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9-Anthryldiazomethane in the Synthesis of Anthracene-Containing Polymers

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ABSTRACT

Methods of the preparation of anthracene-containing monomers and polymers have been developed. They are based on the ability of 9-anthryldiazomethane to react with carboxylic groups of macromolecules and unsaturated carboxylic acids, to copolymerize with diazoalkanes, and to generate 9-anthrylcarbene. These methods are used to obtain: (1) polymers with a low content ($<$ 0.1 mole %) and different arrangement of anthracene groups in macromolecules (i. e., polymers with luminescent marks used to investigate macromolecules by luminescent methods) and (2) polymers with a high content (up to 100%) of anthracene-containing units, (which imparts to polymers specific photophysical and photochemical properties).

INTRODUCTION

The preparation of polymers with covalently attached anthracene groups involves the solution of several scientific and technical problems. It is possible to distinguish two main trends in the synthesis of anthracene-containing polymers. (1) New properties which result from the properties of the anthracene nuclei themselves (photoconductivity, stability to radiation, photochemical activity, scintillation properties etc.) [1-4] are imparted to the polymers. The investigation of specific properties of the anthracene nucleus which appear when it is bonded to polymer molecules (e. g., in photoionization processes [5]) can be included in this group of problems. (2) Anthracene groups bonded to polymers are used as markers for investigating the properties and structure of polymers by optical methods. In this case the addition of anthracene groups should not essentially affect the properties of polymer systems.

One of the methods using the "labeling" approach is the method of polarized luminescence (PL) based on the measurement of the luminescence of luminescent groups or markers (LM) covalently bonded to macromolecules of the polymer investigated in the amount of 0.1 mole % [6, 7].

The PL method makes it possible to obtain information on such important properties of synthetic and natural macromolecules as intramolecular mobility (IMM), which affects various physical properties of polymers and their chemical behavior [6-10]. The physical dynamics of polymer chains are related to their chemical structure. They are sensitive indicators of changes in inter- and intramolecular interactions, the structural state and conformational transformations in macromolecules, and permit the investigation of changes occurring under the effect of any factors. Intramolecular mobility determines to a great extent relaxational phenomena in polymers on different levels of the organization of polymer chains in solution and in the solid state which are shown in the physicomechanical and chemical properties of polymers. Depending on the position of LM in the macromolecule (in the main chain, in the side group or at the chain end), the method of polarized luminescence makes it possible to investigate the peculiarities of the relaxational behavior of various parts of macromolecules [6, 7]. Of particular interest is the use of the polarized luminescence method as a labeling method for investigating complex multicomponent polymer systems (block copolymers or polycomplexes), since the alternative incorporation of LM into different components of the system makes it possible to follow separately the processes characterizing the behavior of each type of macromolecule (or blocks) forming a multicomponent system [7, 9].

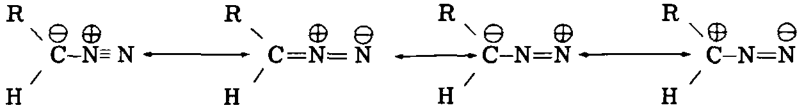
One of the advantages of the polarized luminescence method is the possibility of carrying out investigations of all polymers in all solvents (including water) at very low concentrations of the polymer in solution (up to 0.001 wt %). This is very important for understanding the mechanisms of intramolecular mobility in single macromolecules.

Structural groups attached to polymers as LM should exhibit certain optical characteristics: relatively high polarization of luminescence, high quantum yield, and the localization of absorption and emission in a spectral region favorable for experiments. Anthracene-containing LM satisfy all these requirements.

The various fields in which anthracene-containing polymers can be used stimulate the search for new methods of their synthesis permitting the preparation of polymers of different structures with different contents (from 0.01 to 100 mole % of anthracene-containing units) and different arrangement of anthracene groups in macromolecules. Anthracene-containing polymers can be obtained both in the formation of macromolecules, i. e., during initiation, propagation, or termination of the kinetic chain in polymerization, and in reactions with the participation of natural or synthetic polymers [6, 11]. The synthesis of anthracene-containing initiators, monomers, or reagents necessary for this purpose is a special and sometimes a complicated problem. The anthracene nucleus readily undergoes hetero- and homolytic reactions of substitution and addition which can occur not only in the most active meso position but also in other positions of the anthracene system [12]. On one hand, in the synthesis of anthracene-containing compounds this can lead to the formation of a great amount of side products including those which have the isomeric structure. On the other hand, when polymers with LM of the anthracene structure are obtained, in general all anthracene-containing units of macromolecules should have a unique and identical structure (and, hence, should exhibit quite definite and identical optical and dynamic characteristics), otherwise a correct interpretation of data obtained by the method of polarization luminescence would be very difficult.

In our search for reagents suitable for the synthesis of anthracene-containing monomers and polymers and satisfying the above requirements, we considered anthracene-containing aliphatic diazo compounds: specifically, 9-anthryldiazomethane (ADM) and its derivatives.

The structure of diazoalkanes with the general formula $RCHN_2$ can be represented by four resonance structures [13, 14].



$$\overset{R}{\underset{H}{\overset{\ominus}{C}}}-\overset{\oplus}{N}\equiv N \longleftrightarrow \overset{R}{\underset{H}{C}}=\overset{\oplus}{N}=\overset{\ominus}{N} \longleftrightarrow \overset{R}{\underset{H}{\overset{\ominus}{C}}}-N=\overset{\oplus}{N} \longleftrightarrow \overset{R}{\underset{H}{\overset{\oplus}{C}}}-N=\overset{\ominus}{N}$$

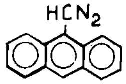
Peculiarities of the structure of diazoalkanes determine their specific chemical properties. Aliphatic diazo compounds with high chemical activity can participate in various reactions exhibiting either electrophilic or nucleophilic character, depending on conditions, generating carbenes or forming polymers of the polyalkylidene type [13, 14]. All this suggested that the use of 9-anthryldiazomethane or its derivatives as reagents would be very advantageous for the synthesis of polymers with different structures and different content and arrangement of anthracene groups.

Using chemical properties of ADM characteristic of diazoalkanes we developed various methods for obtaining polymers with anthracene groups and employed these methods for the synthesis of anthracene-containing polymers of many classes: polyolefins, polyalkylidenes, linear and crosslinked polymers based on acrylic acids, poly(alkylene oxides), cellulose derivatives (such as carboxymethyl cellulose), synthetic polypeptides, and proteins (such enzymes as invertase and ribonuclease).

