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23. Copolymers of 9-Anthrylmethylmethacrylate with Acryloyl-β-Hydroxyethyl-3,5-Dinitrobenzoate and Acryloyl-6-Hydroxyhexyl-3,5-Dinitrobenzoate

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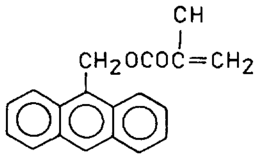
Dedicated to Professor H.-J. Cantow on his 60th birthday

SUMMARY

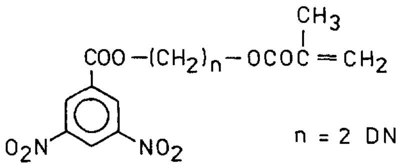
The copolymerization mechanism and the complexation properties of the copolymers of 9-anthrylmethylmethacrylate with acryloyl- β -hydroxyethyl-3.5-dinitrobenzoate and acryloyl-6-hydroxyhexyl-3.5-dinitrobenzoate are presented. The degree of complexation was found to increase by decreasing the difference between the side chain lengths and by increasing the flexibility of the main chain. The strength of complexation was estimated by considering the dependence of the chemical shifts of the aromatic protons on copolymer composition.

INTRODUCTION

In some previously papers (GRIGORAS et al.1982,PERCEC et al.1981a) the strength of complexation in methacrylate-methacrylate and acrylate-acrylate copolymers of poly(donor-co-acceptor) type was evidenced to be dependent on the structure ,length and flexibility of the side chains bonding the pendant groups to the main chain.To extend the structure-properties correlation,this paper is concerned with two similar copolymers but having a methacrylate-acrylate structure of the main chain, namely poly(9-anthrylmethylmethacrylate-co-acryloyl- β -hydroxyethyl-3.5-dinitrobenzoate) and poly(9-anthrylmethylmethacrylate-co-acryloyl-6-hydroxyhexyl-3.5-dinitrobenzoate).



9-AMMA



n = 2 DNBA

n = 6 DNBHA

EXPERIMENTAL

9-AMMA was obtained from 9-methylolanthracene and methacryloyl chloride (IWATSUKI and INUKAI 1978).

DNBA was synthesized as previously described (PERCEC et al. 1981b).

DNBHA was synthesized from acryloyl chloride and 6-hydroxyhexyl-3.5-dinitrobenzoate,as follows:

A mixture of 10 ml (0.12 mole) acryloyl chloride and 50 ml benzene was added dropwise (during 30 minutes) under vigorous stirring to a solution of 30 g (0.10 mole) 6-hydroxyhexyl-3.5-dinitrobenzoate and 17 ml (0.12 mole) triethylamine in 200 ml anhydrous benzene,the solution being maintained at 8°C. The resulting mixture was stirred 3 hours at 8°C and 6 hours at room temperature.The obtained precipitate ($NEt_3.HCl$) was filtered and washed several times with benzene .The benzene solution was washed with water and dried on $CaCl_2$. After benzene evaporation the viscous liquid was recrystallized twice from methanol giving 25 g (71 %) white crystals (m.p.39-40°C).

Anal. calc'd for $C_{16}H_{18}N_2O_8$ (366.33);C,%=52.46;H,%=4.95; N,%=7.65 and O,%=34.94.

Found:C,%=52.79;H,%=4.80 and N,%=7.58.

^{1}H-NMR ($CDCl_3$):1.5-2.3 ppm ($-CH_2-CH_2-CH_2-CH_2-$), 4.1-4.7 ppm ($-O-CH_2-$) ,5.72-6.35 ppm ($-CH=CH_2$) and 8.9-9.1 ppm (aromatic protons).

The copolymerization reactions were performed at 60°C,in dioxane solutions under argon in sealed ampoules.The total monomer concentration was 0.5 mole/l and the initiator (AIBN) was 1 % from the monomers .The copolymers were precipitated in methanol and purified by dissolving in tetrahydrofuran and reprecipitated with methanol. Their composition was determined from ^{1}H-NMR spectra,which were obtained at 90°C in dioxane. A JNM-C-60HL spectrometer working at 60 MHz was used.

