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Copolymerization of 9-Anthrylmethylmethacrylate with Maleic Anhydride

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SUMMARY

Copolymerization of 9-anthrylmethylmethacrylate with maleic anhydride is presented. The copolymerization reaction appears to be associated with the cycloaddition of maleic anhydride at the anthracene nucleus. It is also shown that for 9-anthrylmethylmethacrylate/maleic anhydride molar ratio lower than 1/2 the copolymers have an alternating structure with 1/2 composition

INTRODUCTION

In a previous paper (1) the radical copolymerization of 9-anthrylmethylmethacrylate (electron donor monomer) with acryloyl-β-hydroxyethyl (and 6-hydroxyhexyl)-3.5-dinitrobenzoate (electron acceptor monomers), leading to copolymers of intramolecular charge transfer complexes (CTC) type was presented. The formation of intermonomer CTC and its participation in copolymerization process was evidenced by different methods.

Maleic anhydride is known to be a strong electron acceptor monomer and it has been generally accepted that it can readily undergo alternating copolymerization with olefins, dienes, ethers and aromatic compounds (2), even in the absence of radical initiators. In most of these copolymerizations it has been assumed that a CTC with a small equilibrium constant was formed between both monomers and it was considered that this complex plays an important role on initiation and propagation reactions.

The present paper will describe the radical copolymerization of 9-anthrylmethylmethacrylate (9-AMMA) with maleic anhydride (MA). The Diels-Alder addition of MA to anthracene is a well known reaction. Therefore, one has to expect that besides the copolymerization reaction of the two monomers the cycloaddition of MA to anthracene nucleus takes place.

EXPERIMENTAL

9-Anthrylmethylmethacrylate (9-AMMA) was obtained from 9-methylolanthracene and methacryloyl chloride (3).

Maleic anhydride (MA) was of commercial grade and purified by recrystallization from chloroform solution and then sublimated.

9-AMMA/MA Diels-Alder adduct was obtained by heating an equimolar mixture of the two monomers in dioxane,for 24 hours at 90°C. The product was purified by recrystallization from acetone . The reaction yield was 92%.
^{1}H-NMR spectrum in acetone-d_6 (δ,ppm); 2.00 (singlet,CH_3 group), 3.80 (doublet, CH-CH group) ,4.90 (singlet,the proton H_{10} of dihydroanthracene nucleus), 5.55 (singlet,CH_2-O group), 5.65 and 6.10 (doublets,=CH_2 group) and 7.30 (multiplet, aromatic protons).
Copolymers Copolymerization **was** carried out at 90°C into sealed ampoules and using dioxane as solvent. The total concentration of monomers was 0.5 mol/l in all cases,and the copolymer composition was varied by the ratio between comonomers. AIBN was used as initiator (1% by weight). The copolymers were precipited with petroleum ether. The total MA content in copolymers was determined by hydrolysis followed by titration with an 0.1 M NaOH solution. The content of anthracene groups was estimated from UV spectra (UNICAM SP 800 B spectrophotometer) using the absorption band at 390 nm and a molar extinction coefficient of 18 $g^{-1}.l.cm^{-1}$.

RESULTS AND DISCUSSION

The copolymerization data are given in Table 1. One observes that the samples 4-7 show a maleic anhydride content higher than 50% although the MA-MA enchainments are not expected for the experimental conditions used in this copolymerization. This is evidently due to the addition of MA at the anthracene nucleus.NMR and UV spectra (Figures 1 and 2) argue for this interpretation. Indeed,the following observations arise from the comparison of ^{1}H-NMR spectra of poly(9-AMMA) and 9-AMMA/MA copolymers;

-the disappearance of the signal at 5.8 ppm,attributed to the methylene groups directly bonded to the anthracene nucleus

-an evident decrease of the intensity of the signals at 7.9 and 8.0 ppm,attributed to aromatic protons

-a shift from 0.7 to 1.2 ppm for the signal of methyl groups,and

-the appearance of new and broad signals at 3.3, 3.6, 4.3 and 5.0 ppm,their assignment being based on the NMR spectrum of 9-AMMA/MA adduct. It has to be mentioned that the decrease of screening for the methyl protons is produced by the decrease of anthracene nucleus aromaticity,which is associated with a restriction of screening regions.

The UV spectra (Figure 2) reflect the addition of MA on the anthracene nucleus as follows: the intensities of absorption bands at 260,320,337,370 and 390 nm for normal anthracene group decrease continuosly from sample 1 to sample 4 becoming neglijable for samples 5-7.In the same time new absorption bands appear at 258,279 and 295 nm due to 9.10 dihydroanthracene nucleus.

Thus,the structure of the copolymers is the following one:

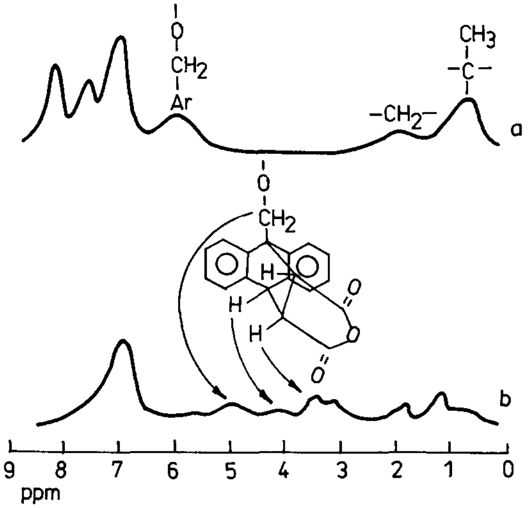


Figure 1- ^{1}H-NMR spectra of poly(9-AMMA)(a) and (9-AMMA/MA) copolymer (sample 3)(b) (CDCl$_3$,60 MHz,room temperature).