RESULTS AND DISCUSSION

Preparation and Properties of 9-Anthryldiazomethane

9-Anthryldiazomethane (ADM) can be obtained by one of the classical methods of synthesis of diazoalkanes [15]: oxidation of 9-anthraldehyde hydrazone with yellow mercuric oxide. The technique of the synthesis developed for diphenyldiazomethane [16] has later been used with success for the preparation of ADM (I) [17].



I

The thermal stability of diazoalkanes is profoundly affected by the nature of the substituents at the diazo carbon atom and usually increases in the case of substituents with a system of conjugated bonds [14]. As compared to alkyldiazomethanes, the 9-anthryl group at the diazo carbon atom greatly increases the stability of diazoalkane and permits its isolation from solution in the form of violet reddish crystals. However, even in the course of the preparation and isolation of ADM or in storage, it undergoes partial decomposition which in an aprotic medium can lead to the formation of 9-anthraldazine and 1,2-dianthrylethylene. The presence of ethanol in the reaction mixture during the preparation of ADM or of moisture in the course of storage can favor the formation of compounds with UV absorption spectra characteristic of 9-alkylanthracenes. Moreover, ADM can be contaminated by the initial compound, 9-anthraldehyde hydrazone. The purification of ADM is a very complicated experimental task owing to its high reactivity and its tendency to thermal or catalytic decomposition. It has not yet been possible to find suitable conditions for its purification by low temperature crystallization. The amount of impurities in an ADM sample can be decreased by its extraction with saturated hydrocarbons which are poor solvents for such compounds as 9-anthraldehyde hydrazone or 9-anthraldazine.

The most effective method for obtaining relatively pure ADM involves the selection of experimental conditions ensuring the lowest amount of impurities. For this purpose it is necessary to develop a rapid method for determining the purity of ADM. Traditional methods (such as titration of diazoalkanes with benzoic acid [18]) require large amounts of material and are very laborious. The characteristics of ADM (decompositon temperature 64°C, the presence of an infrared absorption band at 2080 cm^{-1} assigned to the diazo group) reported by the authors who have developed the method of its synthesis [17] do not allow an evaluation to be made of the purity of the compound obtained. A method based on the use of UV spectra can be used to assess the purity of ADM.

The UV absorption spectrum of ADM in toluene contains a strong ($\log \epsilon \simeq 4$) featureless band in the region of 30,000-20,000 cm^{-1} (Fig. 1, curve 1). A distinct absorption band on its background due to impurities of the type of 9-alkylanthracenes has an allowed vibrational structure (Fig. 1, curves 2 and 3). At the same time the absorption bands of such compounds as 9-anthraldehyde hydrazone, 9-anthraldazine, or 1,2-dianthrylethylene are masked by the ADM band (e.g., Fig. 2, curves 3 and 4). A fast reaction of ADM with carboxyl-containing compounds can be used to develop the absorption bands of possible impurities of this type. When one drop of acetic acid is added to a cell with ADM solution, the latter is quantitatively transformed into 9-anthrylacetoxymethane [17] whose spectrum in the range of 30,000-24,000 cm^{-1} is similar to that of 9-alkylanthracene (Fig. 2, curve 2). In this case absorption bands of impurities can be revealed (Fig. 2, curves 5 and 6). This method can be used both for evaluating the purity of ADM obtained and for analyzing its stability in storage. When the synthesis is carried out accurately, without any additional purification, ADM contains no more than 5 mole % of anthracene-containing impurities. In the crystalline form, ADM can be stored at a temperature of 0 to -10°C for 7-10 days without any visible signs of decomposition.

This method makes it possible to obtain a pure reagent sufficiently stable for practical purposes. Similar methods of synthesis and evaluation of purity can be used for the preparation of 10-methyl and 10-phenyl derivatives of ADM [19].

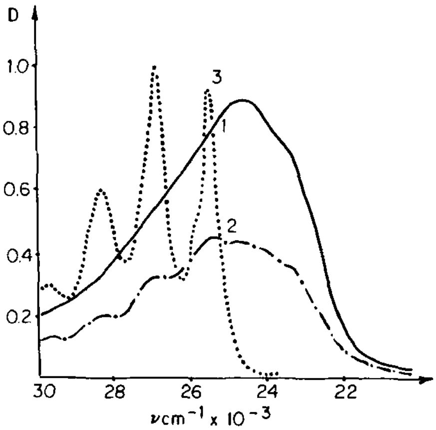


FIG. 1. UV absorption spectra of solutions in toluene: (1) 9-anthryldiazomethane (c = 1.04 × 10^{-4} mole/liter); (2) mixture of 90% 9-anthryldiazomethane (c = 0.52 × 10^{-4} mole/liter) and 10% 9-oxymethylanthracene (c = 0.05 × 10^{-4} mole/liter); (3) 9-methylanthracene (c = 1.03 × 10^{-4} mole/liter).

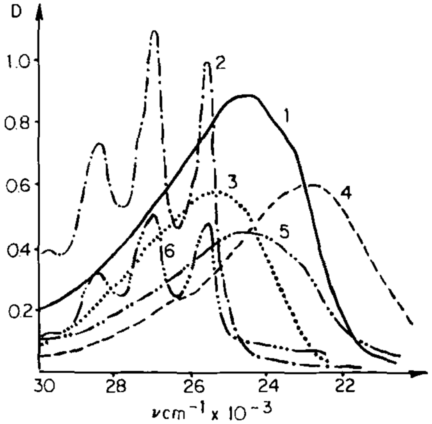
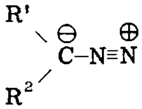


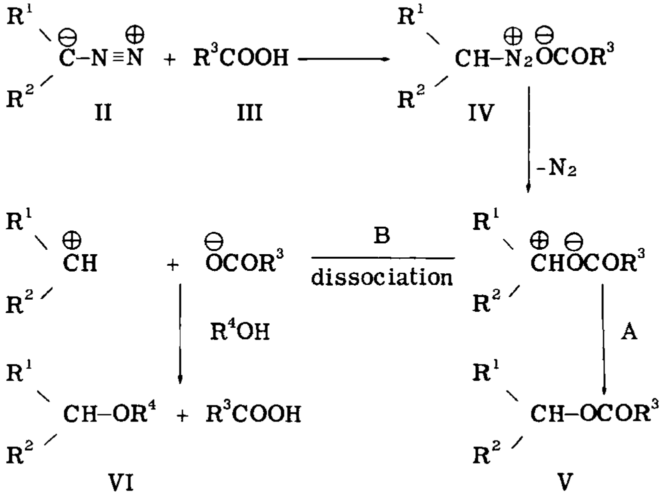
FIG. 2. UV absorption spectra of solutions in toluene: (1) 9-anthryldiazomethane (c = 1.0 × 10^{-4} mole/liter; (2) same solution after addition of one drop of acetic acid; (3) 9-anthraldehyde hydrazone (c = 0.49 × 10^{-4} mole/liter); (4) 9-anthraldazine (c = 0.18 × 10^{-4} mole/liter); (5) mixture of 95% anthryldiazomethane (c = 0.46 × 10^{-4} mole/liter) and 5% of anthraldazine (c = 0.09 × 10^{-4} mole/liter); (6) same mixture after addition of one drop of acetic acid.

