-like liquid crystals, which can be represented, in the first approximation, as rods, considering the rotation around the longer molecular axis (Fig. 1). Compounds of this type consist, most often, of a rigid central nucleus comprising cyclic moieties (C) and bridging groups (B) and terminal (R^1, R^2) and lateral (L) substituents.[19]

As cyclic moieties diverse aromatic, heterocyclic and alicyclic groups are used, in particular, benzene, naphthalene, biphenyl, anthracene, pyridine, pyridazine and other. The bridges can be represented by simple bonds or groups such as CH=CH, CH=C(CN), C≡C, CH=N, N=N, N=N(O), C(O)O and CH=CHC(O)O groups. Hydrocarbon groups or groups incorporating them such as Alk, OAlk, SAlk, CO_2Me, OC(O)Et, $OC(O)Pr^n$, SC(O)Alk and so on can serve as the terminal substituents. Most often, the terminal substituents contain normal saturated hydrocarbon groups with 1 to 12 carbon atoms. A lot of attention is paid to liquid crystals with branched saturated or normal unsaturated hydrocarbon groups. In addition, Hal or CN, NH_2, NHAlk, $NAlk_2$, NO_2, NCO and some other groups can serve as terminal substituents. The lateral substituents L are, in most cases, small groups such as Hal, Me or CN.



○ is a structurally rigid substituent (CN, CHO, CO_2H, *etc.*)
〰 is a flexible substituent (usually C_nH_{2n+1}, OC_nH_{2n+1}; $n = 2–18$)

Figure 1. Schematic view of the molecule of a rod-like mesogen (see text).

The noticeable anisotropy of both mesogen and polymer molecules gives rise to a number of specific macroscopic properties. In polymers, this implies existence of oriented state, especially in the case of fibres or films, while in mesogenic compounds, this is the presence of liquid crystalline phases possessing orientational ordering and anisotropy of physical properties. Presumably, traditional applications of liquid crystals in electrooptical devices, display devices, gas liquid chromatography, *etc.*, do not exhaust the whole potential of mesogenic compounds. A possible application is modification of polymers, in particular, *via* efficient mutual orientational correlations. These correlations should allow the mesogen molecules, first, to be efficiently incorporated into supramolecular structures of the polymer and, second, to affect substantially the phase and relaxation transitions.

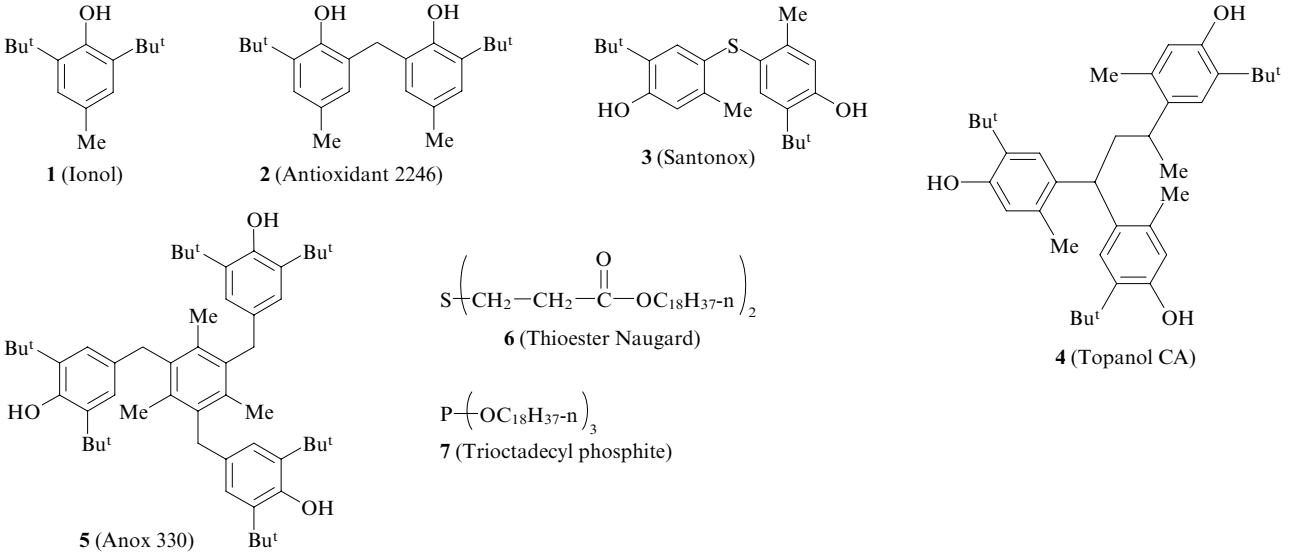
The review considers the key achievements in the investigation of the stabilizing action of various compounds, in particular, thermotropic rod-like mesogens, in compositions based on polyolefins and poly(vinyl chloride), including the authors' own results concerning the structure and physical state as well as the physicomechanical, thermal, strain, relaxation, tribological and other properties of polymer–mesogenic modifier systems. As regards the application of mesogens in polymer chemistry, these studies were started at the Ivanovo State University of Chemistry and Technology and this approach is completely original. Nevertheless, the results obtained by the authors give hope that implementation of this line of research would make it possible not only to diversify the structural series of polymer stabilizers and propose efficient, versatile, multifunctional antioxidants and light stabilizers combining various mechanisms of action on the polymer matrix but also to produce novel materials with high strength and tolerance of adverse factors and to endow them with some specific properties by deliberately forming surface nanostructures.

II. Achievements in the stabilization of polyolefins and poly(vinyl chloride)

During ageing, any polymer undergoes two types of transformations: degradation and structuring.[20] This results in a change in the initial polymer characteristics, resulting in the loss of practically valuable properties. A stabilizing system suitable for a given polymer is chosen taking account of the polymer nature; in addition, processing and operation conditions of the polymer material should be considered.

The process of ageing occurs as an interplay of a number of factors that are responsible for the change in the polymer properties with time. Depending on the causes of ageing,

Structures 1 – 7



photo, thermal, thermal oxidative and ozone types of ageing can be distinguished. Practically, the polymer properties vary with time under the action of the whole set of factors, first of all, in contact with oxygen.[21,22] Polymer stabilization can, in principle, be achieved in two ways: by introducing special additives — stabilizers (antioxidants) and by modifying the polymer structure by physicochemical methods. Stabilization by adding minor (in relation to the stoichiometry) amounts of antioxidants which inhibit the chain reactions of polymer degradation is most popular.[14]

II.1. Polyethylene and polypropylene

Polyethylene (PE) reasonably ranks first in the world production of polymerization plastics.[23,24] The large-scale manufacture and popularity of PE are caused by combination of valuable properties (high dielectric characteristics retained over a broad temperature range, chemical resistance, considerable thermal stability and cold resistance, strength, and relatively low density)[25] with the processability by any known highly productive process used for thermoplastics. Polyethylene is fairly stable during long-term storage away from light at room temperature. However, processing and operation without stabilizers results in fast ageing of the polymer accompanied by sharp deterioration of the performance characteristics of PE-based materials.[26]

Polypropylene (PP) is the second most produced and applied polymer after PE.[25] In the absence of oxygen, PP, like PE, is relatively stable to high temperature. However, PP is oxidized much faster than PE and is processed only with addition of antioxidants.[14,25] Generally, stabilizers for polyolefins should slow down the decrease in the viscosity of the melt during processing; reduce the brittleness caused by thermal oxidation of polymers during thermal and atmospheric ageing; decrease the colouring on heating caused, as a rule, by the products of transformation of composition components; deactivate transition metals because the remainders of metal-containing catalysts induce oxidative decomposition and colouring of polymers; and increase light- and atmospheric stability of polymeric materials.[25]

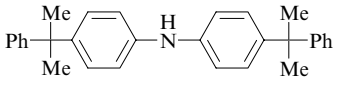
The main stabilizers used for polyolefins are alkylphenols, for example, 2,6-di-*tert*-butyl-4-methylphenol, or ionol (**1**); alkyl-bis-phenols, for example, antioxidant 2246 (**2**); thiobisphenols, for example, Santonox (**3**); polyphenols, for example, Topanol CA (**4**) and Anox 330 (**5**); terpene-substituted phenols, for example, 2,6-isobornyl-*p*-cresol; hydroxyphenylalkanoic acid esters, phenol-substituted *sym*-triazines, *etc*., which are practically used, as a rule, in synergistic mixtures with sulfur or phosphorus compounds such as esters of thiodicarboxylic acids (*e.g*., compound **6**) or trioctadecyl phosphite (**7**).[25]

Rather recently, the following stabilizers for high-density PE (HDPE) were proposed: a synergistic mixture of phenolic antioxidant with T_m = 54 °C and sulfur-containing phenolic antioxidant with T_m = 70 °C; liquid phenolic antioxidant with T_m < 10 °C; a synergistic mixture of liquid phenolic antioxidant with T_m < 10 °C and sterically hindered phosphite.[27]

