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Intramolecular Charge Transfer Complexes

20. Copolymers of Acryloyl and Methacryloyl-2'-hydroxyethyl-2-(N-phenothiazinyl)Propionate with Methacryloyl-2'-hydroxyethyl-3,5-dinitrobenzoate

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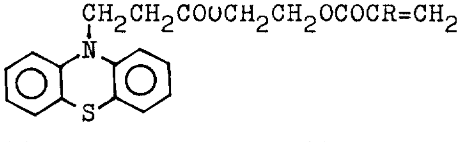
SUMMARY

Radical copolymerization of acryloyl (PtA)- and methacryloyl (PtM)-2'-hydroxyethyl-2-(N-phenothiazinyl)propionate with methacryloyl-2'-hydroxyethyl-3,5-dinitrobenzoate proceeds through a mechanism which implies intermonomeric complex participation. There are indirect proofs that the intramolecular charge transfer complexes obtained present a total electron transfer phenomenon at high temperatures.

INTRODUCTION

The electrono-donor monomers used up to now in the synthesis of intramolecular charge transfer complexes (CTC) by radical copolymerization with electrono-acceptor monomers were naphthyl (1), fluorenyl (2), carbazolyl (2-18) and N,N-dimethyl-p-aminobenzyl (19) derivatives. Of these, N,N-dimethyl-p-aminobenzyl methacrylate (DMABM) had the lowest ionization potential (7.21 eV with chloranil as acceptor (19)). Its copolymers with acryloyl (DNBA)- and methacryloyl (DNBM)-2'-hydroxyethyl-3,5-dinitrobenzoate heated in solution presented the irreversible phenomenon of total electron transfer, giving strong salt-like intramolecular charge transfer complexes.

Phenothiazine nucleus has a strong electrono-donor character. Having in mind the ionization potential values for two monomers based on phenothiazine :



R = H PtA
R = CH_3 PtM

of 7.23 eV, with chloranil as acceptor (20), and the very promising electric properties of some phenothiazine polymers (21), we present in this paper the synthesis of two intramolecular CTC by radical copolymerization of acryloyl (PtA)- and respectively, methacryloyl (PtM)-2'-hydroxyethyl-2-(N-phenothiazinyl)propionate (M_1) with DNBM (M_2).

EXPERIMENTAL

PtA, PtM (20) and DNBM (10) syntheses are presented else-

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where. Copolymerizations were performed in dioxane solutions, at 60°C, under argon, in sealed ampoules, at a total monomer concentration of 0.5 M. Copolymers were precipitated in methanol and purified by reprecipitation in methanol from tetrahydrofuran (THF) solutions. Copolymer composition was determined from the ^{1}H-NMR spectra registered in DMSOd_6 on a Jeol C-60HL spectrometer. A typical NMR spectrum is presented in figure 1. Electronic absorption spectra were recorded on a Unicam SP 800 spectrophotometer.

Copolymerization data are presented in table 1.

TABLE 1.
Copolymerization data

x	PtM-DNBM				PtA-DNBM			
	Sample	Time h	Conversion(%)	y	Sample	Time h	Conversion(%)	y
	poly(PtM)	22.0	84.7	-	poly(PtA)	22.0	82.3	-
7.00	1	3.0	14.2	6.69	8	3.8	4.2	2.85
3.00	2	3.7	17.7	2.70	9	7.2	7.1	1.44
1.67	3	4.9	20.8	1.50	10	7.3	7.7	0.82
1.00	4	5.0	19.0	0.89	11	7.4	8.6	0.52
0.60	5	5.0	13.8	0.54	12	7.4	10.6	0.30
0.33	6	5.1	11.6	0.30	13	7.5	12.3	0.15
0.14	7	5.2	9.6	0.12	14	7.5	12.3	0.06

Homopolymerizations were performed at 80°C.
$x = [M_1]/[M_2]$; $y = d[M_1]/d[M_2]$

RESULTS AND DISCUSSION

Copolymerization diagrams for the two systems are presented in figure 2.