Preparation of Anthracene-Containing Monomers and Polymers by the Reaction of ADM with Carboxylic Compounds

Aliphatic diazo compounds $R_1R_2CN_2$ (II) exhibit nucleophilic behavior in the interaction with carboxylic compounds owing to the resonance structure:



The reaction proceeds through the intermediate formation of a diazonium salt IV caused by proton transfer from the carboxylic acid (III) to the α-carbon of diazoalkane (II) [Eq. (1)] [13, 14, 20].



(1)

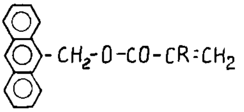
The reactivity of diazoalkanes (II) towards carboxylic acid depends on the nature of the R^1 and R^2 substituents and on their effect upon the nucleophility of the α-carbon of diazoalkane; thus, the incorporation of an aryl radical into the diazoalkane molecule decreases its reactivity. However, even when R^1 is 9-anthryl (R^2 is H), under mild conditions diazoalkane (i. e., ADM) can react with carboxylic acid (e. g., acetic acid) forming the corresponding ester [17]. It is interesting to note that the reactivity of ADM towards carboxylic compounds is much higher than that of diphenyldiazomethane (II, $R^1 = R^2 = C_6H_5$) the reactions of which with carboxylic acid have been investigated in great detail [20].

The composition of reaction products in the interaction of II and III is to a great extent determined by the properties of the medium [Eq. (1)]. Thus, in nonpolar aprotic solvents (saturated or aromatic hydrocarbons) the main reaction product is the corresponding ester V (reaction path A). In protic media (alcohols), apart from V, ether VI is also formed (reaction path B) [20].

The possibility of the occurrence of 9-anthrylmethylation of carboxylic groups by the action of ADM under mild conditions permitted the development of methods for the preparation of monomers and polymers containing 9-anthrylmethylcarboxylate groups.

Synthesis of Anthracene-Containing Monomers of the Acrylic Series

An attempt to obtain monomers of type VII, i. e., 9-anthryl derivatives of widely used and investigated monomers, methyl acrylate and methyl methacrylate, has already been made [21].

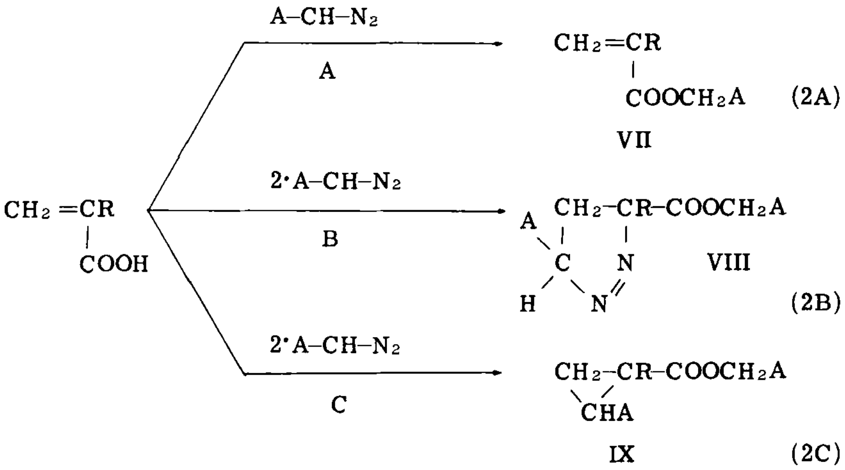


VII R = H; CH_3

However, individual anthracene-containing acrylates have not been isolated from the products of interaction of 9-anthrylmethyl alcohol with acyl chloride of acrylic acids in the presence of triethylamine and phenyl-α-naphthylamine. To obtain monomers VII we have used the reaction between ADM and acrylic acids [22].

Usually the reaction of ADM with carboxylic acids occurs readily and quantitatively but in principle the interaction of diazoalkanes with unsaturated carboxylic acids can be complicated by other reactions: 1,3-dipolar addition [Eq. (2B)] or the formation of cyclopropane derivatives [Eq. (2C)], where A = 9-anthryl- or 10-methyl-9-anthryl-.

The 1,3-dipolar addition between diazoalkanes and conjugated olefins is known to lead to the formation of pyrazolines [Eq. (2) VIII] [13, 14]. Thus, methyl acrylate or methyl methacrylate form the corresponding pyrazolines in high yield not only by the action of diazomethane [23] but also by the action of diphenyldiazomethane [24]. On the other hand, when ADM interacts with methyl methacrylate at 60°C for 15 hr, a cyclopropane derivative (IX) is formed in



50% yield [Eq. (2)] [25]. However, our investigations have shown that under mild conditions the reaction of ADM with acrylic acids introduced into the reaction mixture in a sufficient excess with respect to diazoalkane leads to predominant formation of 9-anthrylmethyl acrylates (VII) [22, 26]. In the case of 10-methyl-9-anthryldiazomethane, the reaction proceeds in a similar manner [27]. In those cases when the reaction cannot be run with an excess of carboxyl-containing compound (e. g., when an attempt is made to obtain bis-anthrylmethyl esters of unsaturated dicarboxylic acids such as maleic or fumaric acid), a complex mixture of products is obtained. Taking into account the fact that maleic and, particularly, fumaric esters [24] are strong dipolarophiles, it can be assumed that under these conditions the 1,3-dipolar addition reaction takes place.

Free-radical copolymerization of 9-anthrylmethyl acrylic or methacrylic esters with other methacrylic esters (0.1 mole % of anthracene-containing monomer in the comonomer mixture) leads to the formation of polymers with macromolecules containing luminescent markers of the anthracene structure [26]. Moreover, special experiments have shown that under the conditions investigated [26] the macroradical of the growing chain interacts only with the vinyl group of monomers VII without attacking either the anthracene nucleus or the α-methylene group. In contrast to methyl methacrylate, in the copolymerization of 9-anthrylmethyl methacrylate with such monomers as styrene or methylacrylate homolytic reactions are possible between the macroradical and the anthracene nucleus; they mainly involve the most reactive 10 position of the anthracene system [28, 29]. In this case the use of 10-methyl-9-anthrylmethyl acrylates decreases the probability of side reactions [27].