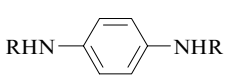
The introduction of combined stabilizers (metal oxide–sulfide type) in amount of 1.0 vol.% – 6.0 vol.% may be a promising trend in the protection of PE from UV radiation. In some cases, for example, in the presence of 2% ZnO and 2% ZnS, the additives show a synergistic effect on the structure stability and physicomechanical characteristics of PE under UV radiation.[28]

Amine antioxidants, for example, Naugard 445 (**8**), *N*,*N*-diphenyl-*p*-phenylenediamine (**9**), *N*,*N*-di-n-butyl-*p*-phenylenediamine (**10**) and other, have higher inhibitory activities than phenolic antioxidants. However, due to pronounced colouring of polymers upon the addition of amine stabilizers, they can be used only with dark pigments.[14]

Structures 8 – 10



8 (Naugard 455)



9, **10** R = Ph (**9**), Bu^n (**10**)

Recent studies [29] demonstrated that gossypol derivatives (1 : 100 by mass with respect to the polymer) have heat and light stabilizing properties and can be considered as a new type of stabilizers for polyolefins. The high stabilizing properties of gossypol derivatives are caused, apparently, by the presence of numerous hydroxyl groups in the molecule, which interact with the products of thermal decomposition of hydrocarbons at high temperature.

The strength and thermal stability of polyolefin-based materials can be somewhat enhanced by adding fillers to the composition.[30] Recommended fillers include alunite, azerit, zeolite, silica gel, *etc.* as powders that have been washed, ground in a mill and sieved to a medium size (50–315 μm particle size); the major components of these powders are silica, alumina and other metal oxides. For better effect, the filler should be pretreated with a coupling agent. The coupling agents are oligoesters obtained by copolymerization of maleic anhydride with hex-1-ene, acrylic or methacrylic acid and propylene oxide. When a mixture of azerit and silica gel is used, a change in the particle size from 50 to 200 μm at a filler content of 10 mass % to 60 mass % induce a 40%–50% increase in the strength and thermal stability of PE composites but the elasticity somewhat decreases (by 20%–30%).

As raw materials for fillers to be used in PP composites,[31] tyre rubber (5 mass % to 30 mass %) was proposed. As the rubber content increases to 15%, the strength characteristics of the PP composite are enhanced but at higher rubber contents, they sharply decrease. The cause is that small amounts of tyre rubber interact with the polymer matrix, while higher contents of rubber loosen the matrix and thus reduce the number of active sites responsible for the filler–polymer adhesive interactions.

The compatibility of PP and rubber can be increased by adding compounds that enhance the interaction of components at the interface.[32] For compatibilization of PP and the rubber, graft copolymers with reactive groups are used, for example, ethylene copolymer with glycidyl methacrylate grafted with maleic anhydride. The compatibilizer content in the PP composition is, as a rule, 3%. The presence of compatibilizer enhances the interaction at the polymer–filler interface, which results in the tensile strength of the PP composite increasing by 20% and tensile elongation increasing by 70%.

A study of the effect of rosin oligoesters on the physicomechanical parameters, structure and processability of PE of various brands based on the changes in the tensile strength, yield point, tensile elongation and melt flow index (MFI) demonstrated that the introduction of up to 1 mass % of rosin oligoester results in a substantial increase in the strength characteristics of pressed PE plates, this effect being more obvious for oligoesters with low contents of epoxide groups. Oligoester increases the temperature of thermal oxidative destruction by 10–15 °C, *i.e.*, it functions as a heat stabilizer.[33]

There are indications of considerable improvement of physicomechanical properties of composite materials containing thermodynamically incompatible additives.[34] However, some characteristics change rather noticeably when modifying agents are compatible with the initial polymer. For example, the ternary ethylene–propylene rubber introduced in an amount of 5 mass %–15 mass % into a PP-based composition not only improves the elasticity and the impact parameters of the material but also enhances the PP stability to thermal oxidative destruction.[35]

A number of valuable physicomechanical properties of the polymer can be improved by structure chemical modification with low-molecular-mass compounds.[36] Indeed, a study of low-density PE (LDPE) modified with acrylonitrile in the presence of *tert*-butyl peroxide and elemental tellurium demonstrated that the resistance of the resulting PE-based material to the light-and-heat ageing increases relative to the initial PE. After 100 h of ageing, the strength characteristics of PE with 0.1–1.0 mass fraction of tellurium remain approximately at the same level, whereas the strength parameters of a similar composite without tellurium decrease by 15%–18% and those of the initial PE decrease by 60%–70%.

It is noteworthy that the selection of a particular stabilizer depends on the conditions of application of the polymeric material. For example, to choose the stabilizing system for film materials for greenhouse covers, it is necessary to take into account the distribution pattern and diffusion behaviour of stabilizers in the microheterogeneous structure of the amorphous-crystalline polymer. It is known [37] that low-molecular-mass polar stabilizers unable to co-crystallize with PE 'sweat out' on the item surface as a result of migration. This means that some of the stabilizer cannot function properly. In order to prevent the sweating-out to the surface, the effective volume of stabilizer molecules is increased by introduction of bulky alkyl substituents into their molecules.[37]

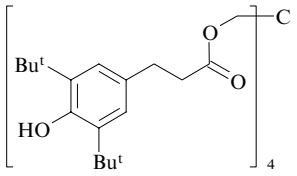
It is of interest to utilize the structural features of amorphous-crystalline polymers, which ensure migration of additives in them, to manufacture film materials with enhanced stability without increasing the stabilizer concentration. This problem can be solved by adding a stabilizer to PE together with a low-molecular-weight additive (LMA).[38] Polar stabilizers are much more compatible with LMA than with PE. Therefore, it can be expected that the main bulk of the stabilizer is displaced, during cooling of the melt, from the crystallizing areas and migrates to less organized parts of the structure, together with LMA. This means that the stabilizer is concentrated, like LMA, in the parts of the structure most accessible for oxygen, namely, in the 'nuclei' of amorphous areas and in the surface layer.

Since polyolefins are universally used for household purposes, in contact with potable water and food products, some studies are devoted to migration of harmful agents, in particular stabilizers, from polymeric materials. It was shown [39] that phenolic and benzophenone-based antioxidants are partly washed out with water. Phosphites are not extracted into water even at 60 °C; therefore, good prospects (as regards health safety) of using phosphites for stabilization of HDPE for pipe applications are obvious. Amine antioxidants are inadmissible as they are washed out with water.

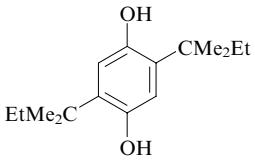
Experimental studies of the solvent (ethanol, isopropyl alcohol, isooctane, ethyl acetate, olive oil, *etc.*) effect on the migration ability of the phenolic antioxidant Irganox 1010 (**11**) from linear HDPE films showed that the antioxidant diffusion is intensified with increase in the maximum solvent absorption and, hence, with increase in the additive solubility in this solvent.[40]

A number of studies [41–47] are devoted to migration of phenolic type antioxidants [pentaerythritol 3,5-di-*tert*-butyl-4-hydroxyphenylpropionate — Irganox 1010 (**11**),

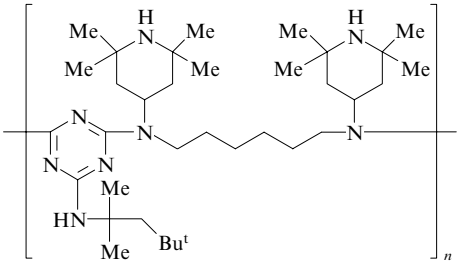
Structures 11 – 15



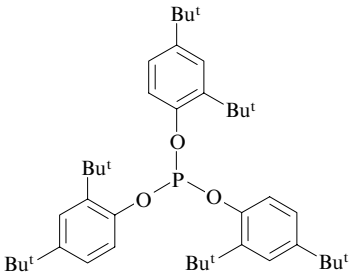
11 (Irganox 1010)



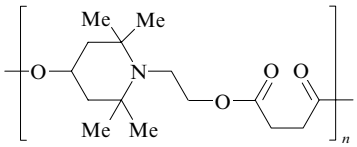
13 (Lowinox AH25)



15 (Chimassorb 944)



12 (Alkanox 240)



14 (Tinuvin 622)