^{1}H-NMR signals characteristic to the two copolymers are the following ones: 8.4-8.8 ppm for the aromatic protons of DNBA and DNBHA , 7.8 and 7.2 ppm for the aromatic protons of 9-AMMA, 5.7 ppm for $-CH_2-O-$ groups of 9-AMMA, 4.3 ppm for $-CH_2-O-$ groups of DNBA and DNBHA ,1.4 ppm for $-C-CH_2-CH_2-C-$ group in DNBHA,and a very broad signal between 2 and 0.6 ppm for the groups on the main chain. All signals are broad and the last one shows a relative maximum at 0.8 ppm due to the $-CH_3$ protons.

RESULTS AND DISCUSSION

Copolymerization mechanism

The copolymerization data for both copolymers are given in Table 1. One observes that the reactivity order in these copolymerizations are the following:

9-AMMA > DNBHA > DNBA

and that both acceptor monomers used here ,DNBA and DNBHA, are less reactive than their methacrylate homologous (GRIGORAS et al.1982).

Table 1

Copolymerization data

	9-AMMA-DNBA			9-AMMA-DNBHA		
x	Sample	Conversion (%)	y	Sample	Conversion(%)	y
7.00	1	56.40	13.49	8	77.60	a)
3.00	2	49.70	8.09	9	51.60	7.85
1.67	3	38.20	5.69	10	45.40	3.40
1.00	4	30.30	3.67	11	29.20	2.39
0.60	5	19.00	2.64	12	19.40	1.74
0.33	6	14.10	1.78	13	11.70	1.19
0.14	7	9.10	0.90	14	-	-

$x=[M_1]/[M_2]$; $y=d[M_1]/d[M_2]$; M_1=9-AMMA ;M_2=DNBA and DNBHA time=100 hours. a) copolymer composition was not possible to be determined by NMR.

The processing of copolymerization data according to the Kelen-Tudos method for high conversions (TUDOS et al.1976) leads to the diagrams presented in figure 1,both diagrams support the possibility of a terminal copolymerization model.

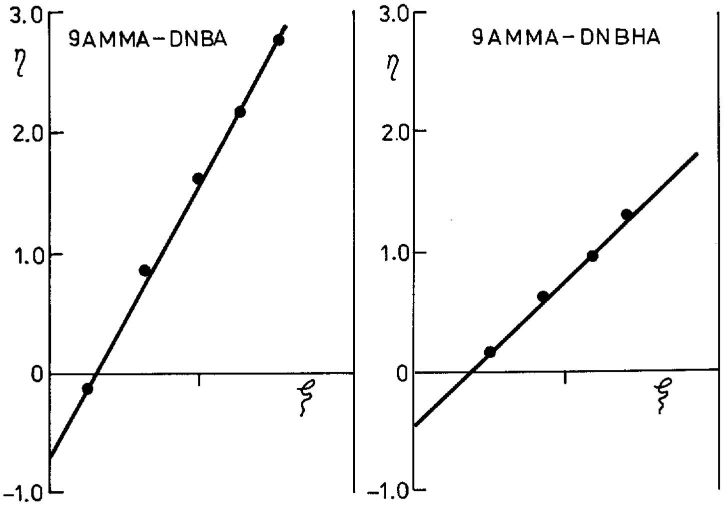


Figure 1- Kelen-Tudos plots

Although both DNBA and DNBHA do not homopolymerize in the same experimental conditions there are copolymers with more 50 % acceptor structural units of this type. One can conclude that the copolymerization mechanism implies in these cases the intermonomeric charge transfer complex (CTC) participation (PERCEC et al.1981b). The formation of such CTC is indicated by the orange colour of the mixture comonomer solutions. It was also proved,by the continuous variation method that the intermonomeric CTC has an 1:1 composition.

Degree of complexation

To estimate the complexation interactions in the two copolymers ,the NMR signals of the acceptor group (dinitrobenzoate) aromatic protons were registered (figure 2).