It is also possible to use 9-anthrylmethyl methacrylate for the preparation of polymethacrylates of high molecular mass with a high content of anthracene groups [2].

Addition of Anthracene Groups to Carboxyl-Containing Polymers

The reaction of ADM with carboxyl-containing polymers shows some peculiarities due to the polymeric nature of one of the reagents. The technique of carrying out this reaction depends on the solubility of the polymer, more specifically, on the existence of a common solvent for ADM and the polymer and on the required amount of 9-anthrylacyloxymethane groups formed on macromolecules during the reaction [30].

The reactions between carboxyl-containing polymers and ADM yielding polymers with LM can be divided into three groups according to the technique by which they are carried out: reactions carried out under homogeneous conditions; reactions proceeding on the liquid-liquid interface; and reactions proceeding on the solid-liquid interface.

When ADM and the polymer have a common solvent, the homogeneous method is the most suitable because it ensures the highest yield of the desired reaction (with respect to ADM) and leads to the most uniform distribution of LM along the chain (when the content of carboxylic groups in macromolecules greatly exceeds the required number of marks). This is confirmed by the fact that the reaction between diazomethane, phenyldiazomethane, or diphenyldiazomethane and syndiotactic poly(methacrylic acid) under homogeneous conditions (dioxane with 5% water as solvent) leads to random distribution of ester groups along the chain [31, 32]. As already mentioned, the nature of the solvent plays an important part in reactions between carboxyl-containing compounds and diazoalkanes. Protic solvents of the ROH type can react with diazoalkane in the presence of carboxylic acids [Eq. (1B)] forming the corresponding ethers [20]. Nevertheless, when it is necessary to attach anthracene groups to polymers of the type of poly(acrylic acid) or poly(methacrylic acid) with a very limited solubility in such aprotic solvents as dioxane or dimethylformamide, lower alcohols or mixtures of ROH or water with dioxane or dimethylformamide should be used as solvents. This decreases the yield of the desired reaction (based on ADM) and, under the conditions used, reduces it to 30-50% [30]. Hence, in those cases when polymers with a low content of carboxylic groups and soluble in aprotic solvents (such as copolymers of nonionogenic monomers of the type of styrene or methyl methacrylate containing several mole % of carboxyl-containing units of acrylic, methacrylic or vinylbenzoic acids), undergo anthrylmethylation, it is advisable to carry out reactions in such media as benzene or toluene [8, 30]. Under these conditions, which ensure the lowest contribution of side reactions, we could observe the correlation between the relaxation properties of polymers (their intramolecular mobility) and the reactivity of carboxyl groups bonded to them towards ADM [8, 9]. In the case of water-soluble natural or synthetic polymers it is possible to use one of the heterophase techniques. When a dilute ADM solution in a solvent miscible with water (such as dioxane) is added to a stirred aqueous solution of the polymer, a fine suspension of ADM is formed and the reaction takes place on the solid-liquid interface.

The reaction on the liquid-liquid interface is carried out by mixing an aqueous solution of the polymer and an ADM solution in a solvent nonmiscible with water (ether, saturated and aromatic hydrocarbons etc.).

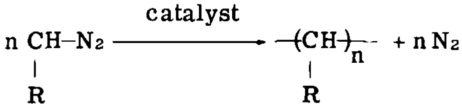
In heterophase methods, a considerable part of ADM is consumed in side reactions. Consequently, in order to obtain polymers with a required amount of 9-anthrylmethyl carboxylate groups, a preliminary experimental selection of the quantitative proportions of the reagents is necessary (see Experimental).

An intermediate case is the incorporation of anthracene-containing groups by the interaction of ADM with crosslinked finely dispersed carboxyl-containing polymers swelling in methanol (e. g., polymers obtained on the basis of acrylic or methacrylic acid [33]).

The use of the above methods for carrying out the reaction between ADM and carboxylic groups of macromolecules made it possible to attach luminescent groups of the anthracene structure to such synthetic and natural polymers as polymers and copolymers of acrylic and vinylbenzoic acids [8, 9, 30], a hydrolyzed copolymer of ethylene and maleic anhydride which is an isomer of poly(acrylic acid) with the "head-to-head" order [7], carboxymethylcellulose [7], poly(glutamic acid) [30] and other synthetic polypeptides [34], and proteins (such as invertase or ribonuclease [7]).

Preparation of Anthracene-Containing Polyalkylydenes in the Copolymerization of Diazoalkanes with 9-Anthryldiazomethane

Aliphatic diazo compounds under the influence of catalysts (some metals and their salts and also some compounds of boron, silicon, and aluminum) form macromolecules of hydrocarbon polymers, polyalkylidenes [14, 35]:

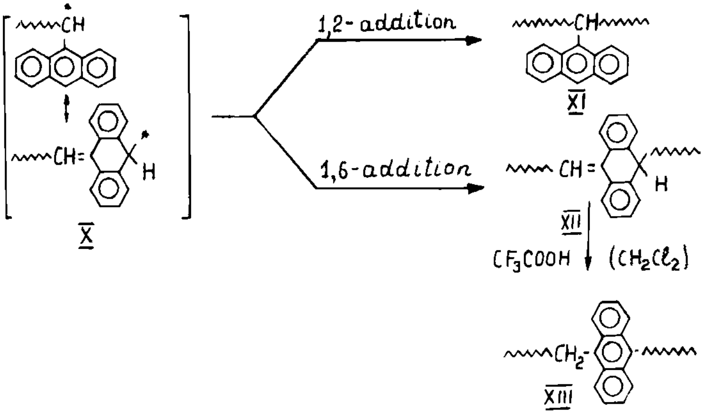


$$n\,\underset{\displaystyle R}{\underset{|}{CH}}-N_2 \xrightarrow{\text{catalyst}} -\!\left(\underset{\displaystyle R}{\underset{|}{CH}}\right)_{n}\!- + n\,N_2$$

Macromolecules of polyalkylidenes formed in the polymerization or copolymerization of diazoalkanes are essentially free of structural defects. Thus, polymethylene obtained in the polymerization of diazomethane has hardly any branches and is identical to high-density polyethylene [36, 37]. Copolymers of diazomethane with higher diazoalkanes are models of an ideal structure of industrial copolymers of ethylene with other alkylenes [14, 38, 39]. Finally, polymers of alkyldiazomethanes are models for the structure of poly-1,2-dialkylethylenes which are virtually unavailable at present [40]. The development of methods for the synthesis of polyalkylidenes with LM would make it possible to use luminescent methods for the study of properties of this important class of model polymers.

