SYNTHESIS AND COPOLYMERIZATION OF ANTHRACENE-CONTAINING ACRYLIC MONOMERS*

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Investigations of the synthesis of polymers containing anthracene groups, involve problems such as the preparation of polymeric scintillating materials, photoconductive coatings, radiation-resistant materials, organic semi-conductors etc. [1–4].

Anthracene groups covalently added to polymer macromolecules were used by the authors as luminescent markers ("tracers") required for investigations of the relaxation behaviour and the conformational transitions of macromolecules by the polarized luminescence method [5–7]. In this case the number of anthracene rings in the polymer must be fairly small so as to prevent distortion of the properties of the macromolecules.

The introduction of anthracene luminescent markers into the macromolecules of polymers containing no reactive functional groups (e.g. into polymethylmethacrylate) is best done by copolymerizing the corresponding monomer (methyl methacrylate (MMA)) with an anthracene-containing monomer. In this case it is important that the chain end growing under polymerization conditions should not interact with the anthracene ring, as this may result in distortions (additional branching, crosslinkages) of the polymer structure and in structural changes, with consequent alteration of the optical properties of the marker. When MMA is used as the main monomer it seems improbable that the growing macromolecule will interact with the anthracene group as it has been shown that when anthracene is introduced into the polymerizing system during the free-radical polymerization of MMA it has only a very weak inhibiting effect [8] and no addition of anthracene to the forming macromolecules takes place [9].

In a previous investigation [10] 9-vinylanthracene was used as the anthracene-containing monomer for the copolymerization with MMA. However in view of the structure of 9-vinylanthracene (conjugation of the exocyclic double bond with the anthracene ring, steric screening of the α-carbon atom of the vinyl group) the yield and molecular weight of the polymer were greatly reduced, and the anthracene content of the copolymer was lower than in the original mixture of monomers.

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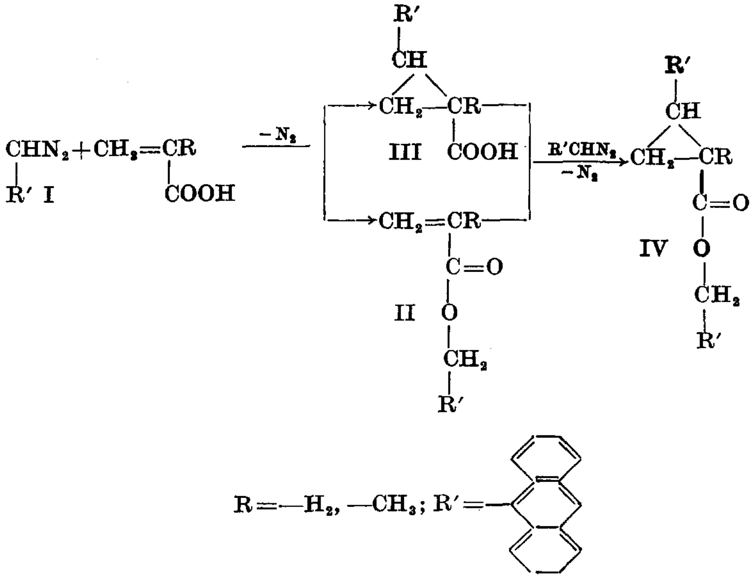
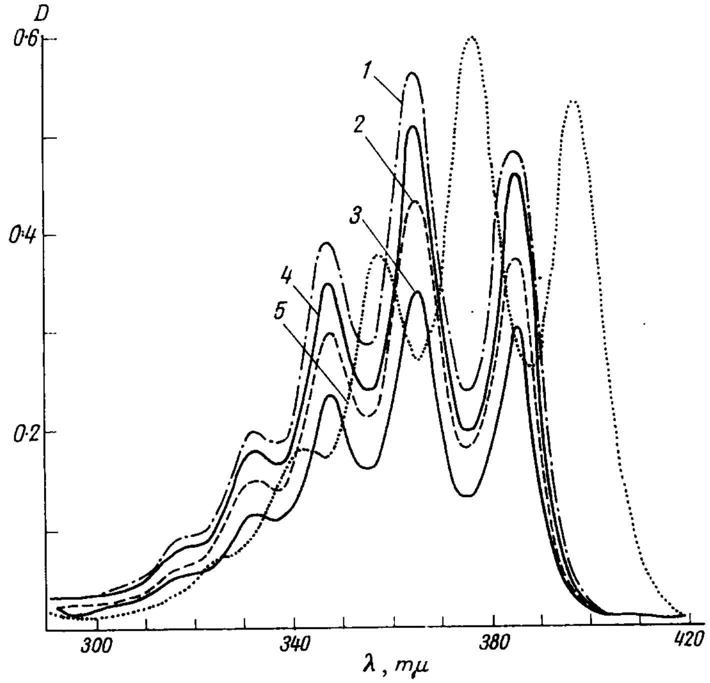
It was thought that 9-anthrylmethyl esters of acrylic acids (structure II) (AMEAA) in which the conjugation of the anthracene ring with the acryloyl groups is disrupted by the introduction of the methylene group, and where the steric hindrances are reduced, would be more active during the polymerization process. The preparation of monomers of type II was attempted in [4]. The interaction of 9-anthrylmethyl alcohol with chloroanhydrides of the corresponding acids in the presence of triethylamine and phenyl-α-naphthylamine resulted in a mixture of products with a melting point at 105–119° from which no anthrylmethyl esters of acrylic acids were separated in the form of individual compounds.