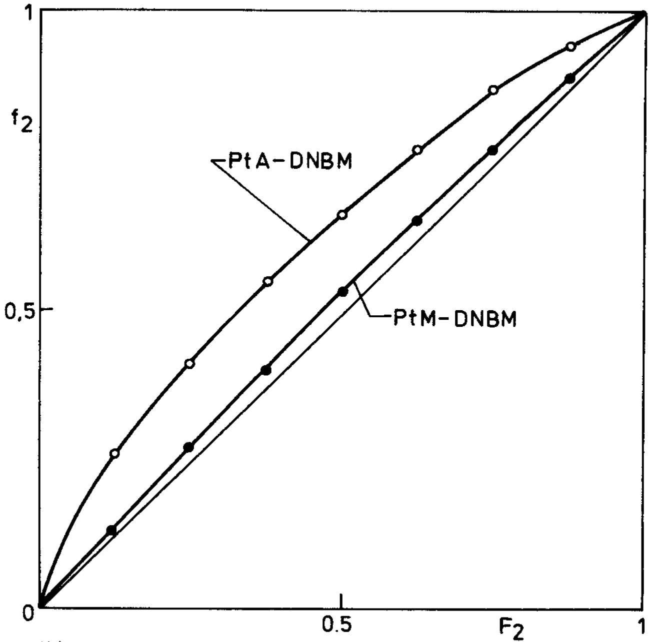

Figure 2. Copolymerization diagrams

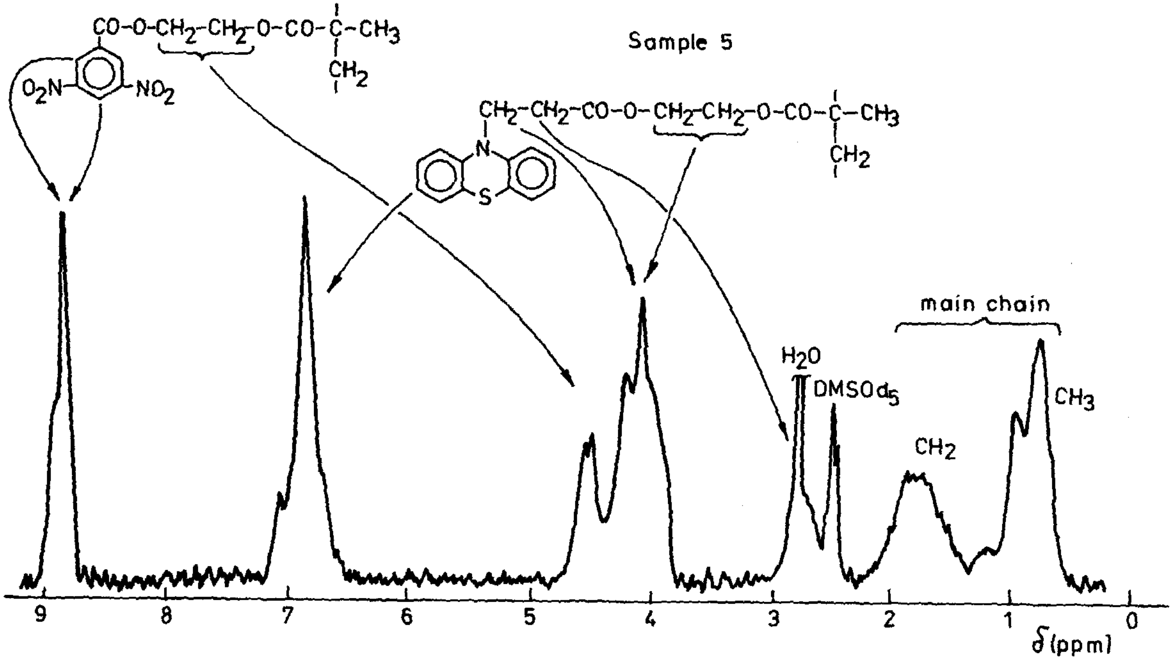

Figure 1. ^{1}H-NMR spectrum of sample 5 (DMSOd_6, 150°C)

Both phenothiazine monomers are less reactive than DNBM, but the methacrylate is more reactive than the acrylate, as in all cases analysed up to now. Data processing with the Kelen-Tüdös method at high conversions (22) gives the plot in figure 3.