To synthesize polyalkylidenes with LM, the copolymerization of diazoalkanes with ADM was used. Investigations have shown that by the action of $BF_3\dot{O}(C_2H_5)_2$ on a mixture of diazomethane and 0.02 mole % of ADM in a toluene solution, polymethylene is formed which contains covalently bonded 9-alkylanthracene groups [41].

It has been shown previously that in chemical transformations of some diazoalkanes, low or high molecular mass reaction products of an isomeric structure can be formed [42-44]. On the other hand, taking as examples homo- or copolymerization with the participation of 9-vinylanthracene, it has been established that during the polymer chain propagation occurring by free-radical or ionic mechanisms, the growing chain end containing a 9-anthryl group on the active α-carbon atom [X, Eq. (3)] can undergo rearrangement. As a result,

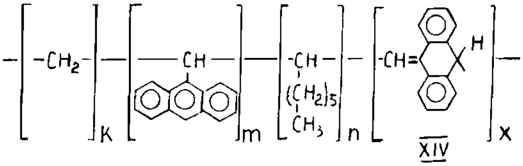


(3)

the macromolecules formed contain not only units of structure XI but also a prevailing amount of units with 9-methylene-9,10-dihydroanthracene structure XII [4, 45-48].

Units of structure XII included in the main chain can be transformed into units of 9,10-dialkylanthracene structure XIII by the action of trifluoracetic acid on a polymer solution in a polar solvent, such as CH_2Cl_2.

It is of interest to determine whether isomerization processes leading to the formation in polyalkylidenes of units of type XII, occur in the copolymerization of diazoalkanes with the participation of ADM. An experimentally suitable solution of this problem involves the preparation of ADM copolymers soluble in CH_2Cl_2 (for example, starting from ADM, diazomethane, and higher diazoalkanes). For this purpose, copolymer XIV was obtained by the action of $BF_3 \cdot O(C_2H_5)_2$ on a toluene solution of a mixture of diazoalkanes containing diazomethane, diazoheptane, and ADM in the molar ratio of 70:50:1 at -78°C. The fraction (25% of the total weight of the polymer) with $\overline{M}_n = 11{,}000$ (osmometry) was investigated. It exhibited good solubility and contained 0.15 wt % of units of type XI.



XIV

The intensities and positions of absorption bands in the spectral region of 28,000 to 24,000 cm^{-1} for the solution of copolymer XIV before and after its treatment with trifluoracetic acid were virtually identical. The positions of maxima of absorption bands for the solution of copolymer XIV in the spectral region between 30,000 and 24,000 cm^{-1} (Fig. 3) are close to those of the corresponding maxima in the spectrum of 9-monoalkylanthracene (a slight displacement towards long wavelengths as compared to the spectrum of 9-methylanthracene shown in Fig. 3 is probably due to the effect of a longer alkyl radical of the polymer nature [49]). Moreover, absorption spectra of solutions of model mixtures of 9-mono- and 9,10-dialkylanthracene derivatives containing 10-20 mole % of 9,10-dialkylanthracene differ markedly from the spectrum of 9-alkylanthracene (e. g., a shoulder in the range of 25,000 to 24,500 cm^{-1}). These facts indicate that polymer XIV contains mainly units of type XI rather than those of type XIII which could be formed as a result of the rearrangement of units of type XII by the action of a Lewis acid, $BF_3 \cdot O(C_2H_5)_2$, during polymerization or in the course of the subsequent treatment of copolymer XIV with trifluoracetic acid. Hence, under the conditions investigated, the copolymerization of ADM with diazoalkanes is not

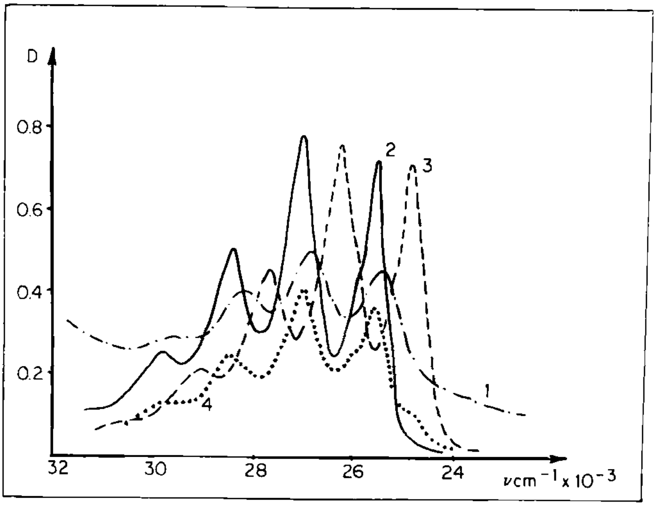


FIG. 3. UV absorption spectra of solutions in dichloroethane: (1) A copolymer of diazomethane, diazoheptane and ADM XIV (C = 5 mg/ml) (2) 9-methylanthracene (C = 8.5×10^{-5} mole/liter) (3) 9,10-dimethylanthracene (C = 7.8×10^{-5} mole/liter) (4) A mixture of 9-methyl and 9,10-dimethylanthracene (20 mole % of 9,10-dimethylanthracene, $C_\Sigma = 7.8 \times 10^{-5}$ mole/liter)

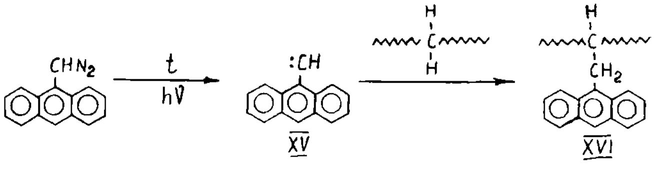
accompanied by appreciable isomerization. It can be assumed that in this case the absence of isomerization in the anthracene-containing active center of the growing macromolecule is associated with the specific chemical structure of such monomers as diazoalkanes in general and diazomethane in particular, and with a peculiar mechanism of the polymerization of aliphatic diazo compounds. It should be noted that up to the present the mechanism of diazoalkane polymerization remains uncertain even for the case investigated in greatest detail, the catalysis by boron compounds [14, 35, 44, 50, 51].

