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# Aryl (meth)acrylates and polymers based on them

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**Abstract. Data on the synthesis, polymerisation and copolymerisation of aryl (meth)acrylates are generalised and systematised. Chemical and photochemical properties of the polymers and copolymers are considered. Basic directions of practical application of poly[aryl (meth)acrylates] and copolymers are demonstrated. The bibliography includes 449 references**.

## I. Introduction

Aryl (meth)acrylates $H_2C=C(R)CO_2Ar$ (hereinafter R = H, Me) occupy a special place in the series of (meth)acrylates due, first of all, to the diversity of functional groups which may be introduced into the aromatic ring of these monomers and the derived polymers. Specificity of physical properties of poly[aryl (meth)acrylates] is determined by the enhanced rigidity of the polymeric chains (because of the presence of aromatic rings). Aryl (meth)acrylates are easily copolymerised with most of the known monomers, which opens broad prospects for their application.

Until recently, the results of numerous studies on the synthesis and properties of aryl (meth)acrylates have not been generalised. The present review is intended to fill this gap.

## II. Methods for the synthesis of aryl (meth)acrylates

Earlier methods for the synthesis of aryl (meth)acrylates were rather complicated and were not of a general character. Thus phenyl acrylate (PA) was prepared by direct esterification of phenol with acrylic acid in the presence of trifluoroacetic anhydride [1] and also by the Reppe reaction, *i.e.*, by the reaction of acetylene and carbon monoxide with phenol.[2] Phenyl [3] and naphthyl acrylates [4] were obtained by pyrolysis of 2-acetoxypropionates $MeCH_2(OAc)CO_2Ar$. The systematic studies of the methods for the preparation of aryl acrylates were initiated by Magagnini and Pizzirani [5] who investigated the reactions of acryloyl chloride with phenols. In addition to PA, these authors described acrylates of isomeric cresols, chlorophenols, thymol, hydroxybiphenyl and 4-methoxyphenol. It should be noted that the reactions were carried out under conditions precluding the addition of hydrogen chloride to the double bond. In earlier attempts of the synthesis of acrylates by this method, this addition took place; therefore, β-chloropropionates were the major products. Conducting of these reactions in the presence of triethylamine allowed a considerable increase in the yields of methacrylates of substituted phenols. This method was successfully used to prepare isomeric phenol di(meth)acrylates,[6] 2-biphenylyl acrylate [7] and 4-biphenylyl (meth)acrylate [8] and mono- and di(meth)acrylates of substituted 2,2′-methylenebisphenols.[9]

Aryl (meth)acrylates are usually synthesised by the reaction of phenols with (meth)acryloyl chloride in the presence of hydrogen chloride acceptors. This process may be carried out in inert solvents in the presence of $Na_2CO_3$,[10] in pyridine,[11] in ethanolic solution of KOH [12] or triethylamine.[7] It is also convenient to use the Schotten – Baumann reaction, which involves the acylation of phenolates with (meth)acryloyl chloride in aqueous solutions at reduced temperature in the presence of an excess of alkali.[13] This reaction occurs efficiently at the interface of the aqueous and organic phases.[14] Monomers based on halogenated 2,2-di(4-hydroxyphenyl)propanes [15] and hydroxyphenyl derivatives of 2*H*-benzotriazole [16] were prepared in this manner.

The methods described above have allowed the preparation of numerous alkyl- (see Refs 4, 6, 13, 17, 18), halogeno- (see Refs 4, 6, 11, 14) and nitro-substituted [4, 10, 19] phenyl (meth)acrylates (PMA). At the same duration and temperature of the reaction, the yields of esters decreased in the following order: *meta*-isomer > *para*-isomer > *ortho*-isomer > disubstituted phenol.[10] Optimum conditions were found for the preparation of 2,6-dimethylphenyl acrylate, 2,4,6-trichloro-, 2,4,6-tribromo-, 2,4,6-trimethyl-, 2,6-diisopropyl- and 2,6-di(*tert*-butyl)-phenyl methacrylates, 2,4,5-trichlorophenyl acrylate [21] and methacrylate.[22]

PMA with substituents in the aromatic ring containing the aldehyde and ketone,[23] carboxy,[24, 25] benzyl,[26] tetracyanocyclobutyl [27] and dioxolane [28] groups have been described. Special mention should be made of (meth)acrylates of hydroxyphenylacetic [29] and hydroxybenzoic [24, 25] acids as well as of surfactant salts [30] of the general formula $CH_2=CMeC(O)OC_6H_4(CH_2)_nX$ [$n$ = 3, 7; X = $CO_2Na$, $N^+(C_nH_{2n+1})_3Z^-$; Z = Cl, Br, I, $MeSO_4$].

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4-(Meth)acryloyloxybenzoic acids form liquid-crystalline polymers upon polymerisation and give birth to a large number of mesomorphic monomers and polymers.[31] Of all monomers of this type, the best studied are the esters of the general formula $CH_2=CRC(O)OYC(O)OYR'$ ($R'$ = H,[32] Me,[33] OR″; R″ = Me,[32–35], Pr,[34] Bu$^n$,[32–34,36] n-$C_6H_{13}$[37] and Alk($C_8-C_{16}$)[36] (hereinafter Y = 1,4-$C_6H_4$). Monomers with more complex structures have been also described, *e.g.*, methacrylates with the mesogenic side groups YC(O)OYOC(O)YOR′ (R′ = H, Alk);[38] or thermotropic bisacrylates R′XR′ (X = $(CH_2)_n$; $n$ = 6–10, 12; R′ = $CH_2=CHC(O)O.$ .YC(O)OYC(O)O.[39] It should be noted that mesomorphic monomers are also found among aryl (meth)acrylates with a different character of substitution. These are acrylates and methacrylates of hydroxybiphenyl with alkyl[40] and alkoxy[41,42] substituents or the CN group[43] at the position 4′. It is noteworthy that poly(4,4′-biphenylene diacrylate) does not possess liquid-crystalline properties.[44]

The group of mesomorphic monomers also includes easily polymerisable acrylates of azomethines derived from 4-hydroxybenzaldehyde. Polymers with Schiff's bases as the pendent groups can be obtained by polymer-analogous transformations from polyacryloyl chloride and the corresponding hydroxybenzylideneaniline.[45] A large group of this type of monomers of the general formula $CH_2=CRC(O)OYCH=NX$ [X = Alk($C_1-C_4$), $C_6H_4Z$; Z = OH, OMe, OEt, $NMe_2$, $NEt_2$, NHPh, naphthyl, pyridyl] has been proposed[46] for the preparation of non-aqueous dispersions of polymers used in polygraphy.

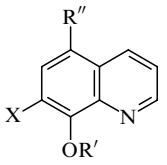
4-(4-Acryloyloxybenzylideneamino)phenyl acrylate[44] and *N*-(4-cyanobenzylidene)-4-acryloyloxyaniline are azomethines based on 4-aminophenol.[47] Mesomorphic monomers (as well as the derived polymers) are rarely found among methacryloylazomethines.[48]

(Meth)acrylates of hydroxyazobenzenes[49–51] and hydroxyazoxybenzenes[52] were used to prepare liquid-crystalline polymers. Azo-monomers possess, as a rule, alkyl, alkoxy or aryl substituents in the *para*-position relative to the azo group. The respective polymers are lyotropic or thermotropic liquid crystals, which undergo reversible changes under the action of UV radiation.[53] Liquid-crystalline polymers based on 4,4′-(bisacryloyloxy)azoxybenzene[44] are also obtained by the reaction of 4-hydroxyazobenzene with poly(acryloyl chloride).[54] Comb-like polymers with liquid-crystalline properties were obtained by polymerisation of hydroquinone mono(meth)acrylates esterified at the second OH group with 4-n-alkoxybenzoic acids.[55–58]

The results of studies on liquid-crystalline polymers derived from aryl (meth)acrylates have been described rather comprehensively in monographs.[59,60]

Syntheses of (meth)acrylates of derivatives of condensed aromatic systems (naphthalene, anthracene, phenanthrene) have been described.[61] Syntheses of α- and β-naphthyl esters of some α,β-unsaturated acids,[62] 2-(β-substituted acryloyl)-1-methacryloyloxynaphthalenes, which are cross-linking agents,[63] and 4-benzoylamino-α-naphthyl methacrylate,[64] which is an efficient thermostabiliser, are documented. Monomeric dyes of the anthraquinone series were obtained by the reaction of unsaturated acid chlorides with 4-amino-1,5-dihydroxy-2,6-diisobutyl-, 5-(3-aminophenylthio)-1,5-dihydroxy-2,6-diisobutyl- and 4,5-diamino-1,8-dihydroxy-2,7-diisobutylanthraquinones.[65] Copolymerisation of these dyes with styrene and butyl methacrylate yields polymers self-coloured in yellow, red and blue. Kimura *et al.*[66] have described 2- and 9-fluorenyl methacrylates. Upon their polymerisation in the presence of a telogen, the degree of telomerisation of the second monomer is lower. A number of monomers based on fluoranthene, including 3-fluoranthenyl methacrylate, produce polymers of the donor type, which form charge-transfer complexes possessing electrical properties with tetracyanoquinodimethane and tetracyanoethylene.[67]

Methacrylates of the 8-hydroxyquinoline series[68] of the general formula




X = H, Br, Cl, I;
R′ = C(O)CMe=$CH_2$;
R″ = H, Br, Cl, $CH_2OMe$, $CH_2OEt$

were synthesised in order to obtain subsequently medicinal preparations with prolonged action.[69,70] Halogens were shown to favour polymerisation. Methacrylates of hydroxyphenyl derivatives of other nitrogen-containing heterocycles are also known, *e.g.*, 1,3-diphenyl-5-(4-methacryloyloxyphenyl)-2-pyrazoline.[71] Of these, the most complex are acrylate and methacrylate of 5-(4-hydroxyphenyl)-10,15,20-triphenylporphyrin[72] (the respective polymers possess semiconducting properties and adsorb oxygen at temperatures below 200 K) and of 5-(4-acryloyloxyphenyl)-15-phenyl-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin.[73]

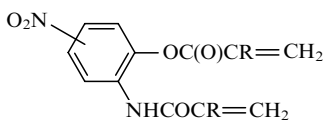
Some monomers contain the methacryloyloxy group bound directly to the heterocyclic ring, *e.g.*, 2-pyridyl methacrylate.[74] Aryl (meth)acrylates with the nitrogen-containing heterocyclic substituents in the *para*- and *meta*-positions of the benzene ring have been described.[75] The initial *N*-(hydroxyphenyl)imides were obtained by condensation of aminophenols with the corresponding anhydrides. Monomers were synthesised by acylation with unsaturated acid chlorides.

As regards aryl (meth)acrylates with nitrogen-containing substituents in the phenyl group, monomers with the nitro (see Refs 4, 10, 19) and cyano[76] groups have been described; a number of monomers with the azo (see Refs 77, 78), azoxy and azomethine groups[79–82] are also known. 4-Azidophenyl methacrylate,[83] salicinide,[84] *N*-benzyl- and *N*-phenyl-4-hydroxybenzamide acrylates and methacrylates[85] were synthesised.

4-Aminophenyl methacrylate proved to be sensitive to oxidation, which reduces the possibility of its practical application.[86] However, 3-(*N*,*N*-dimethylamino)phenyl methacrylate is fairly stable,[76] it forms charge-transfer complexes with electron acceptors and is promising for the synthesis of polymeric photosemiconductors.

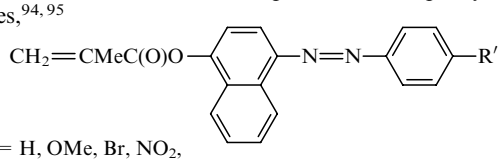
Many reactive monomers, *e.g.,* acylaminophenyl methacrylates of the general formula $R'C(O)NHC_6H_4OC(O)CR=CH_2$ (R′ = H, Me, Et, Pr, Bu, $C_5H_{11}$, $PhCH=CH$, $O_2NC_6H_4$ and $BrC_6H_4$) were obtained by *N*-acylation of isomeric aminophenols with equimolecular amounts of carboxylic acid chlorides (in anhydrous acetone, methanol or DMF) with subsequent esterification by the Schotten–Baumann reaction with acryloyl or methacryloyl chlorides.[87–90] If 4-, 3- or 2-aminophenols are esterified with methacrylic acid, both functional groups react to give 4-, 3- or 2-(meth)acryloylaminophenyl (meth)acrylates. These reactive monomers undergo cross-linking in the polymerisation.[14,91,92] Di- and tri(meth)acryloyl derivatives of 2,4-diaminophenol (amidol) were synthesised by successive acylation.[92]

Diacryloyl and di(meth)acryloyl derivatives of nitroaminophenols




were prepared[93] by acylation of 2-amino-4-nitro- and -5-nitrophenols with unsaturated acid chlorides in tetrahydrofuran in the presence of triethylamine.

