

Synthesis and photochemical transformations of an anthracene containing methacrylic copolymer

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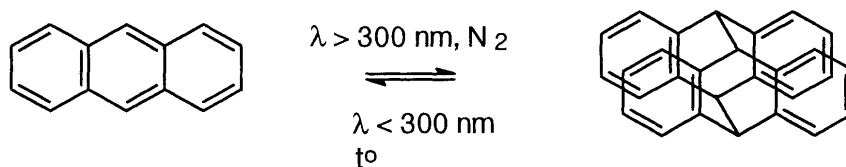
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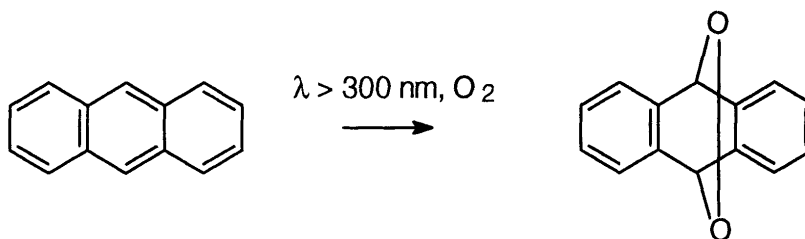
Summary : A new methacrylate monomer containing anthracene moiety connected with long flexible spacer was prepared and copolymerized with n-butyl methacrylate. It has been found that upon illumination in inert atmosphere photodimerization of the anthracene rings takes place to a considerable extend. The reverse decomposition of the photodimers by thermal treatment is also facilitated by the long flexible spacer. In ambient air the only photoreaction is endoperoxide formation.

Introduction

Polymers with pendant anthracene rings have been prepared and investigated by many authors (1-6). The interest in these polymers is mainly due to the expectations to create photoresponsive materials using the photosensitivity of anthracene. It is well known that anthracene undergoes $[4\pi+4\pi]$ photodimerization upon illumination with light $\lambda > 300$ nm (7, 8). The reaction is reversible. Illumination with light $\lambda < 300$ nm or thermal treatment leads to a degradation to the initial compounds (1, 6). However, photodimerization reaction takes place only in the absolute absence of oxygen.

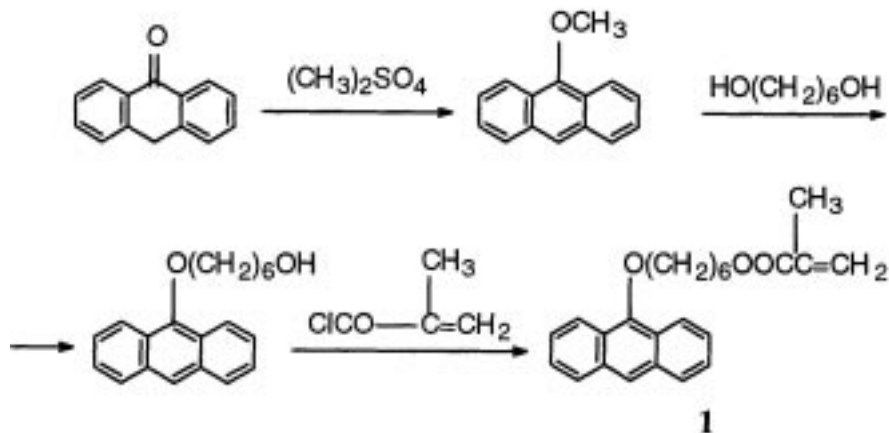


Upon illumination in the presence of oxygen formation of endoperoxide occurs (9, 10)



Many authors pointed out that the anthracene mobility in the polymer matrix is more important for the successful photodimerization than the anthracene density (5, 6, 12). It is the same even for the decomposition of the photodimers. The anthracene moieties have to move apart which needs a mobility (6). The anthracene rings of almost every anthracene containing polymers obtained till now are connected at 9th position with the polymer chain and with a short spacer (1-6). But it is well known from the chemistry of side chain liquid crystalline polymers (11) that the mesogenic units are able to build up ordered structures only when they are connected with the polymer main chain with long, flexible spacers.