Hence, all our data show that the copolymerization of ADM with diazomethane and other diazoalkanes provides a method for the preparation of polyalkylidenes with luminescent groups.

9-Anthrylcarbene in the Synthesis of Anthracene-Containing Polymers

Usually thermal or photolytic decomposition of diazoalkanes leads to the intermediate formation of carbenes, highly reactive compounds with the general formula ($R_1\ddot{C}R_2$) [14, 52, 53]. In this sense, 9-anthryldiazomethane is not an exception because it decomposes with the formation of 9-anthrylcarbene (XV) [54]. Carbenes can participate in various chemical reactions, for example, addition to multiple bonds, insertion on C–H bonds, or hydrogen abstraction [52, 53]. This permits the use of carbenes for modifying the polymer properties [55-57]. The use of 9-anthrylcarbene for reactions with polymers provided possibilities of developing the addition of anthracene groups to polymers of various structures, including polymer without reactive functional groups.

Investigations showed that 9-anthrylcarbene formed by the thermal or photolytic decomposition of 9-anthryldiazomethane in a polymer solution is incorporated on C–H bonds of macromolecules. Thus, as a result of the carbene reaction, anthracene groups are covalently bound (XVI) to macromolecules [58].

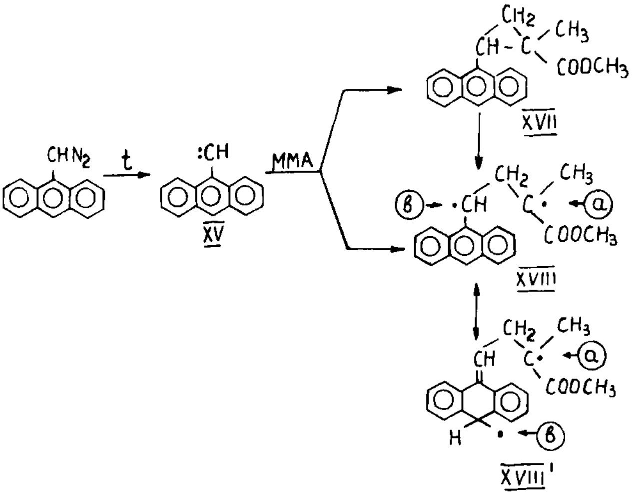


In the regions characteristic of anthracene groups, absorption and luminescence spectra of solutions of anthracene-containing polymers obtained by the carbene reaction show a band assigned to 9-alkyl substituted anthracene groups. The amount of these groups bonded to polymer macromolecules in the course of this reaction is usually small and under our experimental conditions it did not exceed 10-15% of the initial amount of ADM. Moreover, the yield of the desired reaction depends to a great extent on the solvent, the structure of the polymer and its concentration in solution. For example, when the reaction is run under comparable conditions (solvent toluene, polymer concentration in solution ~ 7%, temperature 90°C, reaction time 6 hr), the yield of the addition of 9-anthrylcarbene to polymer macromolecules is 5-10-fold higher for polyethylene glycol ($M = 20{,}000\text{-}30{,}000$) than for high-density polyethylene (10-15% and 1-2% of the theoretical value, respectively).

The reaction of 9-anthrylcarbene with polymer macromolecules can involve various C–H bonds. For example, when 9-anthrylcarbene interacts with poly(methyl methacrylate), anthracene groups can be bonded to both types of methyl groups and to the methylene group of the main chain and the main contribution to the reaction seems to be that of methyl groups. This conclusion is based on data obtained by the method of polarized luminescence (PL method) with the use of additional model samples of labelled poly(methyl methacrylate) in which the structure of anthracene-containing units was known. Consequently, in those cases when it is necessary to ensure a unique structure of the bond between the anthracene group and the polymer macromolecule (e. g., for a rigorous interpretation of data obtained in the study of intramolecular mobility by the PL method) it is advisable to use the carbene method for bonding luminescent groups to polymers with one type of C–H bonds [polyethylene, poly(ethylene oxide) etc.].

The initiation of polymerization of methyl methacrylate by products of the thermal decomposition of ADM is another example of the use of 9-anthrylcarbene in the synthesis of anthracene-containing polymers [59-61]. It has been shown that the polymerization proceeds by a free-radical mechanism [59, 60]. In these papers the scheme of processes occurring in the initiation of the polymerization proposed is shown in Eq. (4).

According to Eq. (4), 9-anthrylcarbene XV formed during the thermal decompositon of ADM in the interaction with a methylmethacrylate molecule generates biradical XVIII (either directly or through the intermediate formation of cyclopropane compound XVII). Its free-radical center (a) initiates the polymerization of MMA. An unpaired electron (b) is delocalized (XVIII⟷XVIII') and cannot take part in the initiation. The latter suggestion does not agree with data obtained in the free-radical copolymerization of MMA and 9-vinylanthracene [Eq. (3)]. The free-radical active



(4)

center (b) in structures XVIII $\longrightarrow$ XVIII' is similar in its structure to the active center of macroradical X [Eq. (3)] capable of bonding MMA molecules [47]. As a result of free-radical copolymerization of MMA and 9-vinylanthracene, macromolecules containing units of structures XI and XII are formed [Eq. (3)]. This comparison induced us to investigate products of the polymerization of MMA initiated by compounds formed in the ADM thermolysis. Our investigations led to the establishment of the following facts.

According to UV spectra, PMMA obtained by this method contains 9-alkyl-substituted anthracene groups. The amount of these groups is comparable to the amount of macromolecules in solution. Investigations of the distribution of anthracene groups in fractions of PMMA samples obtained in the polymerization initiated by products of ADM therolysis, showed that the content of anthracene groups in fractions decreases with increasing molecular mass of these fractions. Thus, fractions with $\overline{M}_\eta$ of 230,000 and 810,000 contained on the average one anthracene group per 2250 and 6200 MMA units, respectively.

Treatment of PMMA with trifluoracetic acid does not increase the amount of anthracene groups in the polymer, whereas units of 9-methylene-9,10-dihydroanthracene structure XII under similar conditions are readily transformed into units of 9,10-dialkylanthracene structure XIII [Eq. (3)].

PMMA samples obtained by using ADM and model PMMA samples with known structure and location of anthracene groups in the macromolecules were investigated by PL method.