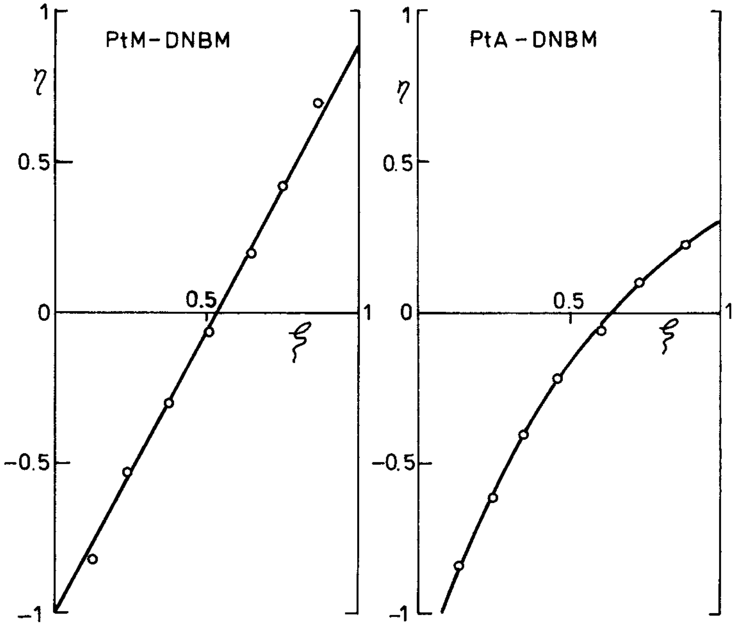

Figure 3. Kelen-Tüdos plots.

The PtM-DNBM system can be approximated by a straight line having the parameters :

$$r_1 = 0.88 \qquad r_2 = 1.11$$

The PtA-DNBM system generates a curve, indicating the non-validity of the terminal model. As demonstrated in previous papers (16-18), DNBM copolymerizes with electrono-donor monomers directly and through the intermonomeric CTC. When the homopropagation rates for both monomers are sufficiently high, the system can be treated as an apparently terminal one (10, 13). When the homopropagation rates are lower, the intermonomeric CTC role increases, and the Kelen-Tudös plots become curves rather than straight lines (18). This is the case for PtA-DNBM system, for instance.

The obtained copolymers are violet colored, unlike the homopolymers, which are white. The color becomes more intense when approaching to 1:1 copolymer composition. Copolymer solubility in dioxan, THF, DMSO and DMF also decreases near 1:1 compositions.

The intramolecular complexation degree is estimated measuring the chemical shift of the aromatic protons from DNBM structural units and plotting it against copolymer composition. In poly(DNBM) this shift is 8.95 ppm (10). For poly(PtA-co-DNBM) the plot in figure 4 is obtained.

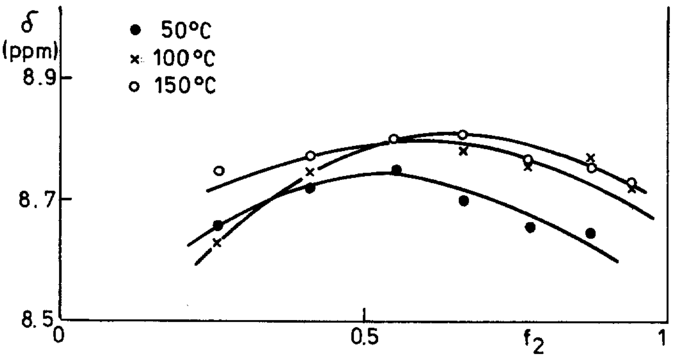

Figure 4. Chemical shift of DNBM structural units aromatic protons against copolymer composition for poly(PtA-co-DNBM).

The spectra registered at 50°C generate a curve having a maximum at ca. $f_2 = 0.5$. Increasing the spectrum registration temperature, the curve becomes flater, and its maximum seems to shift to higher f_2 values (0.55-0.6). A quite similar plot was obtained for poly(DMABM-co-DNBM) (19), where a cation-radical formation was evidenced.

The electronic absorption spectra of the mixture poly(PtM) - acetyl-2'-hydroxyethyl-3,5-dinitrobenzoate (registered in $CHCl_3$ and in THF) and of the copolymers (registered in THF), present a maximum at $\lambda = 450$ nm. In order to evidence the cation-radical appearance in the copolymer, the spectrum of sample 3 was registered in DMSO at room temperature, 50° and 100°C (figure 5).