Ethanox 330, antioxidant 2246 (**2**)] and sterically hindered phosphite Alkanox 240 (**12**) from HDPE, linear HDPE and PP into water, ethanol and corn oil. Out of the three polymers studied, the minimum migration was found for HDPE. Rafii *et al.*[47] detected traces of 2,6-dialkylphenol in water extracts. The migration of low-molecular-mass compounds into water was shown[43] to be 10 and more times less pronounced than into model fatty media. A study of ageing of PE stabilized by Irganox 1010 (**11**) or Ethanox 330 in water at 60 °C detected no change in the antioxidant concentration over a period of three months.[42] The migration of the Lowinox 2246 (**13**), Santonox R and Irganox 1076 antioxidants in cross-linked PE is considerably lower than in linear polymers.[45]

Finally, noteworthy are the works in which organic europium(III) complexes in amounts of 0.2 mass % – 1.0 mass % were added to PE-based compositions in order to enhance the light stabilizing efficiency of Tinuvin 783 [50% Tinuvin 622 (**14**) + 50% Chimassorb 944 (**15**)].[48]

II.2. Poly(vinyl chloride)

Poly(vinyl chloride) (PVC) is one of the best known practically valuable polymers produced on a large scale. It is used for the manufacture of thousands of hard, semi-hard and soft (plasticized) materials and articles used almost in all branches of economy and in household,[49] which is caused by its reasonable and stable cost as well as good physicomechanical and performance characteristics and a broad range of processability.[50]

Poly(vinyl chloride) is stable to moisture, acids, alkalis, salt solutions, industrial gases, petrol, kerosene, alcohols and fats and is almost incombustible.[51] The major problem in the operation of PVC articles is relatively low stability. Under the action of heat, UV radiation, oxygen, high-energy radiation and so on, it easily decomposes to give off hydrogen chloride and to afford C=C double bond sequences in the macromolecules, which give rise to undesired colour (from yellow to black). Therefore, during the storage, processing and operation of PVC and during manufacture, storage and use of PVC-based materials and articles, it is necessary to utilize a set of methods for increasing the PVC stability to various factors, *i.e.*, PVC stabilization is required.[51 – 57]

In the general case, a stabilizer is a compound that removes labile chlorine atoms, prevents oxidation, absorbs hydrogen chloride and restricts the growth of polyene sequences without formation of chlorides accelerating the degradation. An ideal stabilizer ensures a good initial colour, transparency, durable stability and resistance to light, effect of weather conditions and processing conditions. It should be fully compatible, highly efficient, stable to electric action and etching, non-volatile, colourless, tasteless, non-extractable, non-toxic and inexpensive.[53]

In the early 1950s, four major chemical classes of heat stabilizers for PVC were proposed: lead, organotin, mixed metal and secondary organic compounds. These compounds, which are still in use, differ in chemical composition, appearance and physical state (liquid or solid).[12, 57]

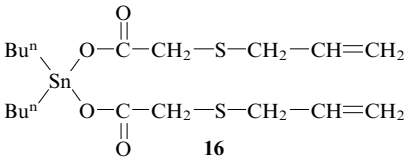
Lead stabilizers represent the longest known and very extensive group of compounds used to stabilize PVC (hard and elastic). The most popular one-component lead stabilizers include tribasic lead sulfate ($3\,PbO\cdot PbSO_4\cdot H_2O$), dibasic lead phosphite ($2\,PbO\cdot PbHPO_3\cdot 2\,H_2O$), dibasic lead phthalate [$2\,PbO\cdot Pb(C_6H_4(CO_2)_2$-1,2], dibasic lead stearate [$2\,PbO\cdot Pb(C_{17}H_{35}CO_2)_2$] and neutral lead stearate [$Pb(C_{17}H_{35}CO_2)_2$].

Lead stabilizers are able to react with HCl to give lead chloride, which, unlike other metal chlorides, does not have a destabilizing action on PVC and is absolutely inert. One more advantage of the basic lead salts is the ability to form complexes needed to stabilize the labile chlorine atoms. Neutral lead stearate has a pronounced lubricating action and is highly compatible with PVC. Dibasic lead phosphite has a unique light stabilizing action.[54] However, lead stabilizers are somewhat non-transparent, which precludes their use in a pure state. A considerable drawback of lead stabilizers is toxicity. Lead compounds are cumulative poisons and are classified as reproductive toxins.[54] European industrial plants took the obligation to exclude them from turnover by 2015.[52, 55]

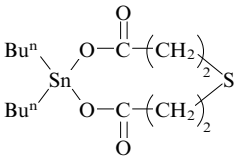
Organotin compounds efficiently stabilize PVC (for the production of pipelines and rigid profiles). Organotin stabilizers can be classified into two types: sulfur-containing compounds — organotin mercaptides and sulfides [for example, dibutyltin didodecylmercaptide, dibutyltin diphenylmercaptide, monobutyltin tributylmercaptide, diaryl- or

dialkyltin sulfides, dibutyltin diallylthioglycolate (**16**), dibutyltin thiodipropionate (**17**), oligomeric mercaptides based on mercaptocarboxylic acid esters **18**] and sulfur-free systems — organotin carboxylates [*e.g.*, dibutyltin maleate, dibutyltin dilaurate (**19**), dibutyltin α-butyl succinate, tetraalkyldi(acyloxy)distannates (**20**) and so on]. Organotin stabilizers can act by several mechanisms: they can substitute labile chlorine atoms, neutralize HCl and generate thiols, which can further destroy hydroperoxides or add to polyene sequences, thus controlling acceleration of dehydrochlorination and preventing the formation of chromophores.[51] The advantages of organotin mercaptides and carboxylates are high efficiency and transparency. The drawbacks restricting their use are associated with high cost and, in the case of organotin mercaptides, with the presence of sulfur atoms (smell, low light stability and colouring). The insufficient light stability can be improved by using UV-absorbers and pigments.[56]

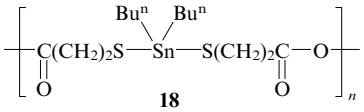
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16

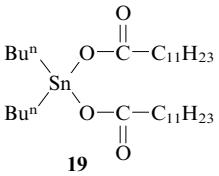


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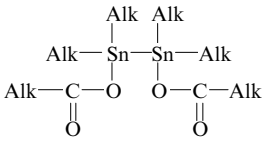


18

$n = 4-8$



19



20

The stabilizing action of mixed metal-containing heat stabilizers is based on interaction of at least two different metal salts with PVC and with each other. For example, stabilizers can include barium – cadmium, barium – cadmium – zinc or calcium – zinc salts.[51] Alkaline earth metal (Ba, Ca) soaps are ionic compounds; their stabilizing function is attributed to neutralization of HCl without substituting labile chlorides. Heavy metal (Cd, Zn) soaps can act as primary stabilizers by the mechanism of nucleophilic substitution of labile chlorides. It is noteworthy that cadmium and zinc chlorides are strong Lewis acids and substantially accelerate dehydrochlorination. Stabilizers of this class are much more compatible with synergistic additives than lead or organotin stabilizers. A composition of mixed metal-containing stabilizers usually contains > 50 mass % synergists — epoxy esters, organic phosphites, blocked phenols, high-molecular-mass alcohols, hydrotalcites, zeolites or 1,3-diketones.

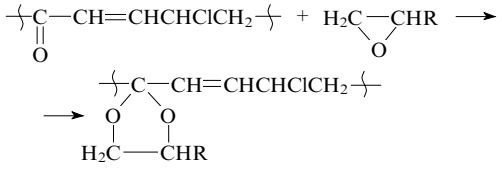
Currently, stearic acid salts (barium, calcium, cadmium, lead and zinc stearates), lead salts (tribasic lead sulfate) or, more rarely, organotin compounds (mainly dialkyltin carboxylates and thiocarboxylates) are now used most widely as heat stabilizers in Russia.[11] Quite a number of works describing the use of various classes of PVC stabilizers are mentioned in the literature.[12, 51, 57 – 61] Data on physical properties of stabilizers can be found in reference books and catalogues.[18, 62, 63]

Although the above-described classes of stabilizers are sufficiently effective, the metal atoms present in these organic metal compounds (Ca, Cd, Pb) can cause serious environmental problems. The research performed did not reveal toxic action of these compounds; however, in 2000, European manufacturers of PVC signed a voluntary commitment (Vinyl-2010) directed at reducing the environmental impact of PVC products throughout the whole life cycle; in particular, cadmium stabilizers had to be eliminated in 2001 and lead stabilizers had to be fully replaced by 2015.[55] In addition, the universal introduction of polymeric materials into articles operating in close contact with humans inevitably toughens the requirements to the quality of plastics. There is a list of stabilizers approved by the Russian Federation health authorities for the manufacture of polymeric materials to be in contact with foodstuffs and for the manufacture of toys, domestic water supply pipes and medical devices.[17]

Organic heat stabilizers are currently used most often as co-stabilizers. Examples are β-aminocrotonates, phosphites, epoxides, *N*,*N*′-diphenylthiourea, 2-phenylindole, β-diketones, β-keto esters, polyols, dihydropyridines and dehydroacetic acid.[51]

Epoxides are widely used in the manufacture processes of PVC materials. They are highly reactive and react with the ketochloroallyl groups present in PVC to give 1,3-dioxolanes.[64] The reaction occurs at 50 – 60 °C in the presence of catalytic amounts of HCl (Scheme 1).