It was shown that not only the polarization of luminescence but also the character of its dependence on the viscosity and the temperature of the solvent and the fluorescence lifetime are very sensitive to changes in the position of anthracene groups in macromolecules [6, 7]. Times describing relaxation processes in those segments of macromolecules which contain anthracene groups provide information on the type of bonding and the position of luminescent groups in polymer chains [6, 7]. It was shown by the PL method that anthracene groups in PMMA obtained by using ADM (curve 1, Fig. 4) are located in more mobile parts of macromolecules than in the case of PMMA obtained in the usual manner and then treated with products of ADM thermolysis, i.e., with 9-anthrylcarbene (curve 2, Fig. 4) or in the case of the MMA-9-vinylanthracene copolymer (curve 3, Fig. 4). On the other hand, the high slope of curve 1 is close to that of curve 4 characterizing a model PMMA sample with anthracene end groups of the 9-anthrylmethylcarboxylate structure. The difference in the parameter $1/P_0$ for curves 1 and 4 (Fig. 4) is due to different structures of groups bonding the anthracene nucleus on the chain end.

The conclusion on the terminal position of anthracene groups in the investigated sample of PMMA is confirmed by the data in Table 1 which presents the values of relaxation times (τ_w) characterizing

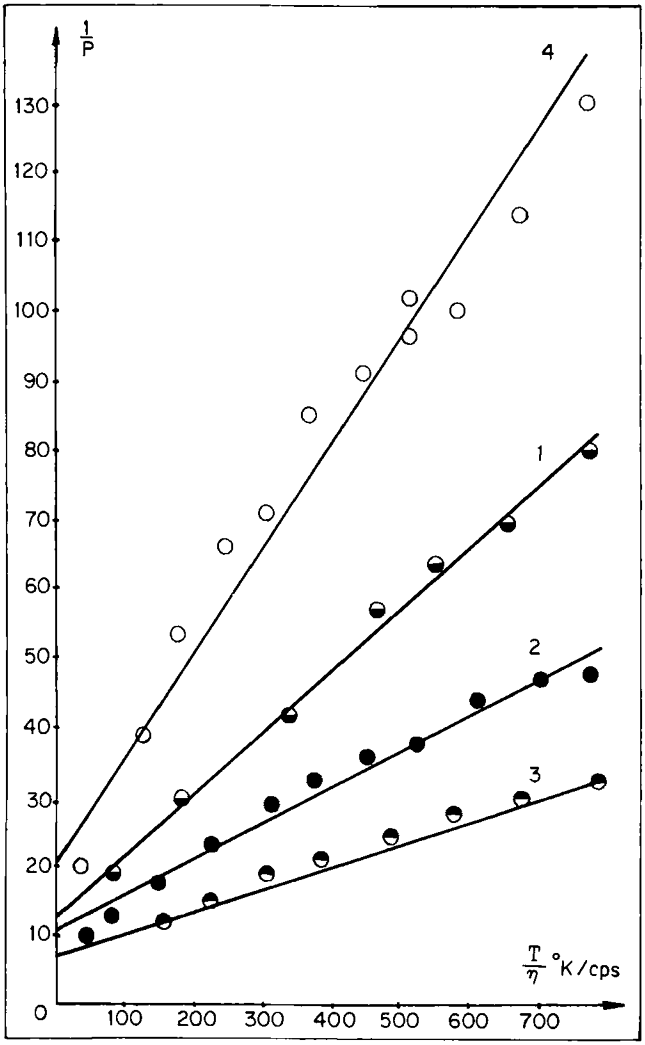


FIG. 4. Dependences of 1/P(T/η) for PMMA solutions at 25°C in the mixtures of methyl acetate and triacetine: (1) PMMA-1; (2) PMMA-2; (3) PMMA-3; (4) PMMA-4 (See Table 1). (T and η denote temperature and viscosity of the solvent, respectively.)

TABLE 1. Relaxation Time (τ_w) for PMMA in Methyl Acetate at 25°C

Code	PMMA Type	τ_w (nsec)
PMMA-1	Initiated by products of ADM thermolysis	3.2
PMMA-2	Model PMMA treated with products of ADM thermolysis	5.0
PMMA-3	MMA-9-vinylanthracene copolymer with anthracene groups bonded to main chain	7.0
PMMA-4	PMMA with anthracene groups at chain ends	1.9

the mobility of parts of macromolecules of the above polymers with anthracene groups.

Hence, our data suggest that PMMA formed in the polymerization of MMA initiated by products of the thermal decomposition of ADM, i. e., by 9-anthrylcarbene, contains anthracene groups mainly at the chain ends and do not contain units of 9-methylene-9,10-dihydroanthracene. In combination with the data obtained in the free-radical polymerization of MMA and 9-vinylanthracene [47], this casts doubt on the scheme of initiation processes proposed by Imoto et al. Unfortunately experimental data available are not sufficient to develop a more correct scheme. As a working hypothesis it is possible, for example, to discuss the abstraction of an H· radical by anthrylcarbene from the reaction medium (as is typical of arylcarbenes [52]) and the formation of a 9-anthrylmethyl radical initiating the polymerization of MMA.

The above data show that the polymerization of MMA initiated by products of thermal degradation of ADM is one of the methods for obtaining polymers with anthracene end groups.

Hence, reactions with the participation of 9-anthrylcarbene formed in the decomposition of 9-anthryldiazomethane provide one of the most suitable methods for bonding anthracene groups to macromolecules of polymers which do not contain reactive functional groups, i. e., to polyethylene and other polyolefins, to poly(alkylene oxides), poly(alkyl acrylates) etc.

EXPERIMENTAL

Preparation of Aliphatic Diazo Compounds

9-Anthryldiazomethane was prepared by oxidation of 9-anthraldehyde hydrazone with yellow mercuric oxide [17]. Its purity was determined by a spectrophotometric method described in the Results and Discussion. For subsequent reactions, ADM samples containing not less than 90-95% of the main substance were used.

Diazomethane and diazoheptane were obtained as toluene solutions by the method of Arndt [62] by base-induced decomposition of the corresponding N-nitroso-N-alkylureas [51, 63, 64]. The concentration of diazoalkanes in solutions was determined by titration with benzoic acid [64].

Below examples are given of typical syntheses of anthracene-containing monomers and polymers based on 9-anthryldiazomethane.

9-Anthrylmethylmethacrylate (VII, R = CH_3)

To a 0.15 g (0.69 mmole) solution of 9-anthryldiazomethane in 45 ml of hexane was added 0.1 ml (1,2 mmole) of twice-distilled methacrylic acid and the reaction mixture was stirred for 10 min at room temperature. The solution was filtered, and the solvent and the excess methacrylic acid were completely distilled off under vacuum at room temperature. The yellow oily residue, which crystallized on standing was dissolved in a mixture of 1 ml of ethanol and 2 ml of diethyl ether. Orange crystals formed by slow evaporation of the solvent at 0-5°C were isolated, rapidly washed with a small amount of cooled ethanol and dried under vacuum to constant weight. The yield of 9-anthrylmethylmethacrylate was 0.155 g (80% of theoretical, mp 85-86.5°C).