Based on 4-amino-α-naphthol, azonaphthyl methacrylates,[94,95]




R′ = H, OMe, Br, $NO_2$,

imidonaphthyl methacrylates [94] and 4-benzoylamino-α-naphthyl methacrylate [95] were synthesised.

Thus, aryl (meth)acrylates with diverse functional groups in the aryl residue have been prepared to date.

## III. Polymerisation of aryl (meth)acrylates

Aryl (meth)acrylates are relatively easily polymerised by a radical mechanism, the polymerisation rate being mainly determined by steric effects of substituents.[96] Thus *ortho*-substituted PMA are appreciably less reactive than the *para*-isomers, the chemical nature of the substituent does not play any substantial role, which has been confirmed by the results of polymerisation of nitro- and methoxyphenyl methacrylates.[13,97,98] Polymerisation was carried out in block and in different solvents in the presence of benzoyl peroxide. Since the electronic effect of the nitro and methoxy groups is opposite, one could expect that the rates of polymerisation of *o*- and *p*-nitrophenyl methacrylates and *o*- and *p*-methoxyphenyl methacrylates would be different; however, polymerisation of *para*-derivatives occurred faster in both cases. The EPR spectra of radicals devoid of *ortho*-substituents, *e.g.*, poly(phenyl methacrylate) (PPMA) and poly(4-methylphenyl methacrylate), are identical, whereas the spectra of radicals of 2,6-diisopropylphenyl methacrylate and 2,6-di-*tert*-butylphenyl methacrylate revealed differences related to the shielding of the growing end of the polymeric chain by the *ortho*-substituents and the α-methyl group.[99]

The overall rate constant of the bulk polymerisation of alkylphenyl methacrylates (alkyl = Et, $Pr^i$, $Bu^t$) is higher for the *para*-substituted monomers than for the *ortho*-substituted ones and is virtually independent of the substituent size, whereas for the *ortho*-isomers this constant decreases with the increase in the substituent size.[100] The reaction order with regard to the initiator (dilauryl peroxide) is 0.5 for non-substituted PMA, while it is 0.64–0.94 for the sterically hindered monomers. The presence of methyl groups in the *ortho*-position (*e.g.*, in 2,6-dimethylphenyl methacrylate) decreases appreciably the ceiling temperature of polymerisation (down to 73 °C) compared to that of non-substituted PMA (140 °C).[101] The overall activation energy (kJ $mol^{-1}$) increases in the following order: 2,6-diisopropylphenyl methacrylate (45.7) < 4-*tert*-butylphenyl methacrylate (49.9) < 4-(1,1,3,3-tetramethylbutyl)phenyl methacrylate (59.6) < 4-methyl-, 4-ethyl- and 4-isopropylphenyl methacrylates (70–76).[102,103]

Substitution of the cyclohexyl radical for the phenyl radical in the molecule of aryl methacrylate affects the polymerisation rate. For example, methacrylate of thymol, which contains a bulky isopropyl residue, is polymerised with difficulty, while methacrylate of menthol (hydrogenated thymol) analogous to the preceding monomer is polymerised easily under the same conditions.[13] This is rationalised by the non-planarity of the cyclohexane ring and, consequently, by a lower rigidity of this monomer molecule compared to the methacrylate of thymol.

Block polymerisation of substituted PMA is accompanied by gel-effect, which is observed in 2,4,6-tribromophenyl, 4-tolyl, 4-cyclohexylphenyl and 4-methoxyphenyl methacrylates at 35%, 35%, 15% and 2% conversions of the monomer, respectively [the concentration of the polymerisation initiator, *viz.*, azobisisobutyronitrile (AIBN) is 0.4%].[104] The kinetic parameters of PMA polymerisation in block and in solvent (60 °C, AIBN) were compared with those for alkyl methacrylates.[105] The overall polymerisation rate has an order of 0.5 with respect to the initiator and 1 with respect to the monomer, *i.e.*, it is described by the usual equation of radical polymerisation. The ratio of the chain termination constant ($k_t$) to the squared chain propagation constant ($k_p$) increases in the following order: (phenyl < isobutyl ≈ n-butyl < ethyl < methyl) methacrylate. According to the radiometric analysis of the initiator fragments, the share of disproportionation in PMA is 89% [72% in methyl methacrylate (MMA)]. The initiation rate of radical polymerisation of PMA by AIBN depends slightly on the nature of the solvent, while $k_p$ (litre $mol^{-1}$ $s^{-1}$) increases in the following series of solvents: benzene (176) < fluorobenzene (180) < chlorobenzene (223) < anisole (230) < bromobenzene (235) < benzonitrile (243).[106] The magnitude of $k_p$ was found to correlate with the difference in chemical shifts of β-alkene protons of monomers depending on the solvent.

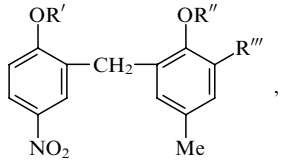
The MO LCAO method was used to calculate the stabilisation energy in the formation of complexes of a radical with a solvent; $k_p$ was found to decrease with the increase in the complexation energy. It was shown later that this trend holds for MMA [107] and PMA.[108] The rate of radiation-induced polymerisation of PMA is proportional to the radiation dose to the power 0.65;[109] in the temperature range 20–34 °C, the activation energy of the process is equal to 14.15 kJ $mol^{-1}$, $k_p/k_t^{0.5} = 0.0198$. At high degrees of conversion, a three-dimensional network is formed owing to the involvement of the terminal double bonds.

Investigation of the influence of substituents on the radical polymerisation of PA has shown that the rate of this process increases in the order: methyl acrylate < 2-chlorophenyl acrylate < PA < 4-chlorophenyl acrylate.[110] This is rationalised by changes in the flexibility of the propagating polymer chains. The increase in the overall polymerisation rate (toluene, 60 °C, lauryl peroxide) was found to increase in the following series:[111] (2-*tert*-butyl- < 2-isopropyl- ≈ 2-propyl- < 2-ethyl- < 2-methyl- < PMA < 4-methyl- < 4-isopropyl- < 4-*tert*-butyl- < 4-propylphenyl) methacrylate. The reaction order with regard to lauryl peroxide is 0.51–0.87 depending on the monomer concentration.

In the radical polymerisation of 2,4,5-trichlorophenyl methacrylate [112] in dioxane ($k_p = 2.73 \times 10^3$, $k_t = 7.22 \times 10^7$ litre $mol^{-1}$ $s^{-1}$), the polymerisation rate is proportional to the monomer concentration to the power 1.5, which is explained by the possible formation of complexes of the monomer with the solvent molecules. In the case of radical polymerisation of nitrophenyl methacrylates, at a low monomer concentration (0.01 mol $litre^{-1}$) one observes an inhibitory effect of the intra- and intermolecular chain transfer, the former being prevalent.[113–115] For this reason, 2,6-dinitrophenyl, 2-methyl-4,6-dinitrophenyl and picryl methacrylates are not polymerised under these conditions, and the conversion of 2,4-dinitrophenyl methacrylate hardly reaches 2.6% in 2 h. The reaction orders of 4-biphenyl methacrylate polymerisation (in DMF with AIBN) are 0.55 and 1.1 with respect to the initiator and monomer respectively; the total activation energy is 58 kJ $mol^{-1}$ (see Ref. 8).

Replacement of an alkyl substituent by the electron-withdrawing acyl substituent in the benzene ring leads to an increase in the polymerisation rate of substituted phenyl (meth)acrylates because of the lower activation energy of the C=C bond cleavage.[17] DTA studies of thermal bulk polymerisation of 4-acetylphenyl acrylate and methacrylate have shown [116] that this process is the first-order reaction with respect to the monomer, the activation energies are equal to 228.1 and 120.5 kJ $mol^{-1}$, respectively. High polymerisation rates were observed for acylaminophenyl (meth)acrylates;[87,88] however, the rate of polymerisation decreased with increase in the length of the acyl radical. On the other hand, 4-diethylaminophenyl acrylate and methacrylate polymerised at a lower rate than non-substituted PMA.[89]

Radical polymerisation of mixed diesters of 2,2′-methylenediphenols with methacrylic and crotonic acids [117]




where R′ and/or R″ are methacrylic and crotonic acid residues and R‴ = H, Me, $Bu^t$, resulted in soluble polymers where R′ = R″ (polymerisation involved the methacryloyl group alone),

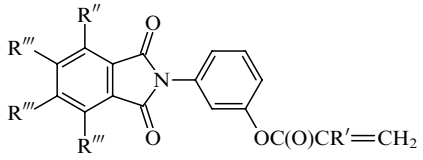
insoluble dimethacrylates where R′ and R″ were the methacrylic acid residues and no polymerisation occurred where R′ and R″ were the crotonic acid residues.

(Meth)acryloyl derivatives of *N*-hydroxyphenyl-substituted phthalimide [118] $R'C_6H_4OC(O)CR=CH_2$ (R′ = phthalimido)

| Monomer | I | II | III | IV |
|---|---|---|---|---|
| R | H | H | Me | Me |
| Position of R′ | *para* | *meta* | *para* | *meta* |

and alicyclic diacylamines [118, 119] polymerise at high rates and are more reactive than PMA, which seems to be due to the electron-withdrawing character of the imide fragment. The reactivity of monomers decreases in the following order: I > III > II > IV > *p*-acetylaminophenyl methacrylate (*p*-AAPMA), acrylates being more reactive than the corresponding methacrylates and the *para*-isomers more reactive than the *meta*-isomers.[118]

The reactivity of *m*-phthalimidophenyl (meth)acrylates [120]



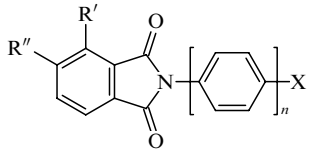
| Monomer | R′ | R″ | R‴ |
|---|---|---|---|
| I | H | H | H |
| II | Me | H | H |
| III | H | Cl | Cl |
| IV | Me | Cl | Cl |
| V | Me | Br | Br |
| VI | Me | $NO_2$ | H |

decreases with in the series: IV > V > II > *m*-AAPMA > VI, *i.e.*, with the weakening of the electron-withdrawing character of the phthalimido group. The reduced reactivity of the monomer with the nitro group in the phthalimide cycle may be explained by its inhibitory action.

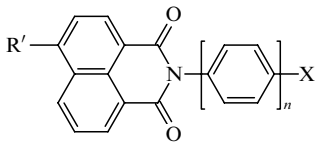
The polymerisation rate of imidonaphthyl (meth)acrylates is lower than that of analogous imidophenyl methacrylates, and, according to Vretik *et al.*, [94] this is due to the reduced reactivity of radicals because of a stronger electronic conjugation in the naphthyl-containing system. The most reactive of all the naphthyl (meth)acrylates studied proved to be bismethacrylate with an additional cycloalkene double bond. This compound was obtained by the reaction of endic dianhydride with 1-amino-4-methacryloyloxynaphthalene.[94]

Irrespective of the initiation mode (thermal or photo-initiation), *m*-(succinimido)phenyl methacrylate (*m*-SIPMA) and acrylate (*m*-SIPA) occupy an intermediate position with regard to their reactivity between *m*-phthalimidophenyl methacrylate (*m*-PTIPMA) and acrylate (*m*-PTIPA), and acetylaminophenyl methacrylate (*m*-AAPMA) and acrylate (*m*-AAPA): *m*-PTIPMA > *m*-SIPMA > *m*-AAPMA > PMA; *m*-PTIPA > *m*-SIPA > *m*-AAPA > PA, *i.e.*, there is correlation between the electron-withdrawing properties of the substituent and polymerisability of substituted phenyl (meth)acrylates.[121] High reactivity of these aryl (meth)acrylates allows the introduction of the above-mentioned heterocyclic fragments into the side chains of macromolecules in order to impart definite photochemical, biological and other properties to the polymeric materials.

Based on imidoaryl (meth)acrylates,[122, 123]



X = $OC(O)CR=CH_2$; R′, R″ = $NO_2$, $NH_2$; *n* = 1, 2;



X = $NH_2$, $OC(O)CR=CH_2$; R′ = $NO_2$; *n* = 1, 2

homopolymers were obtained with the controllable intramolecular energy transfer. In such polymers, movement of singlet or triplet excitons from one part of the macromolecule to another or from one unit chain to another is observed. The prerequisite for such a transfer is the presence of isolated aromatic systems with different excitation energies in each of the neighbouring units; the initial excitation should be generated in a definite element of the system. Such compounds are promising for the design of microelectronic devices in which advantage is taken of photophysical processes at the molecular level.[124]

Polymerisability of bifunctional monomers deserves special mention. Cross-linked polymers are formed upon polymerisation of *p*- and *m*-phenylene di(meth)acrylates; *o*-phenylene diacrylate can undergo cyclopolymerisation [7] with the formation of ladder polymers; the extent of cyclisation increases with the decrease in the monomer concentration and the increase in the polymerisation temperature.[125] At a monomer concentration above 0.5 mol litre$^{-1}$, an insoluble polymer is formed. The intramolecular chain growth in the cyclopolymerisation follows mostly the 'head-to-tail' mechanism, and a small number of units are formed by the 'head-to-head' mechanism.