Favorable special ordering of two anthracene rings is obviously a prerequisite for the occurring of the photodimerization reaction (2). This condition could be better fulfilled when the anthracene rings are connected with the main polymer chain with long flexible spacers. A polymer of this type as we mentioned have not been prepared and investigated so far. That is why in this paper we prepared the monomer (**1**) as shown below:



In monomer **1** the anthracene ring is connected with the polymerizable unit not via methylene group, but through an ether bond and a long spacer. This would be probably an advantage since it was pointed out that anthracene derivatives with ether bond at 9th position dimerize upon illumination very easily, even in the presence of oxygen (12). The ether bridge imports also higher degree of mobility.

An unsolved problem is the ratio between the two anthracene bleaching reactions - the photodimerization and the endoperoxide formation. It was established that under oxygen atmosphere the formation of endoperoxide is the dominating reaction (6). But these investigations were performed with poly[(9-anthrylmethyl) methacrylate], a polymer with very short spacers between the anthracene rings and the main chain. A study of a polymer of **1** where the conditions for photodimerization are expected to be more favorable will show which one of the two photochemical reactions will predominate.

For practical purposes the photoreactions have to be performed in the solid state at room temperature. Since the segment mobility is essential for photodimerization T_g of the polymer must be below the processing (room) temperature (2). This was our reason not to homopolymerize **1**, but to prepare its copolymer with *n*-butyl methacrylate. Better adhesion of the copolymer could be expected in this case as well.

Experimental

Materials

9-Methoxyanthracene (MA) was obtained acc.(13), *n*-butylmethacrylate (Fluka) was distilled before use, 1,6-hexanediol (Fluka), purum, toluene-4-sulfonic acid monohydrate, purum, triethylamine (Fluka), purum, tetrahydrofuran (Fluka), purum was dried over KOH, sodium wire and distilled before use. Chlorobenzene (Fluka) and toluene (Fluka) were distilled before use.

Measurements

UV-VIS spectra (solutions or thin films on quartz plates) were recorded on a spectrophotometer Specord M42, Carl Zeiss, Jena, Germany. The ¹H-NMR spectra were recorded on a Bruker Spectrospin 250 MHz apparatus. GPC analysis was performed on a Waters apparatus (columns 100, 500 and 1000 Å) equipped with model 440 UV and R401 refractive index detectors. The values were determined versus polystyrene standards. DSC determinations were made on a Perkin-Elmer DSC 7 apparatus, heating rate was 10°/min.

Synthesis of 1-(9-anthryloxy)-hexan-6-ol

11,2 g (53,9 mmol) of MA; 27,39 g (1,08 mmol) of 1,6-hexanediol; 0,16 g of p-toluenesulfonic acid and 215 ml of toluene were placed into a round-bottom flask equipped with a Dean and Stark separator containing solid CaCl_2 . The mixture was stirred vigorously and refluxed for 53 hrs. CaCl_2 was changed twice. Then the mixture was filtered off and 40 ml 2n NaOH were added to the filtrate. The organic extract was washed with water and stored over Na_2SO_4 . The solution was purified by column chromatography over neutral Al_2O_3 . The concentrated solution of the product crystallized in yellow-brown crystals, 14,2 g (91% yield), m.p. 69°C.

Elemental analysis: $\text{C}_{20}\text{H}_{22}\text{O}_2$ (294,38) Calc. C 81.60 H 7.50
 Found C 80.87 H 7.46

$^1\text{H-NMR}$ (CDCl_3 , 250 MHz): $\delta = 7,9$ (m, H^9); 4,15 (t, H^2) 3,65 (m, H^2);
 2.0 (m, H^2); 1,6 (m, H^6); 1,5 (t, H^1)

Synthesis of 6-(9-anthryloxy)-hexylmethacrylate, **1**

In a round-bottom flask equipped with a stirrer and nitrogen inlet were placed 5 g (17 mmol) of 1-(9-anthryloxy)-hexan-6-ol, 3,15 ml (22 mmol) of triethylamine, 37 ml of dry THF and some hydroquinone. A solution of 2,15 ml (23 mmol) methacryloylchloride in 10 ml of THF was added to the continuously stirred mixture, so that the temperature did not rise over 5°C. After stirring for 24 hrs at room temperature the mixture was filtered off, THF was evaporated, the residue was washed with water and extracted with chloroform. The chloroform solution was washed with water and dried over Na_2SO_4 . After removal of the solvent a thick syrup like product was obtained, 4,3 g (71,9% yield).