Scheme 1



The following compounds were tested as organic heat stabilizers for PVC at 180 °C in air: barbituric and thiobarbituric acids;[65] (benzimidazol-2-yl)acetonitrile and some its unsaturated derivatives;[66] phenylurea and its derivatives;[67] anthraquinone and 1-aminoanthraquinone;[68] 2-methoxy-4-(propen-2-yl)phenol;[69] N-aryl derivatives of itaconic acid imide (Ar = C_6H_4X-*p*; X = H, Me, OMe, OH, Cl, Br, NO_2, CO_2H; $n = 1-3$);[70] aromatic hydrazines and their derivatives;[71] 1,3,4-oxadiazole derivatives;[72] *N*-acryloyl-*N*′-arylthioureas (aryl is *para*-substituted phenyl);[73] 4-(*p*-methoxyphenyl)-2-sulfanyl-5,6,7,8-tetrahydroquinoline-3-carbonitrile;[74] *N*-benzoyl-*N*′-(4-maleimidobenzoyl)hydrazine[75] possessing antimicrobial action, *etc*. The efficiency of these agents was estimated from the induction period (t_s) (*i.e.*, the period in which no evolution of gaseous HCl was observed), from the level of dehydrochlorination measured by continuous potentiometric titration and from the degree of decoloration of aged PVC sample compared with the PVC samples containing dibasic lead carbonate, dibasic lead stearate, Ba – Cd – Zn stearate and other stabilizers. The tested organic compounds showed high heat and colour stabilizing efficiency. It is worth noting that combination of the above-listed

Table 1. Activation energy of the thermal degradation of PVC stabilized by some organic compounds.[76]

Stabilizer	E_a /kJ mol^{-1}
EDTA	117
Propylene glycol	115
Benzoic acid	112
Phenol	198
None	101

substances with commercial stabilizers provides synergistic action of components.

Taghizadeh and Fakhimi [76] studied the degradation and stabilization kinetics of rigid PVC containing ethylenediaminetetraacetic acid (EDTA), propylene glycol, benzoic acid or phenol in a nitrogen atmosphere in the temperature range of 160–190 °C. Calculations of the activation energy for thermal degradation (E_a) of polymer samples showed a fairly high stabilizing effect of organic stabilizers (Table 1).

Thiols containing ester groups can efficiently operate as stabilizers when taken in an amount of 3.0 parts by mass per 100 parts of PVC.[77,78] These systems are free from metals and can deactivate labile defects *via* nucleophilic substitution of the chloride. They can also prevent or remove the colour owing to addition to polyene double bonds and trap free radicals.[78]

Hydroxybenzylthioethers were investigated as organic heat stabilizers for hard PVC.[79] The stabilizing efficiency of these compounds is higher than that of Ca–Zn stearates [the efficiency was estimated using a Haake PolyDrive extruder and thermogravimetric analysis (TGA)]. This phenomenon can be attributed to the ability of these thioethers to prevent the formation of polyene structures. Hydroxybenzylthioethers and epoxidized soybean (ES) oil show synergistic effect at the ES oil : hydroxybenzyl thioether ratio of < 0.5 (by mass).

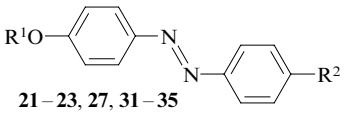
Nafikova *et al.*[80] estimated the thermal stability of PVC in the presence of glycerol monoesters of α-branched saturated isomeric higher $C_{10}-C_{28}$ monocarboxylic acids by measuring the 'dehydrochlorination rate' and 'time of thermal stability' characteristics. These glycerol derivatives were found to be effective mechanochemical stabilizers and lubricants for PVC and to be able to substantially (1.5–2-fold) decrease the polymer dehydrochlorination rate by acting as heat stabilizers.

To date, no perfect stabilizer has been developed. The selection of the particular compound is always dictated by the objective to improve as much as possible the properties needed for further application of the product, while less important characteristics are neglected.[51]

III. Stabilizing action of mesogens in polyolefin-based composites

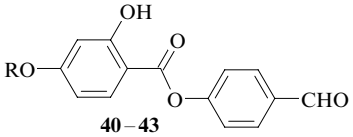
The following mesogenic compounds were synthesized, isolated and characterized to be tested as possible light and heat stabilizers for polyolefin-based composites: 4-(4-hexyloxyphenylazo)cinnamic acid (**21**);[81] 4-butoxy-4′-formylazobenzene (**22**);[82] 4-hexyloxy-4′-formylazobenzene (**23**);[82] 4-formylphenyl 4-propoxybenzoate (**24**),[83] 4-butoxybenzoate (**25**)[83] and 4-hexyloxybenzoate (**26**);[83] 4-formyl-4′-(2,3-epoxypropoxy)azobenzene (**27**); 3-hydroxy-4-propoxy-4′-formylazobenzene (**28**);[84] 4-hexyloxy-3-hydroxy-4′-formylazobenzene (**29**);[84] 3-hydroxy-4-octyloxy-4′-formylazobenzene (**30**);[84] 4-(2-hydroxyethoxy)-4′-formylazoben-

Structures 21–46



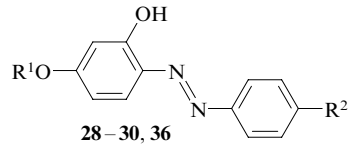
21–23, 27, 31–35

Compound	R^1	R^2
21	n-C_6H_{13}	CH=CHCO$_2$H
22	Bu^n	CHO
23	n-C_6H_{13}	CHO
27	2,3-Epoxypropyl	CHO
31	$(CH_2)_2$OH	CHO
32	$(CH_2)_3$OH	CHO
33	$(CH_2)_6$OH	CHO
34	$(CH_2)_8$OH	CHO
35	$(CH_2)_4$Br	O$(CH_2)_4$Br



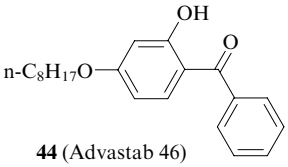
40–43

Compound	R
40	Pr^n
41	n-C_6H_{13}
42	n-C_7H_{15}
43	n-C_9H_{19}

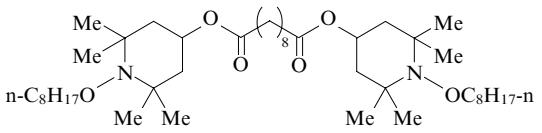


28–30, 36

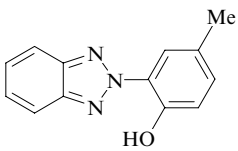
Compound	R^1	R^2
28	Pr^n	CHO
29	n-C_6H_{13}	CHO
30	n-C_8H_{17}	CHO
36	n-C_6H_{13}	CN



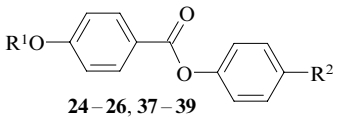
44 (Advastab 46)



45 (Tinuvin 123)



46 (Benazol P)



24–26, 37–39

Compound	R^1	R^2
24	Pr^n	CHO
25	Bu^n	CHO
26	n-C_6H_{13}	CHO
37	n-C_6H_{13}	CH=CHCO$_2$H
38	n-C_9H_{19}	CH=CHCO$_2$H
39	n-$C_{11}H_{23}$	CH=CHCO$_2$H

zene (**31**);[85] 4-(3-hydroxypropoxy)-4′-formylazobenzene (**32**);[85] 4-(6-hydroxyhexyloxy)-4′-formylazobenzene (**33**);[85] 4-(8-hydroxyoctyloxy)-4′-formylazobenzene (**34**);[85] 4,4′-bis(4-bromobutoxy)azobenzene (**35**); 4-hexyloxy-3-hydroxy-4′-cyanoazobenzene (**36**); 4-(4-hexyloxybenzoyloxy)-cinnamic acid (**37**);[86] 4-(4-nonyloxybenzoyloxy)cinnamic acid (**38**);[86] 4-(4-undecyloxybenzoyloxy)cinnamic acid (**39**);[86] and 4-formylphenyl 3-hydroxy-4-propoxybenzoate (**40**), 4-hexyloxy-3-hydroxybenzoate (**41**), 4-heptyloxy-3-hydroxybenzoate (**42**) and 3-hydroxy-4-nonyloxybenzoate (**43**).