Radical polymerisation of 2-allylphenyl (meth)acrylates is a two-step process:[126] at an 18%–30% monomer conversion, a soluble low-molecular-mass polymer is formed, which is then cross-linked. The low molecular mass of the product and the absence of the gel-effect are associated probably with the ability of the allyl group to undergo chain transfer. A detailed study of the polymerisation of 2-allylphenyl acrylate in toluene at 60 °C in the presence of AIBN revealed high content of the residual double bonds in the pendent allyl groups of the polymer.[127] Subsequent cyclopolymerisation occurs due to the reaction of the C=C bonds of the acryloyl and allyl groups. Cyclopolymerisation of 2-allylphenyl, 2-(*o*-allylphenoxy)ethyl and 4-(*o*-allylphenoxy)butyl acrylates catalysed by alkylaluminium chlorides [127–129] yields 8-, 11- and 13-membered rings; however, the catalyst's activity is insignificant for the formation of the 15-membered ring from 6-(*o*-allylphenoxy)hexyl acrylate.

Polymerisation of *ortho*-, *meta*- and *para*-(meth)acryloylaminophenyl (meth)acrylates initiated by AIBN occurs with the formation of cross-linked polymers.[92] A decrease in the reactivity in the order *meta*- > *ortho*- > *para*-aminophenol di(meth)acrylates is associated with the character of conjugation in these monomers. Tri(meth)acryloyl derivatives of 2,4-diaminophenol (amidol) are more reactive than the corresponding (meth)acryloylaminophenyl (meth)acrylates, whereas di(meth)acryl derivatives of amidol (with a free OH group) do not polymerise. Upon polymerisation of monomers based on 2-amino-4- and -5-nitrophenols, no formation of cross-linked polymer is observed even at a 60% conversion,[93] as is the case of polymerisation of di(meth)acryloyl derivatives of 2-aminophenol. The presence of the nitro group decreases the number of active centres in the system resulting in the higher probability of chain transmission and formation of cyclolinear structures in macromolecules.

Cinnamoylaminophenyl (meth)acrylates [90]

$H_2C=CRC(O)OYNHCOCH=CHPh$

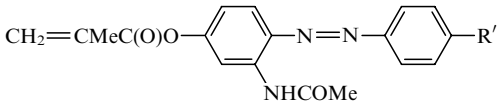
polymerise at a lower rate than di(meth)acryloyl derivatives of isomeric aminophenols; the early chain termination at low conversions appears to be due to the inability of the cinnamoyl C=C bond, which acts as a trap for free radicals, to polymerise. This conclusion is prompted by comparison of the IR spectra of

the monomer and the polymer. Photosensitivity of such monomers (photoinitiator, benzoin), like that of 4-cinnamoylaminophenol, confirms the non-reactivity of the cinnamoyl double bond in radical polymerisation and its capability of photoaggregation.[130] The nitro group in 4-nitrophenyl cinnamate or in 4-nitro-1-naphthyl cinnamate exerts a photosensitising effect. These monomers are light-sensitive and belong to the group of self-sensitised ones.[131] Poly(4-cinnamoylphenyl methacrylate) obtained in the presence of benzoyl peroxide as an initiator with a degree of conversion of 78% is insoluble in common organic solvents.[132]

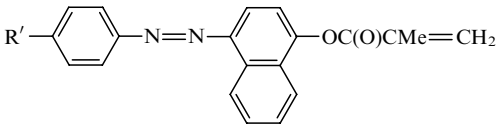
In contrast to MMA, radical telomerisation of aryl (meth)acrylates with the use of bromotrichloromethane as the telogen is not accompanied by the formation of lactones;[133] however, the distribution with regard to the degree of polymerisation and tacticity are analogous. Pyrolysis of telomers at 150–200 °C leads to the formation of unsaturated compounds and in part lactones.

The behaviour of 4-methacryloyl- and 4-acryloyloxybenzoic acids is highly specific under thermal treatment.[134] At 250 °C (above the upper limit of polymerisation temperature), the former undergoes polycondensation with the elimination of methacrylic acid and formation of a rigid-chain polymer, *viz*., poly(4-hydroxybenzoate). The latter undergoes simultaneous polymerisation and polycondensation. In the polymerised state, both acids undergo polycondensation upon thermal treatment.

Methacrylic monomers with the azo group based on aminophenols [77, 135,] and 4-amino-α-naphthol [136]



$R' = H, Me, NO_2$;



$R' = H, Br, OMe, NO_2$

attract attention because of the possibility of using them for the preparation of 'self-coloured' polymers containing dye residues incorporated into the polymeric chain. Of the monomers based on azo compounds of 3-aminophenol, only the azo-coupling products at the *para*-position relative to the methacryloyl group can polymerise. The monomers based on 4-amino-α-naphthol are incapable of radical homopolymerisation because of a decreased reactivity of their radicals due to high electronic conjugation in the azo system. However, they copolymerise with styrene forming coloured polymers. Copolymers of *trans*-4-(phenylazo)-1-naphthyl acrylate and *trans*-4-(phenylazo)phenyl acrylate with (−)-menthyl acrylate are optically active.[137]

The data on ionic polymerisation of aryl (meth)acrylates are scarce. They are known to polymerise by an anionic mechanism. Polymerisation of PMA on organolithium catalysts proceeds more slowly than that of alkyl methacrylates;[138] this process is characterised by the existence of a 'limit' of monomer conversion and the fact that the degree of polymerisation does not increase as the process proceeds further. Anionic polymerisation of PMA, cresyl acrylate [139, 140] and 4-(α,α-dimethylbenzyl)phenyl methacrylate [141] in the presence of n-butyllithium, as well as anionic polymerisation of *p*-cresyl methacrylate [142] with naphthyllithium, butyllithium and $LiAlH_4$ in the hydrogen atmosphere are documented. Reduction of the polymers thus obtained with lithium aluminium hydride yields poly(α-methylallyl alcohol) (in the case of *p*-cresyl methacrylate) and polyallylic alcohol (in the case of *p*-cresyl acrylate). Phenyl (meth)acrylate also polymerises readily with alkylaluminium chlorides by an anionic mechanism.[143] Some PA, *e.g*., 4-nitrophenyl acrylate, do not polymerise by an anionic mechanism.[140]

Comparative studies of radical and anionic polymerisation of 9-fluorenyl and 9-phenylfluorenyl methacrylates [144] in THF or toluene at temperatures from −78 to −60 °C in the presence of AIBN or butyllithium revealed substantial differences in the reaction course. Upon initiation with AIBN, the yield of polymers amounted to 60%–95%, the degree of polymerisation ranged from 9 to 37 with $M_w/M_n = 1.8–3.6$, while upon initiation with butyllithium, the yield of polymers ranged from 3% to 40%, and $M_w/M_n = 1.9–2.0$.

## IV. Aryl (meth)acrylates in copolymerisation reactions

Aryl (meth)acrylates copolymerise easily with most monomers. For example, copolymers of PMA with ethylene [145] and butadiene [146] have been described. But of greatest interest are numerous data [147, 148] on copolymerisation of substituted phenyl (meth)acrylates with styrene, acrylonitrile and MMA. Parameters of copolymerisation (AIBN, in bulk or in benzene at 60 °C) of PMA and its derivatives with substitutions in the ring with styrene are presented in Table 1.

It was noted that the reactivity of monomers towards styrene radical ($1/r_1$) is determined by the polar ($\sigma$) and resonance ($E_r$) effects of substituents and is satisfactorily described by the modified Hammett equation [149]

$$\log\frac{1}{r_1} = \rho\sigma + \gamma E_r$$

for $\rho = 0.21$ and $\gamma = 1$. Low values of the copolymerisation constants $r_1$ and $r_2$ point to the tendency of aryl methacrylates for the alternation with styrene in the copolymerisation. The electron-donor substituents in PMA decrease polarity ($e_2$), while the electron-withdrawing substituents, especially those in the *para*-position, increase polarity. This is accompanied by a decrease in the frequencies of stretching vibrations of the −C=C− and >C=O groups.[150] Linear correlation is observed between the Hammett constants and the $e_2$ criteria as well as between $\log Q_2$ ($Q_2$ is the criterion of the monomer reactivity) and $E_r$.[147] In the case of *p*- and *m*-nitrophenyl methacrylates, the linear dependences are distorted because of the inhibitory effect of the nitro group. Introduction of several functional groups enhances the effect, as is observed for the criteria $Q_2$ and $e_2$ in 2,4,6-tribromophenyl and pentabromophenyl methacrylates.[151, 152] The azo group manifests rather strong acceptor properties ($e_2 = 1.0$).[153] *ortho*-Substituents, *e.g*., the carboxy group, strongly increase the values of $Q_2$ but virtually do not affect the $e_2$ values, which is well explained by considering the increased steric hindrances.[154, 155]

In copolymerisation with styrene, 2-naphthyl methacrylate (2-NMA) manifests a weaker (compared to PMA) trend for alternation, which is, however, enhanced in polar solvents (*e.g*., in acetonitrile).[156–158] Irrespective of the solvent nature, the polydispersity and molecular mass increase with the increase in the content of 2-NMA. In complex aromatic systems, the methacryloyloxyphenyl group behaves in the usual manner, as it does in PMA.[159]

Parameters of copolymerisation of substituted PA with styrene are presented in Table 2. Comparison of the data presented in Tables 1 and 2 shows that the values of the parameters $Q$ and $e$ are higher for PA than for the corresponding MA, which is associated with the absence of the effect of the α-methyl group.[160] For example, $e_2$ is equal to 1.32 for 2,4,6-tribromophenyl acrylate [161–163] and to 0.91 for the corresponding methacrylate.

Copolymers of PA with MMA [164] are characterised by the predominance of MMA units ($r > 1$) in the macromolecule. In this case, the reactivity of substituted PA [165] is determined by their ability to form π-complexes with the double bond of MMA, which decreases in the series: PA > 2-chlorophenyl acrylate > 4-chlorophenyl acrylate. The values of parameter $e$ increase in the same order (up to 1.46 for the latter member).

**Table 1**. Parameters of copolymerisation of substituted PMA with styrene.

| Substituent in PMA | $\sigma$ | $E_r$ | $r_1$ | $r_2$ | $1/r_1$ | $Q_2$ | $e_2$ | Ref. |
|---|---|---|---|---|---|---|---|---|
| – | – | – | 0.30 | 0.60 | 3.33 | 1.17 | 0.51 | 147 |
| 4-Chloro | 0.226 | 0.10 | 0.22 | 0.45 | 4.55 | 1.35 | 0.72 | 147 |
| 3-Chloro | 0.373 | 0.08 | 0.21 | 0.40 | 4.76 | 1.36 | 0.77 | 147 |
| 2-Chloro | 0.560 | – | 0.40 | 0.38 | 2.50 | 0.83 | 0.83 | 20 |
| 4-Nitro | 0.778 | 0.41 | 0.19 | 0.22 | 5.26 | 1.27 | 0.98 | 147 |
| 3-Nitro | 0.710 | 0.35 | 0.18 | 0.36 | 5.56 | 1.47 | 0.86 | 147 |
| 2-Nitro | 0.650 | – | 0.13 | 0.36 | 7.69 | 1.90 | 0.95 | 20 |
| 2,4,6-Trichloro | – | – | 0.19 | 0.34 | 5.26 | 1.40 | 0.86 | 20 |
| Pentachloro | 1.07 | – | 2.00 | 0.35 | 0,50 | 0.31 | −0.20 | 152 |
| 2,4,6-Tribromo | – | – | 0.20 | 0.27 | 5.00 | 1.27 | 0.91 | 151 |
| Pentabromo | – | – | 0.09 | 0.26 | 11.10 | 2.35 | 1.14 | 151 |
| 4-Methyl | 0.170 | 0.03 | 0.30 | 0.70 | 3.33 | 1.23 | 0.45 | 147 |
| 4-Methoxy | 0.268 | 0.11 | 0.28 | 0.60 | 3.57 | 1.23 | 0.53 | 147 |
| 2-Methoxy | – | – | 0.33 | 0.66 | 3.03 | 1.13 | 0.43 | 20 |
| 4-Formyl | – | – | 0.27 | 0.50 | 3.70 | 1.20 | 0.61 | 23 |
| 4-Acetyl | 0.516 | 0.21 | 0.15 | 0.49 | 6.67 | 1.82 | 0.82 | 147 |
| 2-Isopropyl | – | – | 0.34 | 0.16 | 2.94 | 0.75 | 0.90 | 20 |
| 2,6-Diisopropyl | – | – | 0.39 | 0.13 | 2.56 | 0.79 | 0.66 | 20 |
| 2-Carboxy | – | – | 0.16 | 1.18 | 6.25 | 2.22 | 0.50 | 154 |
| 2-Carboxy (DMSO) | – | – | 0.80 | 0.41 | 1.25 | 0.54 | 0.25 | 155 |
| 2-Methoxycarbonyl | – | – | 0.27 | 0.47 | 3.70 | 1.18 | 0.63 | 154 |
| 2-Phenyl | – | – | 0.57 | 0.39 | 1.75 | 0.66 | 0.43 | 20 |
| 4-Phenylazo | – | – | 0.29 | 0.14 | 3.45 | 1.28 | 1.00 | 153 |
| 2,4,6-Tricyano | – | – | 0.18 | 0.10 | 5.55 | 1.56 | 0.82 | 76 |
| 4-(1,3-Diphenyl)-2-pyrazolyl-5 | – | – | 0.26 | 0.39 | 3.85 | 1.15 | 0.71 | 71 |
| 4,4-Bishydroxyphenyl-*o*-carboranyl | – | – | 0.56 | 2.53 | 1.78 | 0.14 | 0.57 | 159 |
| 2-Naphthyl (dioxane) | – | – | 0.49 | 0.34 | 2.04 | 0.70 | 0.54 | 158 |
| 2-Naphthyl (acetone) | – | – | 0.63 | 0.54 | 1.58 | 0.69 | 0.24 | 158 |
| 4-Cinnamoylamino | – | – | 0.62 | 0.31 | 1.61 | 0.58 | 0.48 | 90 |
| 4-Acetylamino | – | – | 0.29 | 1.23 | 2.81 | 1.75 | 0.31 | 148 |
| 3-Acetylamino | – | – | 0.63 | 4.45 | 1.59 | – | – | 148 |
| 3-Butyrylamino | – | – | 0.38 | 0.75 | 2.67 | 1.08 | 0.33 | 148 |
| 4-Methacryloylamino | – | – | 0.14 | 0.18 | 7.14 | 1.53 | 1.13 | 148 |
| 3-Methacryloylamino | – | – | 0.26 | 0.03 | 3.85 | 0.66 | 1.39 | 148 |
| 4-Nitro-2-methacryloylamino | – | – | 0.023 | 3.66 | 43.48 | 12.37 | 0.77 | 148 |
| 3-Methyltetrahydrophthalimido | – | – | 0.55 | 0.21 | 1.82 | 0.56 | 0.67 | 119 |
| 3,5-Bis(*N,N*-dimethylamino) | – | – | 0.32 | 0.28 | 3.13 | 1.03 | 0.75 | |