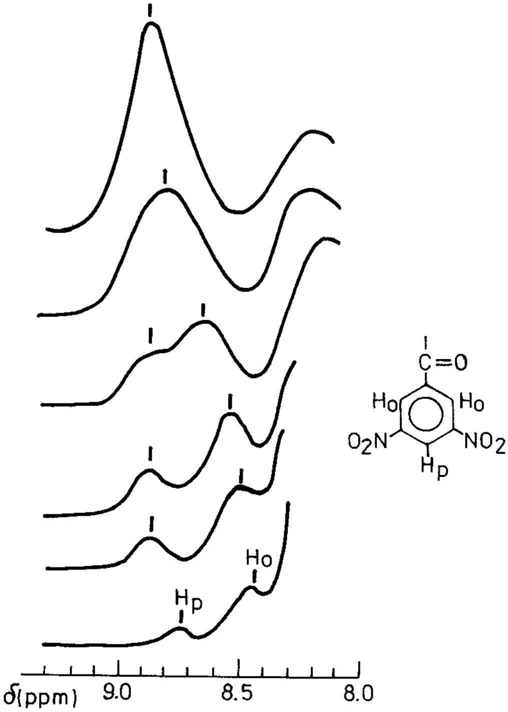


Figure 2- The NMR signals of the acceptor group aromatic protons in 9-AMMA-DNBA copolymer of various composition.

The first observation is that these protons give two distinct signals (at least for low content of acceptor units),while the same protons give only one signal in similar copolymers having a methacrylate-methacrylate main chain (GRIGORAS et al.1982).The assignment of signals in figure 2 is based on their relative intensities. The position of these signals dependence on copolymer composition may be explained if one supposes that the acceptor group mobility decreases by increasing the donor unit content. The fact that the chemical shift dependence on copolymer composition is stronger for the ortho protons than for the para ones is well illustrated in figure 3 and can be explained by the difference between their positions relative to the anthracene nuclei (donor groups) . Taking into account the slope of δ_0 curves (figure 3) it can

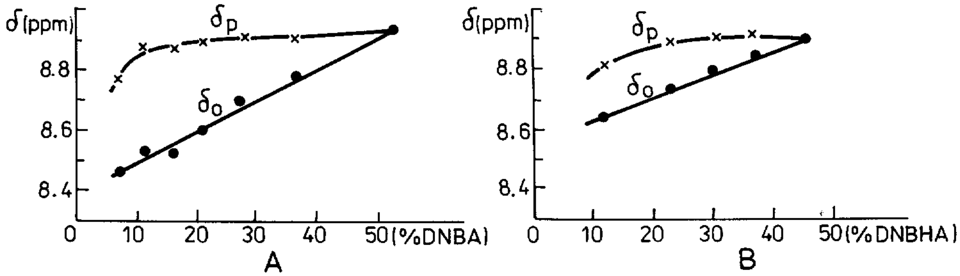


Figure 3- The chemical shifts of aromatic protons of acceptor units in 9-AMMA-DNBA (curves A) and 9-AMMA-DNBHA (curves B) copolymers against the composition.

stated that the donor -acceptor interactions are stronger in the 9-AMMA-DNBA copolymer,where the slope is of $1.1x10^{-2}$ ppm/ % DNBA, than in the 9-AMMA-DNBHA,where the slope is of $0.8x10^{-2}$ ppm/ % DNBHA. These could be explained by the difference between the side chain lengths,which is of 7-4 =3 bonds in the first case,and 11-4=7 bonds in the second one. Considering the same criterion,the 9-AMMA-DNBA copolymer is characterized by a higher degree of complexation than the 9-AMMA-methacryloyl- β-hydroxyethyl-3.5-dinitrobenzoate copolymer (GRIGORAS et al.1982),where the slope was found to be of about $0.7x10^{-2}$ ppm/ % DNBM and this fact may be interpreted by the main chain flexibility higher in the first case.

CONCLUSIONS

9-AMMA-DNBA and 9-AMMA-DNBHA copolymers show CTC characteristics as follows:an orange colour and an evident dependence of the ^{1}H-NMR spectral chemical shifts of the aromatic protons on copolymer composition.The complexation is stronger for 9-AMMA-DNBA copolymer than for 9-AMMA-DNBHA copolymer. These copolymers,which are of methacrylate-acrylate type,are characterized by stronger complexation interactions than similar copolymers of methacrylate-methacrylate type.The degree of complexation increases by decreasing the difference between the side chain lengths and by increasing the flexibility of the main chain.

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