Elemental analysis: $\text{C}_{24}\text{H}_{26}\text{O}_3$ (362,45) Calc. C 79.53 H 7.23
 Found C 79.60 H 7.03

$^1\text{H-NMR}$ (CDCl_3 , 250 MHz): $\delta = 8,22$ -7,18 (m, H^9); 6,04 (s, H^1); 5,47 (s, H^1); 4,12 (t, H^2); 3,63 (t, H^2); 1,92 (m, H^2); 1,88 (t, H^3); 1,63 (m, H^4); 1,48 (m, H^2).

Polymerization

The copolymer was prepared via radical copolymerization of **1** and n-butylmethacrylate, molar ratio 1:1, with azobisisobutyronitrile as initiator in toluene solution at 60°C for 5 days (monomer : toluene = 1:8 wt; initiator - 1 mol-% towards the monomers). The solution was poured into ethanol and the precipitate was filtered off, washed with ethanol and dried. Yield 40,5%; $M_n=23\ 000$; $M_w=48\ 000$, polydispersity 2,07. Tg of the copolymer is 22°C.

Elemental analysis: $(\text{C}_{32}\text{H}_{40}\text{O}_3)_n$ (504,67) Calc. C 76,16 H 7,99
 Found C 75,35 H 7,63

IR (film) 3050 (Ar C-H stretch), 2958 (CH_3 stretch), 2953 (CH_2 stretch), 1725 (C=O stretch), 1465, 1341, 1265, 1155, 1090, 879, 842, 793, 739 cm^{-1}

Photoreactions

The samples deposited on quartz plates were illuminated with high pressure mercury lamp at $25\pm 2^\circ\text{C}$. Cut off glass filter was used to exclude deep UV light ($\lambda < 345$ nm). The light intensity was 30 mW/cm^2 . Some of the samples were illuminated in a closed quartz cell flushed with nitrogen.

The samples were prepared by spin coating of 5% polymer solution in chlorobenzene on quartz plates. After solvent evaporation the layers were dried for 30 min at 100°C. The average layer thickness was 0,3 μm . After illumination, both in air and in inert atmosphere, the samples are no more soluble in the initial solvent. No Tg could be determined of these samples, which confirms their cross-linking.

Results and discussion

It was found that copolymerization of **1** with n-butyl methacrylate is a rather slow reaction. Even after 120 hrs the copolymer yield is only 40%. This result could be expected since anthracene is well known as an inhibitor

of radical processes (14). Due to its high electron donating properties anthracene can form charge transfer complexes with the macroradicals exhibiting high electron affinity (15). The result is a low polymerization rate. The GPC of the copolymer shows a monomodal distribution which indicates the absence of any homopolymerization. The weight content of anthracene in the copolymer is 28% and was determined from the calibration curve extinction-concentration of anthracene at $\lambda=356$ nm. This corresponds to a molar ratio of 1 to n-butyl methacrylate in the copolymer equal to 0,35:0,65.

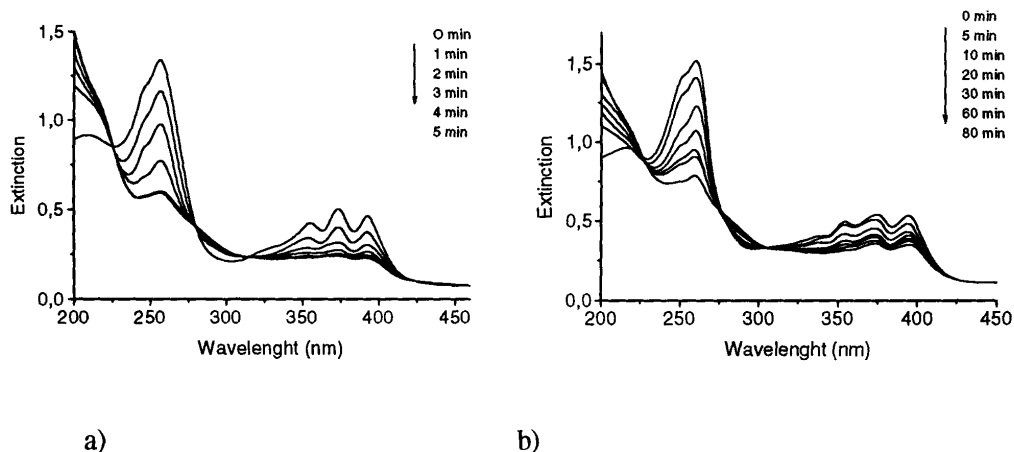


Fig. 1. Time dependent UV-Vis spectra of the copolymer in: a) ambient air; b) argon atmosphere.