**Note**. The subscripts 1 and 2 in the parameters refer to the first (styrene) and the second (PMA) monomers, respectively; here and in other tables, the solvent for copolymerisation is indicated in parentheses.

**Table 2**. Parameters of copolymerisation of substituted PA with styrene.

| Substituent in PA | $r_1$ | $r_2$ | $1/r_1$ | $Q_2$ | $e_2$ | Ref. |
|---|---|---|---|---|---|---|
| – | 0.37 | 0.50 | 2.70 | 0.96 | 0.50 | 20 |
| 2,6-Dimethyl | 0.36 | 0.15 | 2.77 | 0.71 | 0.91 | 20 |
| 2,4,6-Trichloro | 0.25 | 0.29 | 42.00 | 1.09 | 0.82 | 91 |
| 2,4,6-Tribromo | 0.14 | 0.08 | 7.14 | 1.31 | 1.32 | 161 |
| Pentachloro | 0.90 | 2.11 | 1.11 | – | – | 163 |
| Pentabromo | 0.09 | 0.26 | 11.11 | 0.81 | 1.14 | 161 |
| 2,4,6-Tricyano | 0.20 | 0 | 5.00 | 1.03 | 1.18 | 76 |
| 2-Carboxy (DMF) | 0.49 | 0.61 | 2.04 | 0.85 | 0.30 | 160 |
| 2-Carboxy (DMSO) | 0.20 | 0.53 | 5.00 | 1.50 | 0.70 | 155 |
| 2-Carboxy (benzene) | 0.06 | 0.64 | 16.60 | 3.90 | 1.02 | 154 |
| 4-Cinnamoylamino | 1.08 | 0.35 | 0.43 | 0.42 | 0.19 | 90 |
| 4-Propylamino | 0.31 | 0.55 | 3.21 | 1.11 | 0.53 | 148 |
| 4-Bityrylamino | 0.83 | 2.34 | 1.20 | – | – | 148 |
| 4-Nitro-2-acryloyl-amino | 0.05 | 0.88 | 20.00 | 4.86 | 0.97 | 148 |

**Note**. The subscripts 1 and 2 in the parameters refer to the first (styrene) and the second (PA) monomer, respectively.

It was noted [165] that the presence of aromatic substituents in copolymers of MMA with phenyl (meth)acrylates increases the number of hetero- and isotactic sequences in macromolecules. As in the case of 4-phenylazophenyl methacrylate,[153] copolymers of MMA with 2-methacryloyloxybenzoic acid are enriched in the units of the latter ($r_1 = 0.74$, $r_2 = 1.22$). The rate of copolymerisation decreases with the increase in the content of the second component.[166] For 4-acetylphenyl methacrylate, the influence of the penultimate unit [167] was observed, which is due to strong steric hindrances and high polarisability of the aromatic oxo group.

Constants of copolymerisation of a number of substituted phenyl (meth)acrylates with acrylonitrile are presented in Table 3; their reactivity towards the acrylonitrile radical varies depending on the nature of the substituent group and its position in the ring.[168] The trend for alternation is not strong, the values of $r_1$ fit well the dependence

$$\log\frac{1}{r_1} = -0.98(\sigma + 1.66\Delta\sigma),$$

where $\sigma$ is the Hammett polar constant, $\Delta\sigma$ is the difference between the Brown and Hammett constants for substituents. Accumulation of substituents in the ring of phenyl acrylates decreases even more strongly the trend for alternation, as is seen in the example of 2,4,6-tribromophenyl acrylate.[169] However, the

**Table 3**. Parameters of copolymerisation of substituted phenyl (meth)-acrylates with acrylonitrile.[a]

| Substituent in phenyl meth-acrylates | $r_1$ | $r_2$ | $1/r_1$ | $Q_2$ | $e_2$ | Ref. |
|---|---|---|---|---|---|---|
| Acrylates | | | | | | |
| – | 0.46 | 0.36 | 2.17 | 0.36 | 1.4 | 168 |
| 4-Chloro | 0.33 | 0.94 | 3.03 | 0.37 | −0.12 | 168 |
| 3-Chloro | 1.26 | 0.86 | 0.79 | – | – | 168 |
| 2-Chloro | 1.12 | 1.16 | 0.89 | – | – | 168 |
| 4-Bromo | 0.82 | 1.02 | 1.22 | 0.07 | −0.77 | 168 |
| 4-Methyl | 0.73 | 0.80 | 1.37 | 0.11 | −0.47 | 168 |
| 2,4,6-Tribromo | 0.96 | 2.05 | 1.04 | – | – | 169 |
| Methacrylates | | | | | | |
| 2,4,6-Tribromo | 0.20 | 0.98 | 5.0 | 0.78 | 0.08 | 170 |
| Pentabromo | 0.28 | 0.12 | 3.57 | 1.09 | 0.64 | 171 |
| 2-Naphthyl (chloroform) | 0.02 | 0.96 | 50.0 | 18.30 | 0.79 | 172 |
| 2-Naphthyl (benzene) | 0.04 | 0.84 | 25.0 | 46.40 | 0.98 | 172 |
| 2-Naphthyl (acetone) | 0.02 | 0.52 | 50.0 | 21.80 | 0.94 | 172 |
| 2-Naphthyl (acetonitrile) | 0.03 | 0.51 | 33.3 | 53.00 | 1.09 | 172 |

**Note**. The subscripts 1 and 2 in the parameters refer to the first (acrylonitrile) and the second (PMA) monomer, respectively. [a] For acrylonitrile $e_1 = 1.2$, $Q_1 = 0.6$.

trend for alternation was observed for 2,4,6-tribromophenyl and pentabromophenyl methacrylates.[170]

Copolymerisation of 2-NMA with acrylonitrile in chloroform or benzene proceeds with the formation of donor–acceptor complexes between the monomers; therefore, the values of $r_1$ and $r_2$ differ in different solvents.[171,172] Complexation was also found to occur in the copolymerisation of 2-NMA with monomethylitaconate;[173,174] thus the alternation of monomers of this pair is different in different solvents: in chloroform, $r_1 = 2.44 \pm 0.19$, $r_2 = 1.20 \pm 0.28$; in dioxane, $r_1 = 0.49 \pm 0.04$, $r_2 = 0.97 \pm 0.29$; in acetone, $r_1 = 0.15 \pm 0.01$, $r_2 = 0.28 \pm 0.03$ and in acetonitrile, $r_1 = 0.10 \pm 0.01$, $r_2 = 0.35 \pm 0.14$. Such changes in the copolymerisation constants reflect interactions between the monomer molecules and the corresponding solvent.

The constants of copolymerisation of PMA with methacrylic acid (MAA) are as follows: $r_1 = 0.40$ and $r_2 = 0.52$ (benzene), $r_1 = 0.21$ and $r_2 = 1.52$ (DMF/benzene), which points to a lower reactivity of MAA and higher reactivity of PMA in the presence of DMF, which appears to act as a complexation agent.[175] Copolymers of pentachlorophenyl acrylate with acrylic acid (AA) are enriched in the AA units.[163] In 2-butanone, PMA and glycidyl methacrylate give a copolymer enriched in PMA ($r_1 = 0.84 \pm 0.51$, $r_2 = 1.57 \pm 0.56$).[176] Optically active copolymers were obtained upon copolymerisation of phenyl, benzyl and 1-naphthyl methacrylates with maleic anhydride in the presence of β-cyclodextrin.[177] Copolymerisation of *N*-vinylpyrrolidone with 2-carboxyphenyl acrylate[160] and 2,4,5-trichlorophenyl acrylate[178] was also studied; in the latter case, copolymers with a high degree of alternation were obtained.

In copolymerisation of *p*- and *m*-phenylene diacrylates with styrene, a copolymer with acrylate pendent groups is formed in the initial stages; these groups then react with styrene to form a cross-linked copolymer, which precipitates from the reaction mixture in the form of a gel. *o*-Phenylene diacrylate forms a non-cross-linked ladder copolymer with styrene due to cyclopolymerisation. The smallest values of the polarity criterion *e* were obtained for the *ortho*-isomer.[6] The values of the copolymerisation constants for isomeric phenylene diacrylates (PDA) are presented in Table 4.

**Table 4**. The values of copolymerisation constants for phenylene diacrylates (FDA) and styrene.

| FDA isomer | Solvent | $r_1$ | $r_2$ | $Q_2$ | $e_2$ |
|---|---|---|---|---|---|
| *ortho*- | THF | $0.55 \pm 0.15$ | $0.48 \pm 0.19$ | 0.74 | 0.37 |
| | benzene | $0.42 \pm 0.28$ | $0.45 \pm 0.19$ | 0.83 | 0.49 |
| *meta*- | THF | $0.33 \pm 0.06$ | $0.17 \pm 0.02$ | 0.78 | 0.90 |
| | benzene | $0.67 \pm 0.11$ | $0.15 \pm 0.04$ | 0.46 | 0.72 |
| *para*- | THF | $0.35 \pm 0.06$ | $0.21 \pm 0.07$ | 0.79 | 0.82 |
| | benzene | $0.30 \pm 0.08$ | $0.35 \pm 0.09$ | 1.00 | 0.70 |

**Note**. The subscripts 1 and 2 in the parameters refer to the first (styrene) and the second (FDA) monomer, respectively.

In radical copolymerisation of *p*-chlorophenyl methacrylate with ethylene glycol, 2,2-di(4-hydroxydiphenyl)propane and hydroquinone dimethacrylates,[179,180] the most reactive is ethylene glycol dimethacrylate as the second monomer, which is devoid of the mesomeric effect. The copolymer produced both upon catalytic and photochemical initiation is enriched in this compound ($r_1 = 0.29 \pm 0.03$ and $r_2 = 1.31 \pm 0.06$).

Methacrylamide[181] and peroxide monomers can be used for subsequent cross-linking in copolymerisation with PMA. The constants of copolymerisation of PMA with *tert*-butyl *p*-vinylperbenzoate are as follows: $r_1 = 1.35$, $r_2 = 0.32$.[182]

Copolymerisation of aryl methacrylates in donor–acceptor complexes bears a special character. For example, complexes of monomers and polymers of carbazolyl methacrylates with dinitrophenyl-containing monomers and polymers were obtained.[183] Charge-transfer complexes (CTC) are formed in copolymerisation of the donor monomers, *viz*., *N*-(2-hydroxyethyl)carbazolyl acrylate (**1**) and -methacrylate (**2**) with the acceptor monomers, *viz*., 2,4-dinitrophenyl acrylate (**3**) and methacrylate (**4**).[114,183,184] The extent of intramolecular charge transfer in copolymers (according to the chemical shift values of aromatic protons in the $^1$H NMR spectra of **3** and **4**) increases as the content of **4** in the alternating diads with **1** is increased and is larger in the **2**–**3** copolymer than in the **1**–**3** copolymer. In copolymers containing only methacrylate units, no intramolecular CTC are revealed, the most stable CTC are formed in copolymers having only acrylate units. In copolymerisation of **1** with **4**, the intermonomeric CTC are not added as a whole,[184] and the relative reactivity is determined solely by the sequence of distribution of units rather than by the configuration factors. With the increase in the temperature, the CTC present in the copolymer disintegrate due to the higher segmental mobility. Intramolecular CTC are also formed in the copolymerisation of picryl (meth)acrylate (incapable of homopolymerisation) with *N*-(2-hydroxyethyl)carbazolyl (meth)acrylate. The copolymerisation constants indicate that the most stable CTC are formed in dioxane.[185–187] Photoconductivity of poly(*N*-vinylcarbazole) increases when electron-acceptor comonomers forming CTC are used, *e.g*., isomeric 2,2-dicyanovinylphenyl (meth)acrylates $(NC)_2C=CHC_6H_4OC(O)CR=CH_2$ (see Ref. 188). Mixing of poly(*N*-vinylcarbazole) with the same amount of the low-molecular-weight acceptor leads to a less pronounced effect.