The listed mesogens were tested as light and heat stabilizers for LDPE, HDPE and PP and compared with a series of commercial stabilizers:[18] Advastab 46 (**44**) (2-hydroxy-4-octyloxybenzophenone), a light stabilizer for polyolefins; Tinuvin 123 (**45**) [bis(2,2,6,6-tetramethyl-1-octyloxypiperidin-4-yl)sebacinate], a light stabilizer for polyolefins; Benazol P (**46**) [2-(2-hydroxy-5-methylphenyl)-benzotriazole], a light stabilizer for polyolefins; cadmium or calcium stearate, a heat stabilizer for PVC; Irganox 1010 (**11**), a heat stabilizer for polyolefins, especially for polypropylene and PVC; Ionol (**1**), a stabilizer for rubbers and a heat stabilizer for polyethylene.

A necessary preliminary testing of potential mesogenic stabilizers is studying their thermal stability. First of all, this check is topical for compounds containing chemically reactive substituents (CHO, CN, epoxy group, *etc*.) bearing in mind their reactivity, especially, at elevated temperatures. According to TGA data, all of the tested mesogens had temperatures of the onset of decomposition sufficiently high to withstand the processing temperatures of polyolefins. In addition, the presence of pronounced absorption in the near-UV region suggests that these compounds being introduced into the polymer composition would shield the polymer matrix from the most harmful part of solar radiation, *i.e*., they can be efficient UV absorbents.[87]

Table 2. Effect of the nature and amount of the stabilizer on the variation of HDPE film characteristics upon ageing.

Stabilizer (concentration) [a]	K_σ (%)	K_ε (%)	Ref.
None	83	15	88, 89
None	83	17	90–92
4,4′-Azobenzenedicarboxylic acid (0.5) + cadmium stearate (1)	92	79	88, 89
23 (0.05)	95	85	88, 89
23 (0.1)	109	96	88, 89
23 (0.5)	129	107	88, 89
21 (0.1)	121	77	88, 89
22 (0.1)	107	94	88, 89
Benazol P (**46**) (1) + Ionol (**1**) (1)	84	63	90–92
28 (0.1)	93	78	90–92
29 (0.1)	93	79	90–92
30 (0.1)	96	76	90–92
31 (0.1)	116	206	90–92
32 (0.1)	116	200	90–92
33 (0.1)	117	235	90–92
34 (0.1)	116	234	90–92
35 (0.1)	120	240	90–92

[a] Here and in Tables 3–5, the stabilizer concentration is expressed in parts by mass per 100 parts by mass of the polymer.

The light and heat stabilizing activity of mesogens was estimated from the relative change in the tensile strength (K_σ) and tensile elongation (K_ε) of the polymer samples subjected to heat-and-light ageing in accordance with GOST 8979–85 (Table 2).

As can be seen from Table 2, single mesogenic additives are more efficient than mixtures of known light and heat stabilizers. They have a versatile action of protecting the polymer from heat and light. The introduction of formylazobenzene **23** (0.05 and 0.1 parts by mass per 100 parts of the polymer) provides better retention of the polymer properties after light-and-heat ageing. The introduction of 0.5 parts by mass of aldehyde **23** eliminates the decrease in the strength, provides full retention of elasticity, whereas the mixture of stabilizers with a total content of 1.5 parts by mass preserves only 92% of the initial strength and 79% of the tensile strain upon ageing. The higher strength of compositions containing mesogenic additives upon light-and-heat ageing is caused by structuring of the polymer. This result is not undesirable as the composition elasticity is completely retained in the presence of aldehydes **22** and **23** or azocinnamic acid **21**.

The results presented in Table 2 also indicate that compounds **28**–**30** possess higher light and heat stabilizing activity than a Benazol P + Ionol mixture. This is indicated by the fact that the polymeric material stabilized by a mixture of commercial stabilizers loses 16% of the initial strength upon the light-and-heat ageing, while the material stabilized by aldehydes **28**–**30** loses 7% to 4% under the same conditions. Even higher efficiency was found for formylazobenzenes **31**–**34**. This is indicated by up to 17% higher tensile strength of HDPE films after light-and-heat ageing. In addition, aldehydes **31**–**34** substantially retard the loss of elasticity by a polymeric material upon ageing. With azobenzene **35** as the light and heat stabilizer, an HDPE-based film material was obtained, which proved to be 20% stronger and 4 times more elastic after light-and-heat ageing than the control sample stabilized by commercial stabilizers.

Table 3 presents the results of testing of LDPE films stabilized by the commercial light stabilizers Tinuvin 123 and Advastab 46 and by mesogenic formylphenyl benzoates **24**–**26** after light ageing. Comparison of the experimental data indicates that the same content of liquid crystalline compounds provides higher strength and especially elasticity of polymer films, which attests to their higher efficiency compared with commercial light stabilizers.

Table 3. Effect of the nature of a light stabilizer on the degradation of LDPE films upon light ageing.

Stabilizer (concentration)	K_σ (%)	K_ε (%)	Ref.
Tinuvin 123 (**45**) (0.5)	81	4	87, 88
Advastab 46 (**44**) (0.5)	79	4	87, 88
24 (0.5)	93	13	87, 88
25 (0.5)	86	15	87, 88
26 (0.5)	95	15	87, 88
Benazol P (**46**) (0.5) + Irganox 1010 (**11**) (0.5)	102	19	86
37 (0.1)	110	25	86
38 (0.1)	107	33	86
39 (0.1)	104	32	86
36 (0.1)	96	52	86

Table 4. Effect of the nature of a stabilizer on the degradation of polypropylene films upon light and heat ageing.[93]

Stabilizer (concentration)	Light ageing		Heat ageing (E_a/kJ mol^{-1})[a]
	K_σ (%)	K_ε (%)	
Irganox 1010 (**11**) (0.5) + Benazol P (**46**) (0.5)	42	0.3	65
40 (0.25)	71	2.6	97
41 (0.25)	82	2.7	84
42 (0.25)	76	2.4	87
43 (0.25)	78	2.6	88
23 (0.25)	81	2.5	94

[a] The accuracy is ± 2 kJ mol^{-1}.

Cinnamic acids **37**–**39** provide 7%–8% higher tensile strength and 36%–73% higher elasticity of LDPE films after light-and-heat ageing. Ageing of LDPE films containing cyanoazobenzene **36** results in somewhat lower strength but almost 3-fold higher elasticity (see Table 3). The samples were compared with an LDPE sample containing a mixture of commercial stabilizers.

Mesogenic aldehydes **23** and **40**–**43** were also found to considerably surpass a commercial stabilizer mixture in PP-based compositions: the degree of retention of tensile strength and tensile elongation after light ageing is higher when these compounds are used as stabilizers (Table 4). The activation energy for thermal degradation of polypropylene stabilized by mesogens is 30%–50% higher than this value for samples containing a commercial stabilizer mixture.

Generally, the performed studies indicate that molecular-anisotropic mesogenic compounds can be promising components of polymer compositions based on polyolefins.

IV. Molecular-anisotropic stabilizers for poly(vinyl chloride)

Considering the results described in Section III, it appeared of interest to find out whether high light and heat stabilizing efficiency of mesogenic compounds would hold for polymeric materials other than polyolefins, for example, for composites based on plasticized PVC.

The data of Table 5 attest to a more pronounced light stabilizing effect of mesogenic derivatives of phenyl benzoate **24**–**26** towards PVC as compared with the commercial light stabilizers Advastab 46 (**44**) and Tinuvin 123 (**45**), which follows from the fact that the same amounts of liquid crystalline compound **24**–**26** provide higher characteristics of polymer films after light ageing regarding both the strength and elasticity.

The possibility of application of mesogenic additives as heat stabilizers for PVC can be evaluated from the results of thermal analysis of plasticized PVC films [40 parts by mass of dioctyl phthalate (DOP) per 100 parts of the polymer] stabilized by mesogens and commercial stabilizers. During ageing of plasticized PVC, the process of separation of the plasticizer under the action of high temperature is superimposed on the purely thermal degradation; therefore, the effective activation energy of thermal degradation can be considered to be an integral characteristics, which formally describes the rate of mass loss of the sample during ageing in the specified dynamic heating mode. It is quite obvious

Table 5. Effect of the nature of a light stabilizer on the degradation of poly(vinyl chloride) films.

Stabilizer (concentration)	K_σ (%)	K_ε (%)	Ref.
Tinuvin 123 (**45**) (0.5)	85	93	83
Advastab 46 (**44**)	93	97	83
24 (0.5)	101	103	83
25 (0.5)	99	107	83
26 (0.5)	110	102	83
Ca stearate (2.0) + Pb silicate (4.0)	92	94	94
OP phosphite (0.5) + Ca stearate (2.0) + ED-20 (2.0)[a]	92	91	94
27 (0.2)	100	89	94
23 (0.2)	91	96	94, 95
47 (0.2)	99	111	94, 96
55 (0.2)	108	130	94
56 (0.2)	107	108	94, 97
57 (0.2)	106	111	94, 98
Vigostab BKC (2)	102	100	99
51 (0.2)	137	136	99
52 (0.2)	105	86	99
53 (0.2)	101	84	99
54 (0.2)	100	100	99

[a] OP phosphite is tris(n-octylphenyl) phosphite; ED-20 is epoxy resin.

that both these processes result in the loss of performance of the polymer sample due to the loss of elasticity, cracking, *etc*. Apparently, E_a can be used as a criterion of stability of the plasticized polymer sample to the action of heat.