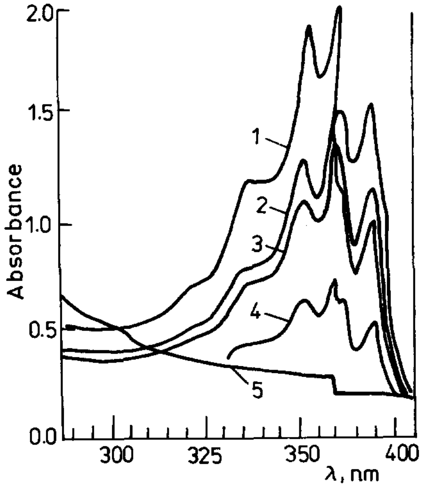
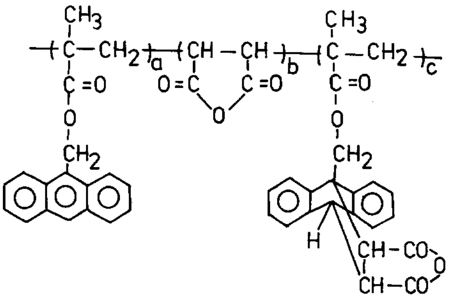


Figure 2

UV spectra of (9-AMMA/MA) copolymers,in chloroform:
1) sample 1,c=0.1777 g/l,
2) sample 2,c=0.0967 g/l,
3) sample 3,c=0.1528 g/l,
4) sample 4,c=0.2107 g/l,
5) sample 5,c=0.3866 g/l.



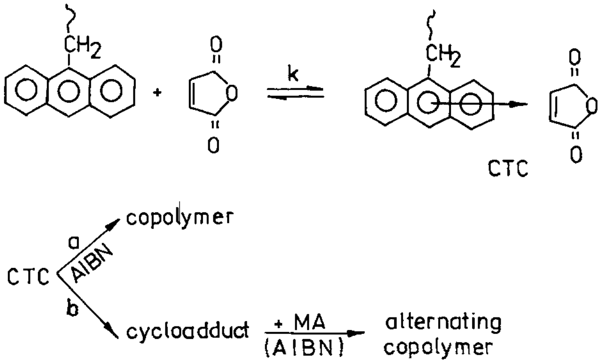
where a,b and c are given in the Table 1.Starting with sample 5,a becomes equal with 0.

Table 1- Copolymerization data of 9-anthrylmethylmethacrylate (M_1) and maleic anhydride (M_2). Reaction conditions:90°C,24 hours,in dioxane.

Sample	f_2	Yield %	F'_2	F_2	F_a	F_b	F_c
1.	0.125	63.1	0.204	0.162	0.746	0.154	0.050
2.	0.250	62.9	0.242	0.176	0.678	0.162	0.080
3.	0.375	57.9	0.406	0.244	0.378	0.190	0.216
4.	0.500	40.3	0.572	0.403	0.145	0.289	0.283
5.	0.625	37.5	0.666	0.500	-	0.333	0.333
6.	0.750	31.6	0.666	0.500	-	0.333	0.333
7.	0.875	9.4	0.666	0.500	-	0.333	0.333

F'_2 - the molar fraction of MA in the reaction product,determined by titration with a 0.1 M NaOH solution
F_a - the molar fraction of anthracene groups in copolymers, determined by the absorption in UV range
F_b - the molar fraction of MA in the main chain
F_c - the molar fraction of MA (or 9-AMMA) in the Diels-Alder adduct.
$f_2= [M_2]/[M_1]$,$F_2 = d[M_2] / d[M_1]$,Relations: $F'_2 + F_a + F_c = 1$, $F'_2 = F_b + F_c$

Therefore,in the 9-AMMA-MA copolymerization two reactions take place: a) the radical copolymerization (by methacryl group) and b) the cycloaddition reaction (on the anthracene nucleus). One can consider that the 9-AMMA is a bifunctional monomer when it is copolymerized with MA. Normally,one can suppose that the cycloaddition of MA at anthracene nucleus is preceded by the formation of a CTC. Such a complex was really confirmed by the NMR spectrum of MA,the proton signal of which is about 0.1 ppm shifted to higher fields when 9-AMMA is added in excess (in dioxane).



The contribution of the intermonomer complex in the copolymerization of MA with electron donor monomers was previously evidenced (4-6) and studied as a function of solvent polarity (7).

In our case ,this complex might be the intermediate for both copolymerization and cycloaddition. However,the decrease of polymerization rate with the MA content in the initial mixture indicates that this complex has a minor contribution to the copolymerization process. Also, from the Table 1 it can be seen that the samples 5-7 are alternating copolymers with 1/2 9-AMMA/MA composition.The homopolymerization of 9-AMMA/MA adduct does not occure. One the other hand it was observed that the copolymerization between this adduct and MA leads to an alternating copolymer with the 9-AMMA/MA ratio equal to 1/2. These observations allow the following suppositions to be considered:

- the Diels-Alder addition is faster than the copolymerization reaction,and
- the copolymerization of Diels -Alder adduct and MA is an alternating one.

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