Analysis: Calcd for $C_{19}H_{16}O_2$: C, 82.59%; H, 5.83%. Found: C, 82.4, 82.64%; H, 6.00, 6.16%.

The structure of VII (R = CH_3) is also confirmed by data of UV and IR spectra and luminescence spectra [26].

Free-radical homo- and copolymerization of 9-anthrylmethyl and 10-methyl-9-anthrylmethyl esters of acrylic acids with monomers of acrylic and vinylaromatic series has been described previously [26, 27, 65].

The preparation of polymers with covalently bonded anthracene groups includes the following stages: (1) carrying out of the chemical reaction leading to the formation of macromolecules with anthracene groups, (2) purification of polymers from unbonded anthracene-containing compounds (monomers, reagents, products of their transformations) and purity control, (3) quantitative determination of the anthracene group content of the polymer.

The purification of the polymer from anthracene-containing compounds not attached to macromolecules can be carried out by extractions from a solid polymer or a solution, by dialysis, chromatographic methods, or repeated reprecipitation alternating with a thorough washing with the precipitant. Purification processes were repeated until the specific absorption of polymers in the spectral region of 25,000-30,000 cm^{-1} characteristic of anthracene derivatives ceases to decrease. The final check on polymer purity can be carried out by the PL method because the polarization of luminescence is very sensitive to the presence of anthracene-containing compounds of low molecular weight in solution.

When the amount of bonded anthracene-containing groups in the polymer was low, (up to 1-3 mole %), it was determined from the optical density of their solutions for one of the absorption bands of the anthracene group in the region of 25,000-30,000 cm^{-1}. Previously it was shown that the investigated systems obey the Lambert-Beers law. Extinction coefficients were determined under experimental conditions by using corresponding model compounds.

When the anthracene group content of the polymers was higher ($>$ 5 mole %), a hypochromic effect can appear [65]. In this case it is advisable to determine the number of anthracene groups in the polymer by other methods, such as IR spectra [65].

IR spectra were measured with a UR-20 spectrometer (DDR) and a DS-301 spectrometer (Japan). UV absorption spectra were measured with a Specord UVVIS spectrophotometer (DDR). The polarization of luminescence was measured with an apparatus described previously [66].

Bonding of Anthracene Groups to Carboxyl-Containing Polymers

Homogeneous Technique. To a stirred solution of 1.5 g (0.021 base moles) of polyacrylic acid (PAA) in 30 ml of methanol at room temperature was added 9 mg (4.13×10^{-2} mmole) of ADM in 4.5 ml of purified dioxane (one ADM molecule per 500 PAA units). After 2 hr the polymer was precipitated with ether and purified by repeated reprecipitations from methanol into ether. The PAA sample obtained in this manner contained one 9-anthrylmethyl carboxylate group per 1500 polymer units.

Heterophase Technique. To a solution of 0.1 g (1.16 mmole) of poly(methacrylic acid) (PMAA) in 3 ml of water stirred at room temperature was added a solution of 0.5 mg (2.3×10^{-3} mmole) of ADM in 0.25 ml of purified dioxane. After 1.5 hr, the reaction mixture was filtered, the aqueous solution was repeatedly washed with ether, and after lyophilic drying the polymer was isolated; it contained one anthracene group per 10000 PMAA units.

Preparation of Anthracene-Containing Polymers by Copolymerization of ADM with Other Diazoalkanes

To 160 ml of toluene solution containing 0.75 g (17.5 mmole) of diazomethane, 1.4 g (12.5 mmole) of diazoheptane, and 0.055 mg (0.25 mmole) of ADM at -78°C was added 0.7 g (6.2 mmole) of $BF_3 \cdot O(C_2H_5)_2$ dissolved in 4 ml of toluene. The reaction was run for 15 hr at -78°C. The polymer was isolated from the reaction mixture by precipitation with methanol. The polymer yield was 0.45 g (34% of the theoretical). The labeled polymer (polyalkylidene) contained 0.125 g (28%) of fraction soluble in toluene which was purified by repeated reprecipitations from a toluene solution into methanol. This fraction had $\bar{M}_n$ = 11,000 (osmometry) and contained 0.15 wt % of covalently bonded 9-monosubstituted anthracene groups.

Bonding of Anthracene Groups to Polymer Macromolecules by the Action of 9-Anthrylcarbene

To a solution of 300 mg of poly(ethylene oxide), $[\eta] = 0.55$ dl/g, in water, 25°C, in 2.5 ml of toluene at 90°C was added a solution of 10 mg of ADM in 0.5 ml of toluene (one ADM molecule per 150 polymer units). The resulting solution was heated at 90°C for 6 hr, then the polymer was precipitated with petroleum ether and purified by repeated reprecipitations from a dichloromethane solution into petroleum ether. The labeled poly(ethylene oxide) contained one anthracene group per 2000 units of the main structure, and its intrinsic viscosity was equal to that of the initial polymer.

CONCLUSION

These methods for the preparation of anthracene-containing polymers based on ADM made it possible to synthesize polymers of various types with the required amount of anthracene groups. Their synthesis, in its turn, facilitated an approach to the solution of a number of general problems of chemistry and physics of polymers. Thus, polyacrylates with a high content of 9-anthrylmethylcarboxylate groups proved to be suitable for studying photophysical and photochemical properties of anthracene-containing polymers [2, 65]. Investigations by the PL method of various polymers with luminescent markers of the anthracene structure permitted the investigation of such problems as the effect of the chemical structure on the intramolecular mobility of polymer chains [6, 7], various types of intra- and intermolecular interactions and conditions of their appearance, the formation, structure, and properties of polymer complexes [6, 7, 67, 68], intramolecular structurization of various types (formation of a compact structure [7, 69, 70], α-helical state [34], and globules [34]), and conformational transformations of macromolecules [34, 69-72]. Finally we have used the ability of ADM to react with functional groups of macromolecules with formation of luminescent markers for investigation of the relationship between intramolecular mobility of macromolecules and their local reactivity [8, 9, 73, 74].

Hence, the use of ADM as reagent for obtaining polymers and for solving some urgent problems of polymer chemistry and physics was found to be very fruitful.

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