Mesogenic formylazobenzenes **22**, **23** and **27**, as well as 4-propoxy-4′-(2,3-epoxypropoxy)azobenzene (**47**), can ensure substantially higher E_a values of plasticized PVC film samples than commercial stabilizers, furthermore, being present in substantially lower concentrations.[94]

The thermal analysis of films based on plasticized PVC stabilized by the commercial heat stabilizer Vigostab BKC (2 parts by mass per 100 parts of PVC) and by mesogenic formylazobenzene **33**, 4-(2,3-epoxypropoxy)propoxy-4′-cyanoazobenzene (**48**), 4-(8-acryloyloxy)octyloxy-4′-cyanoazobenzene (**49**) and 4-(10-hydroxydecyloxy)-4′-cyanoazoxybenzene (**50**) (only 0.2 parts by mass per 100 parts of the polymer) resulted in the following sequence of the additives in terms of heat stabilizing efficiency towards plasticized PVC: Vigostab BKC (E_a = 115 kJ mol^{-1}) < aldehyde **33** (E_a = 118 kJ mol^{-1}) < acryloyloxy-substituted azobenzene **49** (E_a = 124 kJ mol^{-1}) < cyanoazoxybenzene **50** (E_a = 127 kJ mol^{-1}) < epoxy-substituted cyanoazobenzene **48** (E_a = 159 kJ mol^{-1}).[100]

More information on the effect of the nature of a heat stabilizer on the rate of dehydrochlorination can be derived from analysis of the IR spectra of gaseous products formed upon degradation of PVC film samples. Hydrogen chloride has absorption peaks at 2886.01 cm^{-1} ($H^{35}Cl$) and 2888.39 cm^{-1} ($H^{37}Cl$).[101] A characteristic peak was also found in samples stabilized by mesogens **33** and **48**–**50** and in a sample containing Vigostab BKC. However, the intensity of this peak in the IR spectra of gaseous products formed upon the thermal degradation of films stabilized by anisotropic additives is much lower than that for the control sample (Table 6). Furthermore, the time before the appearance of this peak considerably increases. In view of the fact that polymer compositions differ only by the nature of the

Table 6. Positions and intensities of IR absorption maxima and the time before the appearance of the peaks.[100]

Sample	ω /cm $^{-1}$	Intensity (rel.u.)	t /s
PVC film with Vigostab BKC	2700 – 3000	0.035	3000
PVC film with compound **48**	2900 – 3000	0.006	3900
PVC film with compound **49**	2900 – 3000	0.010	3800
PVC film with compound **50**	2900 – 3000	0.010	3800
PVC film with compound **33**	2950 – 3000	0.015	3700

stabilizer, the intensity of HCl evolution could decrease owing to the hear-stabilizing efficiency of anisotropic compounds.

A considerable increase in the effective activation energy of thermal degradation was noted for films based on plasticized PVC stabilized by some dicyanoethenyl derivatives, in particular, 4-(2,3-epoxypropoxy)-4′-(2,2-dicyanoethenyl)azobenzene (**51**), 4-hexyloxy-4′-(2,2-dicyanoethenyl)azobenzene (**52**), 4-(2,2-dicyanoethenyl)phenyl 4-dodecyloxybenzoate (**53**) and 4-acryloyloxy-4′-(2,2-dicyanoethenyl)azobenzene (**54**).[99] It is noteworthy that a positive trend is attained at a 10 times lower content of mesogens **51** – **54** in the polymer composition compared with the content of commercial heat stabilizer Vigostab BKC. This may be attributable to the chemical reaction of the reactive terminal substituents of the anisotropic additives with hydrogen chloride evolved upon the degradation of PVC films, which was confirmed by IR spectroscopy.

The introduction of multiwalled carbon nanotubes (MWCNTs) dispersed in a melt of mesogenic aldehydes **26** and **33** into the composition appeared to be a successful approach to enhancing the thermal stability of film materials based on plasticized PVC. A considerable increase in the temperature of the onset of decomposition and E_a of the polymer samples was noted in the dehydrochlorination stage; this requires only 0.2 – 0.3 parts by mass of mesogens and 0.01 parts by mass of MWCNTs per 100 parts of the polymer.[102]

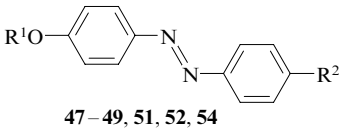
As a rule, the efficiency of stabilizers is evaluated from the stability coefficients (strength K_σ and elasticity K_ε), which define the degrees of retention of parameters (in %) after light-and-heat ageing. The data presented in Table 5 indicate that the introduction of mesogenic aldehydes **23** and **27** or glycydyl-containing modifiers **47**, 4-hexyloxy-4′-(2,3-epoxypropoxy)azoxybenzene (**55**), 4,4′-bis(2,3-epoxypropoxy)biphenyl (**56**) or 4-cyano-4′-(2,3-epoxypropoxy)biphenyl (**57**) into PVC-based composite provides the same stabilizing effect as the synergistic mixtures of commercial stabilizers and epoxy resins, the former being present at 10 – 20 times lower concentrations. The introduction of one test compound brings about both heat- and light-stabilizing action, which makes the polymer composite much simpler and cheaper. Mesogenic modifiers are relatively harmless, unlike heavy metal compounds; they are also readily compatible with the polymer and are not sweat out during sample processing and storage.[95]

The strength characteristics of the film samples obtained by stabilizing the compositions based on plasticized PVC with anisotropic dicyanoethenyl derivatives **51** – **54** measured after light-and-heat ageing are almost not inferior to these characteristics of the control sample, *i.e.*, a light stabilizer is not required in this composition (see Table 5).[101] The content of mesogens is 0.2 parts by mass per 100 parts of PVC, which is 10 times lower than the content of Vigostab BKC.

Mesogenic azo- and azoxybenzenes **33**, **48**, **49** and **50** are also not inferior in the light- and heat-stabilizing efficiency to the commercial stabilizer Vigostab BKC. After ageing under laboratory conditions for two years, the hardness index of the sample containing Vigostab BKC and Benazol P (**46**) increases by 14%, which is caused by sweating out of the plasticizer. Conversely, the samples containing mesogens became softer (Table 7). All of the tested film samples retain almost completely their initial strength and elasticity after ageing for 2 years.[103]

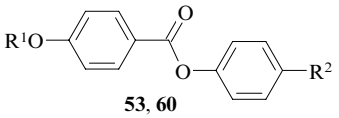
4-Cyano-4′-[3-(2,3-epoxypropoxy)propoxy]biphenyl (**58**),[104] 4-(8-acryloyloxyoctyloxy)-4′-cyanobiphenyl (**59**)[104] and 4-(2,3-epoxypropoxy)phenyl 4-propoxybenzoate (**60**) are good light and heat stabilizers for composites based on plasticized PVC.[105] These compounds provide complete retention of both strength and elasticity of film materials even after long-term (100 h) accelerated light-and-heat age-

Structures 47 – 60



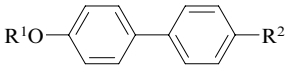
47 – **49**, **51**, **52**, **54**

Compound	R^1	R^2
47	Pr^n	2,3-epoxypropoxy
48	3-(2,3-epoxypropoxy)propyl	CN
49	$CH_2{=}CHC(O)O(CH_2)_8$	CN
51	2,3-epoxypropyl	$CH{=}C(CN)_2$
52	n-C_6H_{13}	$CH{=}C(CN)_2$
54	$CH_2{=}CHC(O)$	$CH{=}C(CN)_2$



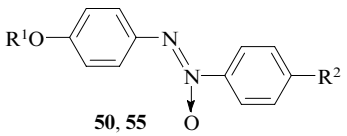
53, **60**

R^1 = n-$C_{12}H_{25}$, R^2 = $CH{=}C(CN)_2$ (**53**);
R^1 = Pr^n, R^2 — 2,3-epoxypropoxy (**60**)



56 – **59**

Compound	R^1	R^2
56	2,3-epoxypropyl	2,3-epoxypropoxy
57	2,3-epoxypropyl	CN
58	3-(2,3-epoxypropoxy)propyl	CN
59	$CH_2{=}CHC(O)O(CH_2)_8$	CN



50, **55**

R^1 = $(CH_2)_{10}OH$, R^2 = CN (**50**);
R^1 = n-C_6H_{13}, R^2 — 2,3-epoxypropoxy (**55**)

Table 7. Comparison of the physicomechanical characteristics of PVC films before and after ageing for two years.[103]

Stabilizer (contents) [a]	Hardness /cN			Tensile strength /MPa			Tensile elongation (%)		
	STP	2 years	Δ (%)	STP	2 years	K_σ (%)	STP	2 years	K_ε (%)
Vigostab BKC (2) + Benazol P (**46**) (1)	7.0	8.0	14.3	25	23	92	240	240	100
33 (0.2)	7.0	6.2	−11.4	33	32	97	240	240	100
48 (0.2)	6.0	5.5	−7.1	41	40	98	240	240	100
49 (0.2)	5.6	4.3	−18.6	32	32	100	240	240	100
50 (0.2)	8.0	7.2	−11.4	31	29	94	220	220	100

[a] In parts by mass per 100 parts by mass of the polymer and 40 parts by mass of DOP.

ing. Mesogens **58**–**60** are white powders; therefore, it is expedient to use them for the manufacture of non-coloured and white-coloured materials, for example, stretch ceilings, sport shoes or medical accessories.