Directed intramolecular transfer of electronic triplet excitations was studied in a copolymer of 1-naphthyl acrylate (1-NA) and 4-acetylphenyl methacrylate.[189] The copolymer contains two π-electronic systems in which unidirectional transfer of electronic excitation is brought about. Upon selective excitation of the singlet level of 4-acetylphenyl methacrylate units, phosphorescence of only 1-NA units is observed. Such a molecular structure can function as a specific exciton gate.[190–192]

In a ternary styrene–acrylonitrile–2,4,6-tribromophenyl (meth)acrylate system, the third component decreases the molecular mass and thermal stability of the terpolymers formed.[193–195] In copolymerisation of phenyl, 4-butylphenyl, 4-nitrophenyl and

1-naphthyl acrylates with $SO_2$ and also in three-component copolymerisation of these monomers with hept-1-ene (see Ref. 196), the maximum content of sulfonyl monomeric units in copolymers ranges from 13% to 24% depending on the inductive steric effects. The composition of terpolymers varies within a wide range depending on the molar ratio of reagents and conversion. It is also possible to copolymerise PMA one with another.[197] Changes in the enthalpy and parameters of PMA copolymerisation with 2-methylphenyl and 2-ethylphenyl methacrylates were studied in the temperature range 80–100 °C.

The problems of the relationship between the structure of polymeric carriers based on cross-linked PA polymers and their copolymers with styrene and the reactivity of such carriers were reviewed.[198]

## V. Structure and properties of poly[aryl (meth)acrylates]

Esterification of atactic, syndiotactic and isotactic polyacrylic acids with phenols yields only atactic polymers. This points to the spatial isomerisation of the tertiary carbon atom in the course of esterification and the impossibility of obtaining stereoregular poly(aryl methacrylates) by polymer-analogous transformations.

Radical polymerisation of PMA yields an atactic polymer which contains nonetheless more syndiotactic structural blocks than the structurally similar poly(benzyl methacrylate) and poly(2-phenylethyl methacrylate).[199] This is related to the higher polarity ($\sigma = 0.6$) of the phenyl groups than that of the alkyl groups ($\sigma$ varies from $-0.3$ to 0.215) rather than to their higher rigidity or small volume. Jimmy *et al.*[200] studied the influence of the side groups and the size of the polymer coil of poly(benzyl methacrylate), poly(triphenylmethyl methacrylate) and poly(diphenylmethyl methacrylate). The overall activation energy of radical polymerisation of PMA is equal to 69.0 kJ mol$^{-1}$, which is somewhat lower than that for poly(methyl methacrylate) (PMMA).[201] In polymerisation with AIBN in the temperature range 30–100 °C, a Bernoulli distribution of stereochemical structures in the PPMA chains is observed. The content of iso- and syndiotactic triads in them decreases as the temperature increases, which is characteristic of α,α-disubstituted monomers. The triads are disposed in the chain in an isolated manner. The phenyl radical is oriented with its maximum polarisability axis along the direction of the main *trans*-chain.[202] In poly(aryl methacrylates), the content of isotactic, atactic and syndiotactic triads is 15%, 40% and 45%, respectively.[203] The use of high-frequency NMR spectroscopy (500 MHz for $^1$H and 125 MHz for $^{13}$C) allowed calculation of isotactic parameters for poly(phenyl acrylate) (PPA) ($P_m = 0.44$) and poly(4-fluorophenyl acrylate) ($P_m = 0.48$)[204] obtained by radical polymerisation. Isotactic PPA can be obtained by anionic polymerisation in the presence of butyllithium.[140] Kempf and Harwood[205] have shown that PPMA of a predetermined configuration can nonetheless be obtained from polymethacrylic acid if certain conditions are met.

Studies of the influence of solvents on the microstructure of poly(1-naphthyl methacrylate) and poly(2-naphthyl methacrylate) (1-PNMA and 2-PNMA, respectively) in comparison with poly[cumylphenyl meth)acrylate] and PMMA have shown[206–208] that the polymerisation of 2-NMA in methanol, acetonitrile and nitromethane occurs heterogeneously. Even in the presence of non-polar solvents, the percentage of isotactic triads in 1-PNMA and 2-PNMA is higher and the percentage of syndiotactic triads is lower than in PMMA. Syndiotacticity of 2-PNMA is higher than that of 1-PNMA. In solvents with higher dielectric constants, PNMA with a still higher content of isotactic triads is obtained. Poly(1-naphthyl methacrylate) possesses a higher heterotacticity than 2-PNMA. In copolymerisation of 2-NMA with MMA ($r_1 = 1.93 \pm 0.16$, $r_2 = 0.33 \pm 0.08$), syndiotactic addition proved to be preferential.[209] The behaviour of PA is analogous.[210] However, PPMA, poly(*p*-cresyl methacrylate), 2- and 4-methoxyphenyl methacrylates, obtained by polymerisation in the presence of butyllithium at low temperatures in toluene, have an isotactic structure with 90% of isotriads,[211] while syndiotactic polymers are formed in THF.[212]

The temperature characteristics of poly[aryl (meth)acrylates] are determined by their structural peculiarities. As was indicated above,[4] the thermostability is determined by the character of the substitution: in the *para*-substituted poly[aryl (meth)acrylates] the glass transition temperature ($T_g$) is always lower than in the *ortho*-substituted ones. This is explained by the shielding effect of *ortho*-substituents on the ester bond. $T_g$ increases with the increase in the size of substituents and their polarity. Thus PPA, poly(*o*-tolyl acrylate) and its *para*-isomer have $T_g$ values of 56.5, 51.5 and 24.5 °C, respectively. For 1-PNMA and 2-PNMA, $T_g$ values are 135 and 119 °C, respectively.[214] The relationship between $T_g$ and molecular mass ($M$) of poly(*o*-alkylphenyl methacrylates) is non-linear and may be described by the following equation:[215]

$$T_g = T_g(0) + k\ln P,$$

where $T_g(0)$ is the temperature characteristic of the monomeric unit and $P$ is the degree of polymerisation. For the infinitely large PPMA molecules, $T_g = 118$ °C, while for poly(2,6-dimethylphenyl methacrylate) (PMPMA) $T_g = 177$ °C. In copolymers of phenyl, 2-chlorophenyl and 4-chlorophenyl acrylates with MMA, $T_g$ decreases with the increase in the concentration of MMA.[216] In this case, the concentration dependence of $T_g$ obeys Johnson's equation, which considers the contribution of diads in the polymer chain to the glass transition effect. A comparative calorimetric study of substituted PPA[217] and poly(vinyl benzoates) made it possible to establish that the dependence of specific heat capacity ($C_p$) on temperature in the range of glassy state is described by the equation

$$C_p = A + BT + CT^2 + DT^2.$$

The increase in $C_p$ in the glassy state was observed for all substituted polymers with increase in the volume of substituents. For a number of alkyl- and alkoxy-substituted PPA the values of $T_g$ were found and the heat capacity jumps in the glass transition region and coefficients $A$, $B$, $C$ and $D$ in the proposed equation were determined.

Thermal stability of poly(aryl methacrylates) was studied by the TGA method;[218] the curves for poly(tolyl methacrylates) (PTMA) and poly(benzyl methacrylate) are S-shaped and similar to the curves for PMMA. For PPMA, the process was characterised by several ranges of decomposition. *ortho*-PTMA proved to be the most stable isomer. Effective activation energies of thermal destruction for the polymers studied vary from 81 to 159 kJ mol$^{-1}$ (210 kJ mol$^{-1}$ for PMMA).

Thermal destruction of poly(2-methacryloyloxybenzoic acid)[219] occurs in three steps in temperature ranges of 140–220, 250–330 and 350–450 °C with mass losses (according to TGA data) of 33%–35%, 30% and 30%, respectively, which corresponds to the stoichiometric content of salicylic acid in the polymer in the first two stages. The effective activation energy in the first stage is 79 kJ mol$^{-1}$. Upon destruction, fragments of the glutaric anhydride type accumulate first in the polymer (up to 330 °C); after this, the macrochains undergo disintegration.

Copolymers of PMA with MMA are more thermostable than the homopolymers;[220] monomers are the main degradation products. At a low content of PMA, oligomers containing anhydride groups are also formed; with the increase in the PMA content the ability to form anhydrides drops. In contrast to homopolymers, the destruction of copolymers is characterised by relatively short kinetic chains of depolymerisation and the cleavage of the principal bonds in the macrochain. Among the copolymers of acrylonitrile with 2,3-dibromopropyl, pentabromophenyl and 2,4,6-tribromophenyl acrylates, the highest thermostability was observed for copolymers with the latter.[221]

In studies of poly[aryl (meth)acrylates], a prominent place is occupied by the investigations of properties of their dilute solutions. By measuring the swelling degree, solubility para-

meters ($\delta$) were determined and their dependence on the character of forces of interaction of polymer with solvent was confirmed.[222] Chloroform, tetrachloroethane, chlorobenzene and ethyl acetate are the best solvents for poly(aryl methacrylates). The values of $\delta$ for poly(alkylphenyl methacrylates) were determined in 20 solvents of different nature, considerably differing in their polarities (the contribution of $\delta_p$) and ability to form hydrogen bonds (the contribution of $\delta_H$), and in the widest possible range of the chain flexibility parameter $\sigma$. The magnitude of $\delta_H$ decreases slightly with the enhancement of the 'paraffinic character' of the solvent.[223] The influence of alkyl residues is weakly manifested and the values of $\delta_H$ found differ somewhat from the calculated ones. Investigation of properties of dilute solutions by the osmometry and viscosimetry methods showed that the *ortho*-substituents in the benzene ring of the side chain increase appreciably the rigidity of the polymer. For PMPMA, the solubility parameter in toluene is equal to 9.6 $cal^{-1/2}$ $cm^{3/2}$ (see Ref. 224). The power index $\alpha$ in the dependence

$$[\eta] \approx M_w^{\alpha},$$

where $[\eta]$ is the specific viscosity, increases as the thermodynamic quality of the solvent is enhanced ($\alpha$ is equal to 0.5 in toluene, 0.59 in THF and 0.69 in chlorobenzene). It was established that $< r_0^2 >^{1/2}$ (characteristic chain ratio) and $T_g$ increase upon transition from PPMA to PMPMA. For poly(2,6-diisopropylphenyl methacrylate), the solubility parameter in toluene is also equal to 9.6 $cal^{-1/2}$ $cm^{3/2}$ (see Ref. 225), while the Mark–Hauwink equation ($[\eta] = KM_n^{\alpha}$) (25 °C) has the following form for THF

$$[\eta] = 1.02 \times 10^{-4} M_n^{0.71},$$

for toluene

$$[\eta] = 1.22 \times 10^{-4} M_n^{0.69},$$

and the THF : water mixture (90.9 : 9.1)

$$[\eta] = 8.51 \times 10^{-4} M_n^{0.50},$$

for the ratio of the mean squared distance between the ends of the polymer coil and the molecular mass of the polymer (see Ref. 225)

$$< r_0^2 > = 0.677 M^{1/2}.$$

For *p*-AAPMA [226] in DMF at 25 °C

$$[\eta] = 1.40 \times 10^{-3} M_n^{0.85}.$$

Investigation of the influence of temperature on the thermodynamic properties and undisturbed dimensions of PPMA macromolecules in isobutyl methyl ketone showed [227] that for all fractions an anomalous dependence of $[\eta]$ on temperature takes place at 20–35 °C, which becomes more pronounced with the increase in the molecular mass. The value of the coefficient $K$ in the Mark–Hauwink equation is maximum at 25 °C, which implies changes in the character of hydrodynamic interactions inside the macromolecular coil, whereas the value of $\alpha$ is a minimum at the same temperature, which means drastic deterioration of the solvent quality. These phenomena point to a conformational transition associated with the increased chain flexibility resulting from the changes in specific interactions between the phenyl groups. The side chains in PMMA, poly(isobutyl acrylate) and poly(cyclohexyl methacrylate) have a strong influence on the temperature of the conformational transition and changes in the undisturbed dimensions of the chains, which is accompanied by the appearance of a jump in the temperature dependence of viscosity, refraction index and partial specific volume of polymers.[228] Gargallo *et al.*[229] analysed the influence of the size and the nature of the side groups in poly(alkylphenyl methacrylates) on the magnitude of partial volumes. The intramolecular character of the conformational transition is confirmed in the example of poly(4-*tert*-octylphenyl methacrylate).[230] It was established for PPMA solutions that the conformational transition occurs owing to the changes in specific near-order interactions between the phenyl rings in the pendent groups of the polymer studied.[231] Comparison of magnitudes and orientation of dipole moments related to the pendent groups of poly(chlorophenyl acrylates) revealed their strong dependence on the position of the substituent in the benzene ring.[232] The example of PPMA with the phenyl benzoate side groups showed [233] that the influence of thermodynamic quality of the solvent on the dipole moment is characteristic of polymers with highly rigid polymeric chains and strong intramolecular interactions of the side groups.