As expected due to the spacer in **1** and to the participation of n-butyl methacrylate the copolymer exhibits a relatively low $T_g=22^\circ\text{C}$, convenient for performing photochemical transformations.

As already stated two main reactions can take place upon illumination: photodimerization and endoperoxide formation (in ambient air). In both cases the conjugated π -electron system of anthracene is destroyed and two separate benzene structures arise. Fig. 1a shows the changes with time in the electronic spectra of the copolymer upon illumination in ambient air. After 5 min. anthracene absorption bands between 350 and 400 nm disappear and an absorption band at about 200 nm grows due to the formation of a benzene-type product. The presence of isobestic points at 228, 276 and 315 nm indicates that only one photoreaction is going on. In the presence of oxygen this could be only the endoperoxide formation. This result shows that in ambient air the endoperoxide formation is a very rapid reaction and no photodimerization takes place, despite to the best conditions for photodimerization determined by the structure of anthracene containing monomer.

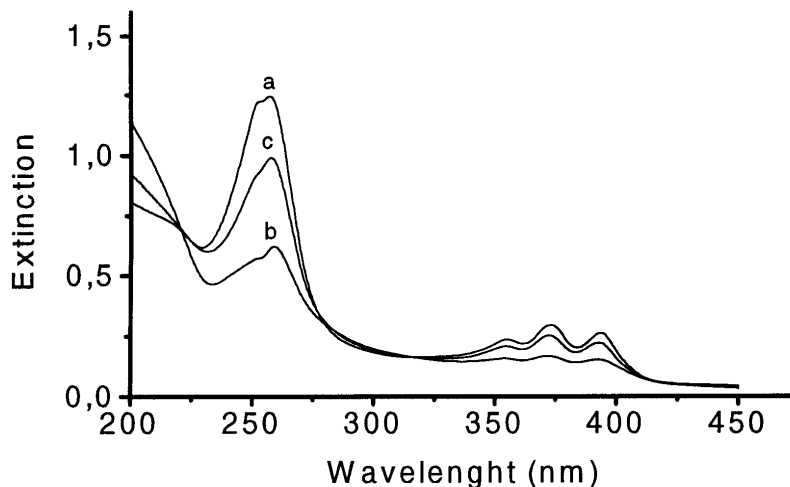
The changes in the spectra during the illumination in inert atmosphere (Fig. 1b) are slower. After 5 min. the decrease of anthracene content in a 0,3 μm thick film is only 10% of the initial. Even after 80 min. of illumination anthracene rings are still present. There are no isobestic points in this case, which is an indication that more than one photoreaction is going on. Obviously photodimerization is the most likely reaction occurring here. However, endoperoxide formation cannot be completely excluded since oxygen traces in the irradiated copolymer film are always present (16). It is hard to determine the ratio between the two reactions.

As already mentioned photodimerization reaction of anthracene is reversible upon illumination with light $\lambda < 300$ nm or upon thermal treatment (1, 7, 8). In a polymethacrylate where the anthracene units are connected with short spacers practically no decomposition of anthracene dimers takes place neither photochemically nor thermally (6). Two explanations are given - low anthracene dimer concentration or low cycloreversion probability. The latter is determined by the low mobility of the anthracene moieties(6). In our case the situation is quite different. We have observed real photodimerization in our copolymer upon illumination in inert atmosphere. Decomposition of the dimers could be expected also since anthracene moieties could move apart more easily due to the long spacers and the flexible ether linkages. We have not investigated the photodecomposition since it was shown that under photoirradiation at $\lambda < 300$ nm both anthryl group and the photodimer absorb photoenergy and the reactions are reversible (1). Thermal treatment however has confirmed our expectations. Thus after treatment for 60 min at 130°C of an illuminated copolymer its anthracene content reaches about 60 % of the initial value (Fig.2).

As results of this investigation we may draw the conclusion that connecting anthracene moieties with the main polymer chain with long spacers really improve the photodimerization and the thermal back reaction.

Nevertheless under ambient air the only photoreaction is the endoperoxide formation, which seems to be a very fast reaction.

Fig. 2. UV-Vis spectra of the copolymer a) before illumination ; b) after illumination for 60 min. in nitrogen ; c) after thermal treatment of the illuminated sample for 60 min. at 130°C



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