The temporary permissible levels (TPL) of mesogenic compounds determined from the biological activities of chemical bonds are 1–7 mg m^{-3}. In accordance with GOST 12.1.007-76, these compounds can be classified as belonging to the III hazard class, whereas Cd and Pb stearates used correspond to I hazard class.[103]

Generally, analysis of the published data unambiguously indicates that as organic stabilizers for plasticized PVC compositions, mesogens can provide an alternative to popular commercial stabilizers based on Cd, Pb, Zn and Ca stearates.

V. Properties of polymer–mesogenic modifier systems

A macroscopic consequence of the geometric anisotropy of mesogens is the formation of thermodynamically stable liquid-crystalline phases,[19] while in the case of polymers, it is the presence of a specific oriented state. In view of the molecular anisotropy of components, intensive orientational correlations can occur in polymer–mesogen mixtures, which results in enhancement of intermolecular interactions and, as a consequence, in the mutual effect of components.

Studies of the bulk, diamagnetic, rheological and orientation properties[86, 106–110] for some liquid-crystalline compounds, in particular, formylazobenzenes **22**, **23** and **31**–**34** and some other, revealed exceptionally high orienting effect of the hard nucleus on the aliphatic terminal substituents present in the molecule. It was found that a similar effect is possible on aliphatic macromolecules.

The introduction of formylazobenzenes **23** and **33** into a polymer during rolling is an additional ordering factor, which is confirmed by the increase in the degree of crystallinity of polyethylene (Table 8). After ageing, the degree of crystallinity of the initial material increases, which is related to polymer restructuring caused by the relaxation processes at the interface between crystallites and the amorphous phase. The degree of crystallinity of the films containing mesogenic additives remains virtually invariable during ageing. Thus, liquid-crystalline aldehydes **23** and **33** prevent the local restructuring and appearance of mechanical stress in the film upon light-and-heat action. This circumstance is largely responsible for the enhanced stability of film materials to ageing.[111]

Table 8. Effect of mesogenic compounds on the degree of crystallinity of HDPE films.[111]

Additive (concentration, parts by mass)	Degree of crystallinity (±1.2) (%)	
	before ageing	after ageing
None	69.5	73.2
23 (0.1)	72.2	71.4
23 (0.2)	71.2	72.8
23 (1.0)	71.9	72.9
33 (0.1)	70.8	71.8
33 (0.2)	70.9	71.9

Analysis of the strain–stress curves of HDPE containing 0.2 parts by mass of mesogenic formylazobenzenes **22** and **27** per 100 parts of the polymer demonstrated (Fig. 2) that they have a straight-line initial segment, which formally obeys the Hooke law, and a maximum corresponding to the yield point. A decrease in the temperature from 14 °C (see Fig. 2 *a*) to 5 °C (see Fig. 2 *b*) leads to increasing yield point in two cases (curves *1* and *3*); this is accompanied by the absence of a maximum and the subsequent 'plateau', which reflects the formation of the neck (*i.e.*, local thinning of the polymer being drawn) in these samples. The effect of mesogenic modifiers on the strain properties of the polymer is manifested, first, as a decrease in the yield point upon the introduction of anisotropic modifiers (see Fig. 2 *a*). This conclusion is supported by the data shown in Fig. 2 *b*: at low temperature, the yield point is manifested only for the composition containing epoxy-substituted formylazobenzene **27**. The second consequence of the introduction of this mesogen is a sharp increase in the tendency of the polymer sample to form a neck. This is indicated by not only a markedly extended range of constant σ values (the plateau in curve *2* in Fig. 2 *a*) but also the ability to form the neck retained at low temperature only in the composition containing formylazobenzene **27** (curve *2* in Fig. 2 *b*). The neck formation is caused by reorientation processes of both the macromolecular segments in the amorphous phase and the axes of supramolecular aggregates of polymers along the strain direction. Facilitation of this process by addition of mesogenic compounds (especially epoxy-substituted ones) may be caused by the orienting action of the additive towards macromolecules.[88, 94]

The results of mathematical calculation of the HDPE relaxation curves demonstrated that mesogenic additives **22** and **27** increase the mobility of the physical nodes of the

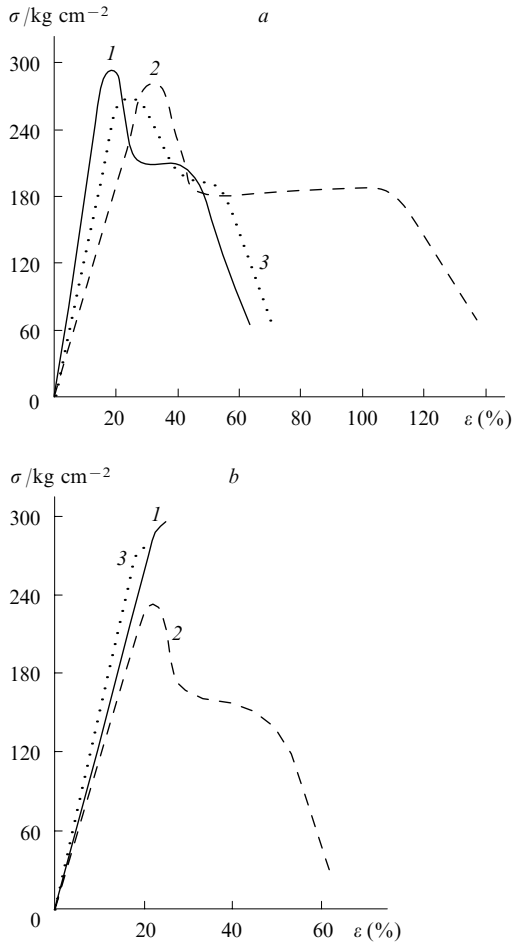


Figure 2. Stress–strain curves for modified HDPE at 14 °C (*a*) and 5 °C (*b*).[88,94]
Modifiers: (*1*) cadmium stearate, (*2*) epoxy-substituted formylazobenzene **27**, (*3*) formylazobenzene **22**.

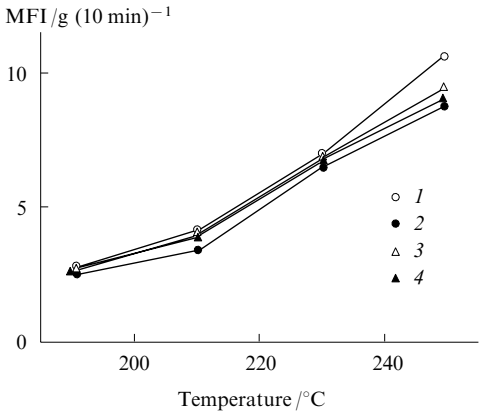


Figure 3. Temperature dependence of MFI for LDPE modified by commercial (Benazol P and Irganox 1010) (*1*) and mesogenic [compounds **37** (*2*), **38** (*3*) and **39** (*4*)] light-and-heat stabilizers.[112]
The curves were recorded at the load $P = 2160$ g.