For poly(2-biphenylyl methacrylate), rather insignificant (5%–18%) variation of $[\eta]$ in different organic solvents was observed,[234] whereas in other poly(aryl methacrylates) the variation of $[\eta]$ is 21%–61%, which is due to the presence of the bulky *o*-biphenylyl group localised close to the basic chain. In poly(4-biphenylyl methacrylate),[235] the undisturbed dimensions of the chain calculated by the Stockmayer–Fixman method with consideration of the dependence of $[\eta]$ on $M$ proved to be three times as large as those in the case of free rotation in the main valent chain, which is indicative of an appreciable inhibition of rotation in poly(aryl methacrylates). For this polymer, the temperature coefficient of undisturbed dimensions of the chain was determined ($2.3 \times 10^{-3}$ at 13–40 °C and $1.2 \times 10^{-3}$ at 40–60 °C);[236] similar calculations were performed for the *ortho*-isomer and for poly(2,4,5-trichlorophenyl methacrylate).[237] In the case of poly(2-biphenylyl methacrylate), the value of the chain flexibility parameter $\sigma$ (2.8) was larger than that for poly(4-biphenylyl methacrylate) ($\sigma = 2.7$), which points to a larger flexibility of the former due to a close position of the *o*-diphenylyl groups to the basic chain.[238] Studies of the mobility in poly(2-biphenylyl methacrylate) by the DSC method pointed to the occurrence of four relaxation processes with the temperature increase, *viz.*, $\gamma$, $\beta$, $\alpha$ and $\rho$. The processes of $\alpha$- and $\beta$-relaxation are related to vitrification and subvitrification, respectively.[239]

For PPA, it was found that the values of temperature coefficients of the undisturbed dimensions range from $-3.4 \times 10^{-3}$ to $-4.7 \times 10^{-3}$, the upper critical temperature of dissolution $\Theta$ in ethyl lactate is 14 °C and the values of $[\eta]$ increase with the temperature increase within the range 7–77 °C.[240] As for PMMA, the constants of the Mark–Hauwink equation for PPMA fit the van Krevelen equation.[241] The use of the light scattering method in ethyl lactate for PPA allowed determination of values of $M_w$, second virial coefficients $A_2$, mean squared radii of inertia $< S^2 >$ and coefficients of swelling at different temperatures.[242] This method was also applied to study PNMA solutions [243, 244] in comparison with polystyrene. The ratios of the threshold concentration $c_0$ in light scattering measurement to the second virial coefficient $A_2$ for these polymers were the same and equal (in non-polar solvents) to 0.93. For dilute solutions of homopolymers with the main methacrylate chain and methoxybiphenyl mesogenic groups and their copolymers,[245] the constants in the Mark–Hauwink equation, parameters of Flory–Huggins interaction and the mean squared distances between the chain ends $< r^2 >$ were determined. The latter parameter is greater than that in PMMA, which indicates an appreciable increase in the rigidity of the polymethacrylate chain upon introduction of the mesogenic side groups. As regards PMA copolymers [246] and substituted PMA,[247] for them, too, the values of $K$, $\alpha$ and $\Theta$ were found in certain solvents, and the undisturbed dimensions of the polymer coils and parameters of the chain rigidity were calculated.

The data on electrical properties of poly(aryl (meth)acrylates) are scanty. The spectra of dielectric losses at different temperatures were studied for specimens of PPMA and polymers of *o*-, *m*- and *p*-PTMA [248] and for polymethoxy-substituted PMA.[249] Three relaxation processes were found to occur. The high-temperature process ($\alpha$-relaxation) occurs in the glass transition range and is related to the micro-Brownian mobility in the basic chain of the polymer. The maximum temperature of this process increases in the following order: *m*-PTMA < *o*-PTMA < PPMA < *p*-PTMA; the crystallinity of polymers increases in the same order. In the middle-temperature range, $\beta$-relaxation is observed due to the micro-Brownian mobility of the side groups, which is particularly

manifested in *o*-PTMA. Increased activation energies of this process were observed for specimens of higher crystallinity (PPMA and *p*-PTMA). The low-temperature γ-relaxation is associated with the motion of the tolyl and methoxyphenyl pendent groups. Investigation of the dielectric relaxation of poly(phenyl and chlorophenyl acrylates) revealed that the intensity of the β-process in PPA and poly(4-chlorophenyl acrylate) is lower than in poly(2-chlorophenyl acrylate) and poly(3-chlorophenyl acrylate); in the last two polymers the intensity of β-process is higher than that of α-process. α-Relaxation is determined by the free volume and is well described by the binding model;[250] in polymers the time of dielectric relaxation is always shorter than the time of mechanical relaxation.[251]

Noticeable changes in the electrical characteristics of polyethylene in strong fields (electrical strength and $I-V$ characteristics in the pre-breakdown voltage range) are observed when small amounts (1% – 2%) of comonomers, such as pentabromophenyl and 2,4,6-tribromophenyl methacrylates, were introduced.[252] The maximum value of breakdown voltage is observed at the content of the former additive of 0.1% – 0.2%, the doping action is produced by units of the above-mentioned PMA. Such an effect is not exerted by benzyl methacrylate.

In a magnetic field, a noticeable effect of the increase in spontaneous orientation of PPMA may be observed only in mesomorphic polymers, in particular in those with the phenyl benzoate pendent groups.[253]

Poly[aryl (meth)acrylates] are very transparent (transmission coefficient > 90%) and possess good mechanical properties.[254] Therefore, copolymers containing up to 99% of these monomers are used as materials for manufacturing lenses.[255] Some of them, in particular 1- and 2-NMA, determine the high refraction index of copolymers.[256]

Some aryl (meth)acrylates and their polymers may exist in the liquid-crystalline state with characteristic anisotropy of optical properties.[31, 257] Their polymeric nature is manifested in considerable enhancement of thermal stability of the mesophase, its temperature range is restricted by the glass-transition and clarification temperatures and is determined to a considerable extent by the nature of the basic chain and its flexibility.[258] In such polymers, structures of various mesophases and different variants of the packing of mesogenic groups can be realised. Most polymers can form lamellar structures of the smectic type. Nematic structures arise in polymers with shorter substituents and flexible hinges. In particular, all polymers with the lateral mesogenic groups possess nematic mesomorphism.[259] Clarification temperatures of polymers with the same mesogenic groups but different chemical composition of the basic chain coincide, whereas in these cases the $T_g$ values decrease with the increase in flexibility of the basic chain or the length of the terminal fragments of the mesogenic pendent groups.

For all the polymers having one mesogenic side unit per elementary unit of the chain, it was established that the global anisotropy is independent of steric inhibition of the α-methyl groups. A decrease in temperature results in a basic polymer chain extension normally to its mesogenic units, which thus acquires an elongated shape.[260] According to the results of X-ray diffraction analysis, the macromolecules of polymers of phenyl and 4-alkoxyphenyl esters of acryloyloxybenzoates,[261] which form anisotropic systems on cooling of melts or concentrated solutions, represent cylinders 8 – 10 nm long and 2.5 – 3.9 nm in diameter formed by aperiodic helices.

Acrylic polymers that contain mesogenic phenyl benzoate groups with short alkyl substituents form only nematic mesophases.[262, 263] In studies of the comb-like liquid-crystalline polymers, which differ in the nature of the basic chain (acrylate or methacrylate) but contain identical phenyl benzoate groups,[264, 265] the low- and high-temperature smectic phases of polyacrylate are referred to the smectic types B and A, respectively. For polymethacrylates, the following scheme of polymorphic transformation was proposed: smectic F → smectic C → smectic A → isotropic liquid. Investigation of conformational changes in poly(methacryloyloxyphenyl 4-n-alkoxybenzoates)[266] in the temperature range including the glassy, liquid-crystalline and isotropic states revealed that the conformational changes are observed in the glassy state 40 – 80 °C before the transition to the liquid-crystalline state depending on the alkyl chain length and that they are accompanied by the homeotropic orientation in the polymeric films. Poly(biphenylyl acrylate) prepared by the reaction of polyacryloyl chloride with 4-hydroxybiphenyl forms a smectic mesophase A at 144 °C, which is totally destroyed at 250 °C. The mesophase – isotropic transition is nearly fully reproduced in repeated cycles of heating.[267] Poly(4-acryloyloxyazobenzene) is in turn in the mesomorphic state at 100 – 240 °C. Polyacrylates and polymethacrylates that contain the cyano-substituted aromatic azomethine and cyanobiphenyl mesogenic groups form liquid-crystalline phases of the nematic type and also of the smectic type A and C.[268, 269] In polymethacrylate with the biphenyl fragments as mesogens in the side chains, a poorly ordered smectic phase exists at 136 – 157 °C and above these temperature, the isotropic phase.[270]

Thus, among poly[aryl (meth)acrylates] it is possible to find polymers that have mesophases in different temperature ranges. Such polymers are capable of reflecting selectively light in the IR, UV and visible parts of the spectrum, manifesting transitions induced by electric and magnetic fields, and in some cases they even possess ferroelectrical properties.[258] Owing to such electrical and other effects, the field of application of these polymers in modern technology is extended.

## VI. Chemical and photochemical properties of poly[aryl (meth)acrylates] and their copolymers

Chemical properties of poly[aryl (meth)acrylates] and their monomers are determined primarily by the presence of the ester group, the aromatic ring and its substituents. The rate of hydrolysis of the pendent groups in PPMA at different temperatures in aqueous DMSO is described by three different constants corresponding to the hydrolysis of the ester groups of the polymer with the adjacent 0, 1 and 2 hydrolysed ester groups.[271] The activation energies that correspond to these constants are equal to 40.6, 58.2 and 74.0 kJ $mol^{-1}$, respectively. Alkaline hydrolysis of PPMA with *p*-Cl, *p*-OMe, *p*-Me and *m*-$NO_2$ substituents in the aromatic ring is of the pseudo-first order;[272] the first two constants increase with the higher KOH concentration, whereas the third constant remains virtually unchanged. The values of these constants correlate well with the values of the Hammett constants for substituents.

Enzymatic hydrolysis of the side ester groups in copolymers of 4-nitrophenyl methacrylate with acrylamide[273] in the presence of lipase did not take place, whereas esterase and α-chymotrypsin acted very slowly. The rate of alkaline hydrolysis increased with the higher content of acrylamide in the copolymer, which was due to the influence of acrylamide units on the reactivity of ester groups in the 4-nitrophenyl fragments. The action of α-chymotrypsin on 2-biphenylyl methacrylate (BPMA) and its copolymers induced hydrolytic liberation of hydroxybiphenyl; the Michaelis constant for the copolymers was lower than for the homopolymer and decreased in the following series of comonomers: methacryloylglycine > vinyl acetate > methacryloylalanine > styrene.[274] The catalytic effect of α-chymotrypsin was weaker in the case of poly(2-biphenylyl acrylate).[275] The possibility of modifying polymers and copolymers of 2,4,5-trichlorophenyl acrylate[276] and 4-nitrophenyl methacrylate[277 – 279] through their aminolysis has been demonstrated.