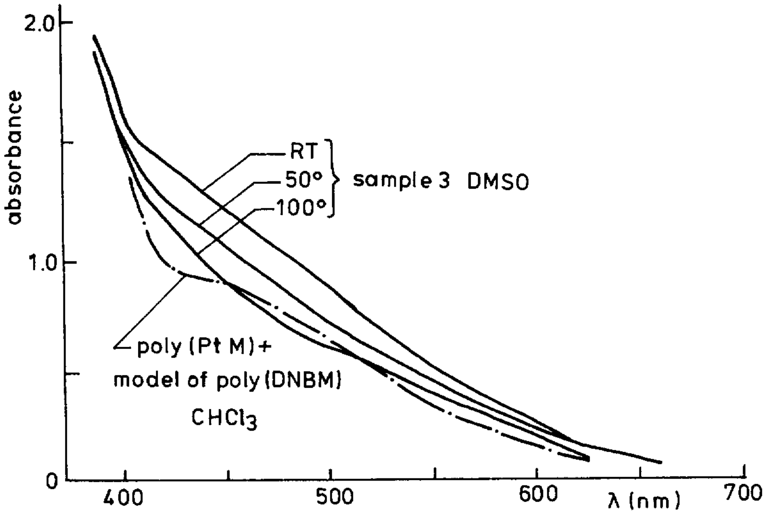

Figure 5. Electronic absorption spectra.

Indeed, by heating, the charge transfer band intensity diminishes and this region of the spectrum becomes flat. We assigned this change to the total electron transfer. The attempt to evidence the concomitent UV absorption appearance, corresponding to the phenothiazine cation-radical, failed, probably because of the overlapping intense absorption at 312 nm due to the phenothiazine nucleus. Therefore, there are no direct proofs for the electron total transfer, but only indirect ones : dissapearance of the CT band and the shape of the chemical shift plot, analogous to that obtained for poly (DMABM-co-DNBM) and poly(DMABM-co-DNBA) where cation-radical appearance was spectrally demonstrated (19). At cooling, the absorbance returns to the initial values, unlike poly(DMABM-co-DNBM) and poly(DMABM-co-DNBA), when the electron total transfer was irreversible. Consequently, one can say that poly(PtA-co-DNBM) and poly(PtM-co-DNBM) are weak CTCs at room temperature, and by heating, the electron total transfer phenomenon appears. The chemical shift plotted in figure 4 reflects the weak complexation which coexists with the strong one. At 150°C, the strong complex predominates and the weak complexation curve is flater.

The ionization potential value of the model for the donor structural unit is slightly higher (7.23 eV (20)) than that of the DMABM structural unit model (7.21 eV (19)) determined in the same conditions. This fact, correlated with the bigger distance between the donor group and the main chain, which can be unfavourable to complexation (20), can explain the stronger CTC character of poly(DMABM-co-DNBM) and poly(DMABM-co-DNBA) as compared with those derived from phenothiazine. For DMABM copolymers, the distance between the donor group and the main chain is much lower than that between the acceptor group and the main chain, consequently the donor group has a low mobility. The electron total transfer, taking place at high temperatures, is irreversible, because, lowering the temperature, the return to the conformation of the weak complex is very improbable.

In poly(PtA-co-DNBM) and poly(PtM-co-DNBM), both the donor and acceptor groups are sufficiently distant from the main chain in order to permit the return to the weak complex state at cooling. Unfortunately, one cannot evidence this state measuring the chemical shifts of the aromatic protons from DNBM structural units, because the copolymer solubility is very poor at room temperature, below the sensitivity limit of the NMR spectrometer. Even at 50° and 100° C the copolymer solubility is low and the error in chemical shift determination increases.

CONCLUSIONS

Copolymerization of PtA and, respectively, PtM with DNBM takes place through a mechanism implying intermonomeric CTC participation. This mechanism is obvious for PtA-DNBM, when the Kelen-Tüdös plot is a curve. Poly(PtA-co-DNBM)and poly (PtM-co-DNBM) are intramolecular CTCs presenting at high temperatures a total electron transfer phenomenon. At room temperature the complex returns to its weak state.

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