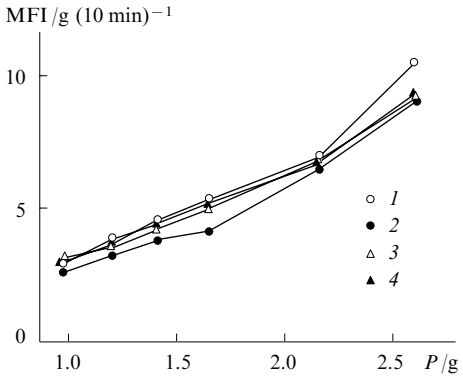


Figure 4. Variations of the MFI for LDPE modified by commercial (Benazol P and Irganox 1010) (*1*) and mesogenic [compounds **37** (*2*), **38** (*3*) and **39** (*4*)] light-and-heat stabilizers *vs.* load.[112]
The curves were recorded at 230 °C.

molecular network in the amorphous phase of the polymer. It was shown that the introduction of mesogenic modifiers decreases the relaxation times and the volume of kinetic units involved in relaxation processes. In the case of PVC, this induces an additional fast relaxation process that is not observed with standard stabilizers.[88,94]

A fundamental characteristics of the polymer that is affected by low-molecular-mass additives is the melt viscosity. The melt flow index (MFI)† is directly related to the polymer viscosity in the viscous flow state. Cinnamic acids **37**–**39**, like commercial stabilizers Benazol P (**46**) and Irganox 1010 (**11**), have a rather minor influence on the MFI. As the temperature and the shear stress increase, the MFI values regularly grow (Figs 3 and 4).[112]

A specific feature of substituted cinnamic acids **37**–**39** is the diphilic nature of their molecules, which accounts for their surfactant behaviour. In the case of liquids, this characteristics of surfactants is related to the change in the surface tension and its estimation faces no experimental difficulties. In a study of a solid–gas interface, direct measurement of the surface tension is problematic and the surface energy is estimated indirectly from the contact angles of various liquids. The replacement of standard stabilizers by cinnamic acid derivatives **37**–**39** improves water wetting of the LDPE surface before water ageing and deteriorates wetting with glycerol, which is accompanied by a considerable decrease in the dispersion contribution (σ^d) and an increase in the polar contribution (σ^p) to the surface energy. These changes can be unambiguously interpreted as surface hydrophilization caused by orientation of diphilic molecules **37**–**39** in the surface layer, namely, by predominant location of the hydrophilic carboxyl groups at the gas–solid interface.

It is of interest that ageing of the sample with commercial stabilizers is accompanied by improvement of wetting with both water and glycerol. This is not surprising because thermal oxidative destruction gives rise to diverse water- and glycerol-solvated groups on the polymer surface. Therefore, a decrease in the contact angles (especially with water) can be regarded as a sort of indicator of the degree of

† Melt flow index is the mass of a polymer (in grammes) that flows under pressure through a standard capillary in a standard time span (ten minutes).

Table 9. Contact angles and surface energies of LDPE films with commercial and mesogenic stabilizers.[112]

Polymer compositions	θ_{water} /deg	$\theta_{glycerol}$ /deg	σ^d /mJ m^{-2}	σ^p /mJ m^{-2}	$\Sigma\sigma$ /mJ m^{-2}
		Before ageing			
LDPE + Benazol P (**46**) + Irganox 1010 (**11**)	80.5	75.5	11.25	15.21	26.46
LDPE + **37**	71.3	77.8	4.12	27.83	31.95
LDPE + **38**	74.4	81.4	3.34	26.32	29.66
LDPE + **39**	69.4	75.4	4.78	28.6	33.38
		After ageing			
LDPE + Benazol P (**46**) + Irganox 1010 (**11**)	78.2	72.6	12.29	16.14	28.43
LDPE + **37**	73.4	71.7	9.73	21.06	30.79
LDPE + **38**	75.9	67.3	16.08	15.68	31.76
LDPE + **39**	75.0	74.6	8.31	20.92	29.23

degradation in the surface layer. It is quite typical that the addition of substituted cinnamic acids **37**–**39** does not provide a decrease in the θ_{water} values after ageing but results in some increase in these values (Table 9) and in the concomitant decrease in the polar contribution to the surface energy upon light-and-heat ageing; this attests to the absence of a significant oxidation of the material surface and, as a consequence, it is possible to speak about light and heat stabilizing activity of mesogenic modifiers.[112]

It should be noted that similar trends are also typical of PVC films containing mesogenic azo- and azoxybenzenes **33**, **48**–**50**.[103]

The specific orientation of mesogenic modifiers in the surface layer affects the tribological properties of LDPE. Although the tribological parameters of wet friction (glycerol and 1% aqueous solution of alkali) are not affected significantly by anisotropic additives, in the case of dry friction, the friction coefficient (f) and friction torque (M) were found to increase by 20%–36% upon replacement of standard stabilizers by substituted cinnamic acids **37**–**39** (Table 10).[112]

In view of the PVC applications for the manufacture of floor coverings, shoe outsoles, *etc*., an important characteristics of PVC films is attrition resistance. Mesogenic additives in the polymer compositions lower attrition and, as a consequence, enhance the wear resistance of films by 10%–30% with respect to the control sample stabilized by Vigostab BKC, which is also a consequence of the specific orientation of mesogens in the surface layer.[96, 103]

Table 10. Wear (Δm, I)[a] and friction coefficients and torques for LDPE films with commercial and mesogenic stabilizers in air environment.[112]

Polymer compositions	M /N m	f	Δm /g	$I \times 10^4$ /g km^{-1}
LDPE + Benazol P (**46**) + Irganox 1010 (**11**)	0.70	0.088	0.0032	7.9
LDPE + **37**	0.85	0.106	0.0097	24.1
LDPE + **38**	0.85	0.106	0.0022	5.5
LDPE + **39**	0.95	0.119	0.0028	7.0

[a] I is the mass wear intensity, *i.e*., the ratio of wear by mass to the distance of friction.

VI. Conclusion

From the material surveyed in the review, it is obvious that the problem of destruction and stabilization of polymers arouses researchers' interest both in Russia and in other countries. Development of the efficient stabilization systems for protecting polymer composites from various types of degradation, mainly during processing, is a topical task.

Extensive information on the methods for enhancing the thermal stability of polymers has been accumulated to date; various stabilizer systems have been developed and recommended almost for all known polymers. Meanwhile, the ever extending scope of application of polymeric materials and increasing requirements for their quality (durability, strength and other performance characteristics) stimulate further research: new practical solutions appear and new expedients and stabilization methods are proposed, which ensure a substantial retardation of ageing processes in polymers under natural and special conditions and saving of chemicals. Approaches dealing with the development of non-toxic, environmentally benign metal-free organic and inorganic stabilizers are especially topical.

The largest number of publications are related to degradation and stabilization of PE and PVC, which is not surprising, as particularly these polymers rank first in the production and application. However, while choosing the stabilizer, one should thoroughly study the mechanism of its action in the polymeric material. It is important to take into account not only the consumption of the anti-agers for the intended purpose (retardation of the degradation reactions in polymers) but also the problems of stabilizer migration into the environment and the destruction of antioxidants themselves under the action of chemically reactive environment.

The available experimental data indicate that the efficacy of mesogenic compounds as light and light-and-heat stabilizers for thermoplastics and PVC exceeds that of commercial stabilizers. The application of mesogens provides an increase in the activation energy of degradation, improvement of the material elasticity and strength. Mesogenic modifiers are versatile, because they are able to protect polymers from both light and heat simultaneously, whereas in the case of commercial stabilizers, the addition of two, three or even more compounds is required, which complicates the polymer composition. Moreover, aniso-

tropic additives are effective at 10 – 20 time lower concentrations than commercial stabilizers. The most effective mesogenic stabilizers belong to the group of azobenzenes — compounds that are widely used to dye textile materials (azo dyes) and that are not hazardous, unlike heavy metal compounds, which are used today as, for example, PVC stabilizers. Mesogens are readily compatible with polymers and do not sweat out during the processing and storage of samples. Finally, mesogenic biphenyl and phenyl benzoate derivatives are white-coloured powders and, hence, they can be recommended as stabilizers for polymer compositions used to produce colourless or white materials.

Elucidation of the mechanisms of action of mesogenic stabilizers is a complicated task requiring extensive experimental and theoretical investigations. We assume that the mechanism of light-stabilizing action may be related to the screening effect of anisotropic compounds having intrinsic absorption in the near-UV range, while the presence of chemically reactive functional groups may result in chemical reactions with particular molecular groups of the polymer or filler and with the low-molecular-mass products of polymer degradation. For instance, aldehyde and carboxyl groups can coordinate to metal ions, which allows considering them as deactivators of transition metals, and can react with hydroperoxides, thus deactivating the sources of free radicals, which initiate the polymer degradation. The epoxide and acryloyl groups are effective acceptors of hydrogen chloride during PVC ageing.

Apart from the stabilizing action, the molecular anisotropic compounds added to a polymer composition function as orienting species during strain and increase the mobility of the physical nodes of the molecular network in the amorphous phase. Modification of polyolefin- and PVC-based compositions by small mesogen amounts would allow the design of new composite materials with not only high strength and stability against the action of adverse factors but also with new specific adhesive, tribological and other properties owing to the formation of surface nanostructures.

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