To obtain compounds II the anthracene-containing aliphatic diazo-compound 9-anthryldiazomethane (compound I) was reacted with acrylic acids [11]. Reaction between diazoalkanes and carboxylic acids leaving to the formation of esters generally proceed readily and quantitatively already at room temperature [12]. However the interaction of unsaturated compounds with 9-anthryldiazomethane may result in the formation of cyclopropane derivatives [13]. The sum total of the possible reactions during the interaction of compound I with acrylic acids may therefore be represented by the following scheme:



The rates of the processes leading to the formation of compounds II and III differ very considerably. To obtain the cyclopropane derivative of II a solution of equimolar amounts of compound I and MMA was heated in benzene for 15 hr at 60° [13], whereas the reaction between the acetic acid and compound I in hexane, modelling the formation of compound II, took place in a few minutes at room temperature [14]. When there is an adequate excess of the acid in relation to compound I the formation of IV is virtually inpossible. Compound II is therefore the most probable product of the reaction. This is confirmed by investigation of the compounds by the IR, UV and luminescence methods, and by elementary analysis. Unlike the IR spectrum of the 9-anthrylmethyl ester of acetic acid [14] the spectra of these compounds have a band at 1630 cm^{-1} characteristic for a double bond, and owing to conjugation with the double bond the band of the C=O group is displaced towards lower frequencies (1710 instead of 1730 cm^{-1}).

The absorption and fluorescence spectra of the compounds are in good agreement with those of the model compound of 9-anthrylmethyl ester of acetic acid (see Figure).



Absorption spectra of the solutions in dioxane: *1*—9-anthrylmethyl ester of methacrylic acid ($c=5{\cdot}5\times10^{-5}$ mole/l.); *2*—9-anthrylmethyl ester of acrylic acid; *3*—9-anthrylmethyl ester of acetic acid ($c=3{\cdot}7\times10^{-5}$ mole/l.); *4*—copolymer of methyl methacrylate and 9-anthrylmethyl ester of methacrylic acid ($c_{polymer}=0{\cdot}1\%$); *5*—9,10-dimethylanthracene.

PMMA samples containing luminescent groups were obtained by free-radical copolymerization of MMA with 9-anthrylmethyl esters of acrylic and methacrylic acids. In all the cases investigated by us the yields and molecular weights of the polymers were practically unaltered by the addition of monomer II to MMA (the data on the copolymerization of MMA and AMEAA are given in the Table as an example). The proportion of anthracene-containing units in the copolymers is lower (1·5–2 times) compared with the corresponding monomers in the initial mixtures.

Special investigations were carried out to estimate the probability of interactions between macroradicals and aromatic or methylene groups of the anthracene-containing units. 1. The polymerization of MMA was carried out under comparable conditions in the presence of a model compound which did not contain the vinyl group of the 9-anthrylmethyl ester of acetic acid (see Table). The introduction of this compound into the polymerizing system had virtually no effect upon the yield and molecular weight of the polymer and did not lead to the appearance of anthracene groups in the PMMA composition. 2. The absorption and fluorescence spectra of the copolymers of MMA and compound II were measured. They are in good agreement with the spectra of monosubstituted anthracene (the corresponding peaks in the absorption and fluorescence spectra of the meso-derivatives of anthracene show displacements of 10–12 mμ into the long-wave region) (see Figure). 3. It was shown that the spectral characteristics and the intramolecular mobility (based on polarized luminescence) of the copolymers synthesized in this investigation are similar to those of the copolymers obtained by the methylation of polymethacrylic acid with 9-anthrylmethacryloylhydroxymethane markers [5]. 4. The investigation of the dielectric relaxation of solutions of PMMA in toluene carried out by Burstein and Malinovskaya showed that PMMA containing one anthracene group per 400 monomer units has the same relaxation characteristics (relaxation time, activation energy) in toluene as ordinary PMMA measured under the same conditions.*