Optimisation of the reaction conditions makes it possible to introduce various substituents, for example, perfluoroalkyl groups,[280] into the phenyl groups of PPMA. Reactive functional groups can be subjected to further transformations[281] and be used for the chelate formation.[282, 283]

Chemical transformations of poly[aryl (meth)acrylates] under the action of different types of radiation are rather diverse. Investigation of the photobehaviour of phenyl-containing methacrylate polymers showed [284] that the lifetime of the singlet state in polymers is shorter than in model small molecules, which is related to the higher sensitivity of this parameter to steric hindrances. A high yield of long-living triplet states was observed in the presence of naphthalene rings.[285] The acetyl groups favour quenching of the triplet. 2,4-Diacetyl-1-naphthyl methacrylate units induce quenching even at their content $\sim 1$ mol. % with a quantum yield of 0.4.[286] In poly(2-naphthyl methacrylate), insignificant migration of the singlet energy occurs.[287] Because of a large difference in the energies of the excited singlet and triplet states, the singlet energy transfer to the ketone traps in a copolymer of 2-NMA with arylvinyl aromatic ketones and the triplet energy is transferred from these traps again to the naphthalene chromophores. The fluorescence (FL) spectrum of 2-PNMA [288] is characterised by the presence of two bands which are attributed to monomeric (340 nm) and excimeric (400 nm) luminescence. The luminescence spectrum of copolymers strongly depends on the amount of a comonomer. In copolymers with MMA, the correlation between the excimeric and monomeric fluorescences is determined basically by the molar fraction of naphthyl methacrylate units.[289] The ratio of intensities of excimeric and monomeric fluorescences is taken as the compatibility parameter of copolymers of naphthyl and anthryl methacrylates with MMA and n-butyl methacrylate (BMA).[290,291] In copolymers of PMA,[292] the band of excimeric FL is at 355 nm. The FL spectra of copolymers of vinyl 3-(1- and 2-naphthyl)acrylate with vinyl hexanoate and vinyl acetate were analysed in order to reveal the monomeric and excimeric FL of the naphthalene groups at 340 and 390 nm, respectively. It was shown [293] that the excimer is formed by two naphthalene groups bound to cyclobutane in the 1,2 or 1,3 positions *cis*-arranged relative to the cyclobutane ring. The curves of FL decay are well described by three exponents attributed to three fluorescence centres: excimers, monomeric chromophores capable of transition to the excimer form and isolated monomeric chromophores incapable of excimer formation.

Copolymers of 2-[(2,4,6-tricyanophenyl)thio]ethyl methacrylate with 3,5-bis(*N,N*-dimethylamino)phenyl methacrylate which are obtained in bulk phase and form rigid films possess photoconductivity. The photocurrent in such films was observed upon illumination with light with wavelengths of 200–700 nm.[294]

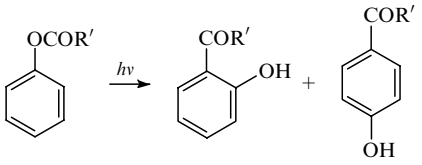
Photodestruction of PPMA in vacuum and in air occurs with the random scission of macrochains and is intensified under shortwave UV irradition.[295] The presence of chlorine atoms in the phenyl radical accelerates photodestruction. For 1-PNMA and its copolymers with BMA it was established that in contrast to thermodestruction leading to depolymerisation, the photo- and radiation destructions involve processes of the basic chain scission, the photodestruction rate depending on the intramolecular excimer formation.[296] For this reason, the quantum yield of the chain scission decreases monotonically (down to 0.015) with the increase in the content of 1-NMA units. Excimers are not formed for the BMA–NMA–BMA sequences.[297,298] Upon irradiation with electrons (20 keV) and UV light, the perfluoroalkylated PPA is cross-linked in contrast to the non-perfluoroalkylated one which is destroyed under these conditions.[299]

In the presence of oxygen, photooxidation of poly[aryl (meth)acrylates] occurs with the formation of carbonyl groups. Investigation of the photooxidation of 2-NMA copolymers with styrene, MMA and acrylonitrile revealed [300] that where the content of 2-NMA was 7 mass %, the concentration of carbonyl groups was considerably higher than in polystyrene (0% of NMA) or in copolymers with 13% or 26% of 2-NMA. The number-average molecular mass is also most strongly decreased in copolymers with 7% of 2-NMA.

On the whole, poly[phenyl (meth)acrylates] are regarded as radiation-resistant materials;[301] however, their resistance is sharply decreased upon introduction of halogens into the aromatic rings. Upon irradiation of poly(4-chlorophenyl methacrylate) with ionic beams,[302,303] the primary process is the elimination of the chlorine atom with the formation of reactive centres in the basic chain under the action of atomic chlorine. Recombination of these two types of polymeric radicals leads to the cross-linking of the polymer. The radiation yield of the basic chain scission in the radiolysis of MMA copolymers with trichloro- and tetrabromophenyl methacrylates [304] is strongly enhanced by small amounts of the latter, which is related to the important role of the processes of dissociative electron capture. The yield drops dramatically with the increase in the concentration of chlorine-containing monomer to 17% when the processes of cross-linking become noticeable. An analogous behaviour is displayed by halogen-substituted PPMA upon irradiation with a beam of electrons.[305]

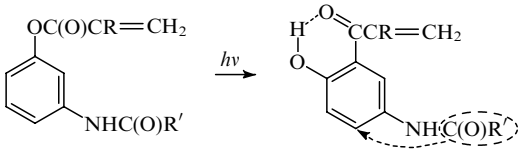
Homopolymers of 4-acryloyloxyazobenzoate and 4-methacryloyloxyazobenzene copolymers with methyl acrylate [306] and MMA,[307] respectively, possess photochromic properties. The azo group in their units undergoes *trans–cis*-isomerisation under UV irradiation ($\lambda = 370$ nm). The increase in absorption is observed at $\lambda < 280$ nm and $\lambda > 400$ nm. Photoisomerisation occurs as the first-order reaction and is reversible, the rate constant for this reaction is independent of temperature. The reverse dark reaction (thermal *cis–trans*-isomerisation) is also of the first order. In homopolymers, the kinetics of photoisomerisation is of a more complex character. For them, this is an energetically more favourable process than for copolymers, which may be explained by the interaction of pendent groups. The absorption band of the azobenzene group corresponds to the $\pi-\pi^*$-transition and is shifted from 321.5 to 324 nm with the decrease in the content of the *trans*-isomer.[307]

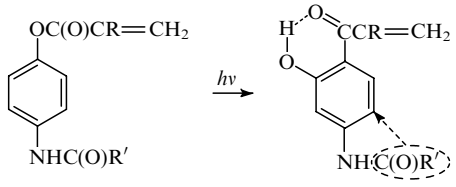
Like other phenyl esters, PA and PMA as well as their polymers and copolymers undergo the photochemical Fries rearrangement under the action of UV light [308–313]




$R^1 = CR = CH_2$.

The rearrangement is inhibited after transformation of certain amount of phenyl esters into *o*- and *p*-hydroxyphenyl ketones (a 2 : 1 mixture). The ketones were identified by the appearance of absorption maxima at 265–270 and 294 nm in the UV spectra of irradiated monomers or new absorption bands at 1620 and 1660 $cm^{-1}$ in the IR spectra of UV-irradiated poly[phenyl (meth)acrylates]. The stability of the polymer with respect to further UV irradiation is associated with the formation of hydroxy ketones on its surface and their photoshielding effect due to higher extinction coefficients. It is known [314] that 2-hydroxybenzophenones are good light stabilisers. It is presumed that their light-stabilising effect is related to the fast tautomerism of excited states. Spectral measurements showed [315] that under prolonged action of the UV light the molecules of *m*- and *p*-(*N*-acylamino)phenyl (meth)acrylates undergo the Fries rearrangement involving mainly the ester groups rather than the acylamino groups and resulting in the appearance of the hydroxy and amino groups, respectively.





$R' = Me, Et, Pr.$

Poly(1- and 2-naphthyl methacrylates) also undergo photochemical transformations by the Fries reaction upon UV irradiation.[316,317] This reaction may be of practical value for the modification of polymeric materials. Yet another type of light-sensitive polymers, *viz*., poly(methacryloyloxybenzylideneacetophenones) [318,319] and copolymers of 4-methacryloyloxybenzylideneacetophenone with BMA,[320] have been described. Upon UV irradiation, they become insoluble in organic solvents because of photodimerisation resulting in the formation of cyclobutane structures. Spectral sensitisation of such copolymers is possible with triplet sensitisers, *viz*., 5-nitroacenaphthene, picramide, *N*-acetyl-4-nitronaphthylamine and some quinones. Evidently, this process is similar to the photoaggregation of cinnamates.

The polymers containing 4-acryloyloxybenzophenone units are highly efficient photoinitiators of polymerisation.[321–323] After light absorption, the units of this monomer pass into the singlet-excited state with subsequent intercombinational conversion into π,π-triplet state and transition to *n*,π-triplet state, which may be quenched by oxygen molecules or be deactivated in the presence of a hydrogen donor with the formation of ketyl radicals.[323] Homopolymer is the most efficient as the polymeric photoinitiator and its copolymers with 4-dimethylaminostyrene are also highly active.[321]

Some PMA copolymers possess unusual photoluminescent properties, whereas the corresponding low-molecular-mass compounds and homopolymers do not luminesce under experimental conditions.[324] The large diversity of properties opens wide possibilities for the application of poly[phenyl (meth)acrylates].

The data on liquid-crystalline aryl (meth)acrylates were generalised in a number of monographs (see, *e.g*., Refs 59, 60), and this allows us not to go into details of this information.

## VII. Practical application of aryl (meth)acrylates

At present, several types of phenyl (meth)acrylates are produced in small quantities and their variety increases continually. An analysis of most recent scientific and patent publications shows that these monomers and polymers, novel for modern industries, will find wide uses basically as modifiers of properties of polymers produced on a large scale.

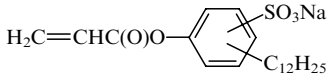
In order to manufacture lenses with high refractive indices (up to 1.67), thermal stability, resistance to shock and solvents and surface hardness, use is made of copolymers of the known monomers (MMA, styrene, *etc*.) with 3%–40% of PMA,[325–328] halogenoaryl methacrylates,[329–332] tribromophenyl methacrylate,[333–337] brominated phenyl acrylates,[338] as well as 1- and 2-naththyl (meth)acrylates and benzylphenyl methacrylate.[339,340] Pentachlorophenyl (meth)acrylates may be used as comonomers in the manufacture of light-conducting fibres.[341] PMA and PA may be the components of oxygen-permeable plastics intended for manufacturing contact lenses.[342] Poly(fluorophenyl acrylates) are used for manufacturing glass for aircraft port-holes.[343]

Halogen-containing phenyl (meth)acrylates [*e.g*., 2,4,6-tribromophenyl (meth)acrylate] were recommended as components of rubbers [344] and plastics [345] in order to increase their fire resistance. For the same purpose, pentabromophenyl (meth)acrylates are incorporated as the third component into a styrene–acrylonitrile copolymer.[346,347]

Aryl (meth)acrylates are introduced into plastics to improve their service properties, *e.g*., shock resistance.[348] Poly[3-pentadecylphenyl (meth)acrylates] are used as pressure-sensitive adhesives for binding various porous materials.[349] 2,2-Di(4-hydroxyphenyl)propane di(meth)acrylates exert a particularly noticeable effect on general properties of plastics.[350–352]

It is proposed to use di(meth)acryloyl derivatives of dihydroxybiphenyl oxides as cross-linking agents for polymeric materials. Fluoro-substituted diacrylates, for example, 1,3-bis(hydroxy-hexafluoropropan-2-yl)benzene diacrylate, are used for making coatings.[353] It is proposed to use alkoxylated dimethacrylates of bisphenol-A,[354–356] xylylene dimethacrylates [357] and aryl or naphthyl (meth)acrylates [358,359] in compositions for photo-solidified coatings and glues. High-strength solidifying compositions may be prepared using hydroxyaryl (meth)acrylates that can form urethanes with diisocyanates or isocyanatoethyl methacrylate.[360]

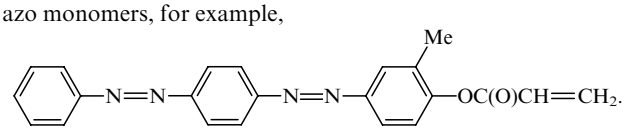
PMA and its derivatives and 2-NMA ($\geqslant 10\%$) are incorporated into copolymers used in the production of precision optical devices and video discs for recording information.[361–364] Low-hygroscopic methacrylic polymers with the water absorption $\leqslant 0.58\%$ at 50 °C have been patented.[365] Polymeric surfactants based on copolymers of hydrophilic and hydrophobic monomers are highly effective.[366] These include di(meth)acrylates of hydroquinone containing in its ring such substituents as halogens, alkyls ($C_1-C_{20}$) and biphenyl. Copolymers which are components of hydrosol compositions with improved adhesive capacity and cohesive strength may contain 2-acryloyloxynaphthalene-2-sulfonic acid along with other monomeric acids.[367] Emulsifying monomers of the general formula



accelerate polymerisation and increase the yield of the target polymer.[368]

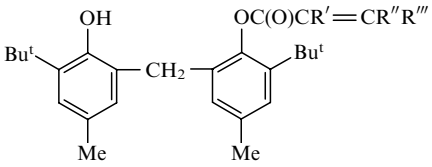
The adhesively strong coatings resistant to the action of water and ethanol were obtained based on film-forming aryl (meth)acrylate copolymers.[369,370] Aqueous dispersions of such copolymers applied onto the polymer surface prevent sweating of plasticising agents from them.

Phenyl (meth)acrylates are used for the modification of well-known polymeric products. In order to prepare self-coloured polypropylene, polycaprolactam or polyethylene terephthalate fibres [371] and films,[372] these are grafted (with the aid of UV light) to azo monomers, for example,



Azo monomers are also used in the synthesis of polymeric luminophores.[373] Units of tribromophenyl methacrylate are incorporated into polystyrene in order to improve its colourability.[374] Coloured polymeric films were prepared by dispersing dyes based on 3,3′-diethoxydicarbocyanine iodide in PPMA.[375]

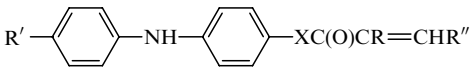
Phenyl (meth)acrylates containing groups with antioxidant or UV-stabilising activities may be introduced into macromolecules as intrachain stabilisers.[376,377] This method of stabilisation is more efficient than the conventional introduction of antioxidants because it prevents their losses from polymers due to volatilisation during processing or diffusion in the course of their service. *p*-Anilinophenyl methacrylate [378] may be regarded as one of the efficient thermostabilisers of this type for polyethylene.[376] Copolymers of dienes and vinylarenes (styrene) are stabilised by introducing up to 1.5% of a complex acrylate [379]



R′, R″, R‴ = H, Alk($C_1-C_{16}$), Ar, cyclo-Alk($C_5-C_9$), AlkAr($C_7-C_{12}$).

Monomeric amines of the type of 4-hydroxydiphenylamine (meth)acrylate belong to the group of non-sweating and non-washed off antioxidants for rubbers.[380] 2-*tert*-Butyl-6-(3-*tert*-butyl-2-hydroxy-5-methylbenzyl)-4-methylphenyl acrylate is a high-temperature thermostabiliser belonging to the group of polymer-bound antioxidants of the phenol type.[381, 382]

Aminophenyl (meth)acrylate derivatives have been used as antioxidants [383]



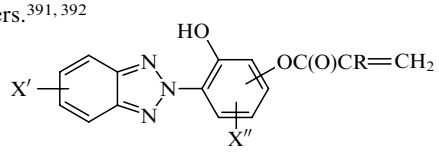
R′ = H, Me, OMe; R″ = H, Me, Ph; X = NH, O.

Such antioxidants are not washed off from rubbers by solvents, are not evaporated and do not cause their bleaching, which is highly important in the technology of rubber processing.

Acylaminophenyl (meth)acrylates, imidophenyl (meth)acrylates and imidonaphthyl (meth)acrylates [384, 385] are efficient light stabilisers for styrene. The mechanism of stabilisation is associated with the intramolecular energy transfer in molecules under the action of UV light. Aryl methacrylates introduced into the polystyrene macromolecule in the amount of 5 mass % undergo the Fries photorearrangement, which is accelerated owing to the intramolecular energy transfer of triplet excitations from the phenyl to the naphthalene moieties of the molecule. The photorearrangement rate is an order of magnitude higher in naphthyl (meth)acrylates than in phenyl (meth)acrylates.

The use of monomers providing for self-stabilisation upon exposure to natural conditions is rather promising for the preparation of copolymers.[316] Under the action of light, the Fries rearrangement occurs in films, for example, of copolymers of 1-NMA or 2-NMA with styrene or MMA, with the formation of structures of the type of 2-acetyl-1-naphthol with absorption at 320–400 nm. Even at a degree of conversion of $\sim 5\%$, one observes a substantial decrease in the photorearrangement rate, which leads to the increased light-resistance of NMA units situated at a distance of $\sim 2.6$ nm from the photoproduct.[386] The application of such light stabilisers is advisable for coatings and fibres. Polymeric absorbers can also be obtained by copolymerisation of monomers which contain light-stabilising fragments or groups, *e.g.*, of phenyl 5-(meth)acryloyloxysalicylate with vinyl acetate, vinylidene chloride and vinyl chloride and of 2-hydroxy-4-(meth)acryloyloxybenzophenone with MMA.[387, 388] The effect of light stabilisation is also achieved by grafting these monomers to polystyrene, polypropylene and polyethylene; the activity of methacrylate is higher and this is explained by additional stabilisation of the radical owing to hyperconjugation with the methyl group.[389] An analogous effect is also observed for di(meth)acryloyl derivatives of 2,4-dihydroxybenzophenone.[390]

To prepare transparent articles with improved UV absorption and weather resistance, it is proposed to introduce phenyl (meth)acrylates with benzotriazole substituents into copolymers.[391, 392]



X′, X″ = H, Hal, Alk, Ar.

The photochemical behaviour of numerous monomers and polymers with benzotriazole fragments has been described in several publications.[393–395] It was shown that the light-protective effect of polymeric UV absorbers depends on the nature of the groups which determine the nearest environment of the fragment and their influence on the strength of the intramolecular hydrogen bond in the benzotriazole fragment. Polyethylene used for manufacturing a packing material containing 4-acryloyloxybenzophenone units (from 0.1% to 40%), which is destroyed under the action of light in 120 h, has been patented. [396]

Monomers with the nitro groups, for example, 4-nitrophenyl methacrylate [397] or 4-nitro-1-naphthyl methacrylate can be used as photosensitisers. Monomers with 4-dialkylaminobenzylideneacetophenone residues, *e.g.*, 4-(4-dimethylaminobenzylidenecarbonyl)phenyl methacrylate can be used as [398] photoinitiators, including the intrachain ones,[399, 400] sensitive to light with a wavelength of 488 nm.

Aryl (meth)acrylates undergo photopolymerisation, which makes them promising components of photopolymerisable compositions (PPC) for printed circuit boards and photoresists. Di(meth)acrylates of the general formula $H_2C=CRC(O)NH-C_6H_4OC(O)CR=CH_2$ are introduced into PPC for improving the technology of manufacturing offset type forms,[401] upgrading printing-technical properties of compositions for obtaining thin copying layers.[402] It was proposed to introduce 3-acetylaminophenyl acrylate into PPC for the same purpose.[403] Dimethacrylates of isomeric aminophenols are also used as light-sensitive compounds in compositions for ideally transparent planographic printed circuit boards.[404] Two preparative methods for obtaining light-sensitive polymers containing *p*-phenylene diacrylate groups (PDAG) have been described. Under the action of radiation from an argon laser, PDAG is photodimerised with a quantum yield of 0.44, which allows one to use these polymers as resists.[405] Comparison of the reactivities of PA in UV-compositions with alicyclic and aliphatic analogues (including diacrylates) showed its highest efficiency.[406] A copolymer of 4-nitrophenyl methacrylate with 2-cinnamoyloxyethyl methacrylate is an efficient negative photoresist with a sensitivity of 17–34 mJ $cm^{-2}$ and a resolution of 1.5–3 μm for a layer 0.5–1 μm thick.[407] Homo- and copolymers of 4- or 2-*tert*-butoxycarbonyloxyphenyl (meth)acrylates are used as binding agents in irradiation-sensitive polymer mixtures and depending on the development technique of the irradiated photoresists, negatives or positives are obtained.[408] The use of phenyl acrylates in resists for X-ray microlithography with the plasma-based development makes it possible to attain submicron resolution ($\sim 0.5$ μm) at a sensitivity of 2.5 mJ $cm^{-2}$ (see Ref. 409). The content of aryl (meth)acrylate in X-ray resists reaches 30%.[410] Positive photoresists with high sensitivity and resolution are obtained by polymerisation of esters of 2-cyanoacrylic acid in the presence of sulfur-containing compounds.[411]

Irradiation of poly(halogenophenyl methacrylates) with electrons induces their cross-linking;[412] therefore, such polymers may be used as negative electron resists. Poly(4-chlorophenyl methacrylate) is an example. However, the increase in the number of chlorine atoms in the ring makes destructive processes more pronounced and the resist may become negative. Poly(phenyl methacrylates) with the perfluoalkyl groups are also regarded as negative electron resists. The sensitivities of $C_3F_7$- and n-$C_6F_{13}$-containing polymers are 20 and 7 μC $cm^{-2}$, respectively.[413] In the case of copolymers, the fluorine atoms may be present in comonomer units. For example, a copolymer of PMA containing up to 50% of α-trifluoromethylacrylic acid is an electron resist with a sensitivity of 10 μC $cm^{-2}$ at a zero residual thickness.[414, 415] The halogen-free poly[aryl (meth)acrylates] are positive electron resists with an insufficiently high electron sensitivity. It is 50 μC $cm^{-2}$ for PPMA, 200 μC $cm^{-2}$ for PNMA, 65 μC $cm^{-2}$ for poly(fluorenyl methacrylate), 550 μC $cm^{-2}$ for poly(anthryl methacrylate) and differs considerably from that for PMMA (10 μC $cm^{-2}$).[416] Introduction of halogen, *e.g.*, by chloromethylation, changes drastically the situation.[417] Electron-ray resists become negative with a sensitivity of 3.7–11.0 μC $cm^{-2}$; their sensitivity increases up to a 20%

content of chloromethyl groups. The crucial role in the cross-linking process is played by recombination of free radicals formed as the result of cleavage of the carbon–halogen bond. In contrast to vinyl and epoxide polymers, virtually no postradiational chain polymerisation, which decreases the resolution obtained, occurs in 2-PNMA. In this particular case it reaches 0.5 μm. This polymer may be sensitised to the action of light with $\lambda = 365$ nm (3% of Michler's ketone), the resultant sensitivity is $\sim 100$ mJ cm$^{-2}$. The above-considered polymers may be used in the so-called hybrid lithography, where relatively large details of microrelief are obtained under the action of UV light, while fine details are obtained with the aid of a well-focused electron beam.

Copolymers of ethylene with halogenoalkyl-substituted PMA are excellent dielectrics.[418,419] Polymers of 4-hydroxystyrene or its halogen derivatives esterified with methacryloyl chloride,[420] exhibit good dielectric properties, heat and fire resistance. These are also suitable for manufacturing bases for semiconductor devices. As in the case of copolymers of styrene with 2,4,5-trichlorophenyl acrylate,[421] modification of functional groups makes it possible to prepare electron-conducting metallocomplexes. Polymethacrylates, containing aromatic amino groups in the side chain, were found to possess the hole-type photoconductivity with rather high mobility of charges comparable to that in polyvinylcarbazole.[422]

There are data on piezoelectrical[423] and magnetic[424] properties of poly[aryl (meth)acrylates]. Specific behaviour of such polymers with liquid-crystalline properties in electric and light fields allows prediction of their wide use in electronics and optics, in particular, in birefringent and colour displays using the 'guest–host' effect, phase lenses and high-resolution laser devices.[425,426]

Like phenols, phenyl (meth)acrylates are antiseptics. Introduction of chlorine atoms into the aromatic rings increases biocidal activity; however, the low rate of the ester bond hydrolysis[427] of poly[aryl (meth)acrylates], *e.g.*, 2,4,5-trichlorophenyl methacrylate, may lead to the total loss of this activity. Nonetheless, materials based on copolymers of styrene with pentachlorophenyl acrylate,[428,429] *p*-chloro-, *p*-cresyl or biphenylyl acrylate and analogous copolymers with MMA and acrylates[429] possess noticeable antimicrobial activities. Homo- and copolymers of pentachlorophenyl methacrylate[430] and 2-carboxyphenyl methacrylate[431] are analogous in this respect. It is proposed to use polymers of 2- and 4-(meth)acryloyloxyphenylacetic acids[432,433] and their alkyl esters as bactericidal agents for the purification of sewage.

High fungicidal activity is displayed by copolymers of pentachlorophenyl (meth)acrylate[434] with vinyl acetate, ethyl and butyl acrylates, MMA and MAA. Their emulsions possess good film-forming properties and may be used as components of fungus-resistant dyes[434] for indoor and outdoor work, while copolymers with acrylamide[435] are applied for impregnation of paper.

It is proposed to use 2,2-bis(4-methacryloyloxyphenyl)-propane in compositions for fillings in dentistry.[436–438] Dentists also make use of solidified compositions which possess enhanced adhesion to metals and the dental tissue and contain from 0.5% to 10% of hydroxybenzoic (meth)acrylate[439] or aromatic di(meth)-acrylates.[440] A hemocompatible polymeric material for coating blood-contacting surfaces was obtained from dimethyl (2-hydroxyethyl)ammonium salt of poly(2-acryloyloxybenzoic acid).[441] Some phenyl methacrylates, *e.g.*, 4-azidophenyl methacrylate, are components of copolymers possessing hemoglobin functions.[442] Others, *e.g.*, 4-nitrophenyl acrylate, are introduced into polymeric carriers for the isolation of biologically specific molecules such as proteins, which may be used for radiodiagnostics of thrombi, antigens and tumours[443] or for immobilisation of enzymes, amino acids, proteins[444,445], *e.g.*, serum albumin.[446,447] Polymers based on 2,4,5-trichlorophenyl, 4-nitrophenyl or 2,4-dinitrophenyl (meth)acrylates are X-ray contrasting preparations.[448]

Introduction of residues of unsaturated acids into medicinal substances and subsequent polymerisation yield drugs with prolonged action.[69–70] Resorption of polymers of acrylic acid with β-naphthyl acrylate as potential coatings of such medicinal preparations was studied by liquid chromatography by monitoring the liberation of the β-naphthol upon hydrolysis of the copolymer.[449]

Thus, aryl (meth)acrylates possess a very broad spectrum of useful properties and their further studies are highly advisable.

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