PREPARATION OF COPOLYMERS OF MMA AND AMEAA

Experiment No.	Anthracene containing compound, (AC), mg	MMA, ml	Molar ratio of MMA and AC	Toluene, ml	DAA, mg	Polymer yield		Ratio of MMA and AMEAA units in copolymer	[η]	$M\times10^{-5}$*
						g	% of theory			
1	—	5	—	7·5	10	3·3	66	—	1·5	6·0
2	9-Anthrylacetoxymethane; 39	5	300 : 1	7·5	10	3·1	62	—	1·4	5·9
3	AMEAA; 12·3	5	1000 : 1	7·5	10	3	60	1700 : 1	1·4	5·9
4	AMEAA; 20·4	5	600 : 1	7·5	10	3	60	1200 : 1	1·3	4·8
5	AMEAA; 61·3	5	200 : 1	7·5	10	2·5	50	390 : 1	1·1	3·9

* The molecular weight (M) of the polymers was calculated on the basis of the intrinsic viscosity of solutions of the latter in dichloroethane, measured at 25°, using the formula $[\eta]=1\cdot7\times10^{-4}\ M^{0\cdot68}$ [15].

In the light of these results one may assume that under the conditions of our experiments the macroradical of the growing chain reacts only with the vinyl group of the monomer of compound II.

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Samples of PMMA with the anthracene-containing luminescent markers were used in an investigation of the intramolecular mobility of the polymer using the polarized luminescence method [6].

As a result of our experiments we have thus been able to obtain individual anthracene-containing acrylates which may be used for the introduction of luminescent markers into polymers by means of free-radical polymerization. It is probable that these monomers will also be active in anionic copolymerization reactions.

EXPERIMENTAL

Preparation of AMEAA. To a solution of 0·52 g (0·0024 mole) of 9-anthryldiazomethane [14] in petroleum ether at room temperature we added 1·5 ml (0·021 mole) of double-distilled acrylic acid, and stirred for 10 min. The solution was filtered, and the solvent and excess acrylic acid were distilled off completely at room temperature, and the yellow oily residue which crystallized when left standing was dissolved in a mixture of 5 ml of diethyl ether and 1·5 ml of ethanol. The orange crystals formed during slow evaporation of the solvent at 0–5° were separated and rapidly washed with a small quantity of cooled ethanol and then vacuum-dried to constant weight. Yield of AMEAA 0·28 g (45% of theory), m.p. 85–87°.

Found, %: C 82·51; 82·67; H 5·59; 5·70. $C_{18}H_{14}O_2$. Calculated, %: C 82·42; H 5·38.

9-Anthrylmethyl ester of methacrylic acid. To a solution of 0·15 g (0·00069 mole) of 9-anthryldiazomethane in 45 ml of hexane was added 0·1 ml (0·0012 mole) of double-distilled methacrylic acid at room temperature. The separation and purification of the product were carried out in the manner described above. 0·155 g (80% of theory) of orange crystals of 9-anthrylmethyl ester of methacrylic acid were obtained, m.p. 85–86·5°.

Found, %: C 82·40, 82·64; H 6·00, 6·16. $C_{19}H_{16}O_2$. Calculated, %: C 82·59; H 5·83.

Copolymers of AMEAA with methyl methacrylate. The free-radical copolymerization of MMA and AMEAA was conducted under argon in sealed ampoules. The inhibitor was dinitrile of azoisobutyric acid (DAA) and the solvent, toluene. As an example the Table gives the results of a series of experiments in the copolymerization of MMA and AMEAA. Apart from the homopolymerization of MMA (experiment 1) the series of experiments included the polymerization of MMA in the presence of 9-anthrylcetoxymethane (experiment 2). The purpose of experiment 2 was to estimate the probability of radical substitution of H atoms of the methylene group or aromatic ring in a 9-anthrylacylhydroxymethane system under polymerization conditions.

In this series of experiments the polymerization was carried out at 60° for 8 hr. The polymers were separated by diluting the contents of the ampoules with a three-fold volume of toluene, and precipitating the contents with petroleum ether. The reprecipitation was repeated three times more, and the separated polymers were washed with petroleum ether. The number of anthracene groups in the samples remained constant on further purification.

The number of anthracene groups in the polymers was determined from the optical density in the absorption band of the anthrylacylhydroxymethane group. 9-Anthrylacetoxymethane was used as a model compound for determining the extinction coefficient of the 9-anthrylacylhydroxymethane group in the polymer samples.

CONCLUSIONS

(1) Anthrylmethyl esters of acrylic and methacrylic acids are novel active anthracene-containing monomers synthesized in order to introduce luminescent groups into a wide range of polymers.

(2) Taking as an example the free-radical copolymerization of these monomers with methyl methacrylate it has been found possible to prepare high-molecular copolymers containing different amounts of luminescent groups.

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THE EFFECT OF THE CRYSTALLINITY OF GUTTA-PERCHA ON ITS DIFFUSION PROPERTIES*

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IN PAPERS [1, 2] we gave the results of a comparative study of diffusion in single- and two-phase polymer–solvent systems over a wide range of compositions. It was found that in binary systems the diffusion coefficients were inversely proportional

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