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Intramolecular Charge Transfer Complexes

7. Radical Copolymers of 2,4-Dinitrophenyl Methacrylate with N-(2-Hydroxyethyl)-3,6-Dichlorocarbazolyl Acrylate and Methacrylate*

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Dedicated to our Prof. C.I. Simionescu in occasion of his 60th anniversary

SUMMARY

Radical copolymerization of 2,4-dinitrophenyl methacrylate (DNPM, M_2) with N-(2-hydroxyethyl)-3,6-dichlorocarbazolyl methacrylate ($HECl_2CM$, M_1) and N-(2-hydroxyethyl)-3,6-dichlorocarbazolyl acrylate ($HECl_2CA$, M_1) takes place by the simple terminal mechanism having the parameters:

r_1=0.13 r_2=1.65 (M_1=$HECl_2CM$)
r_1=0.13 r_2=1.20 (M_1=$HECl_2CA$)

Intramolecular complexation differences for the two obtained systems are explained by configurational differences.

INTRODUCTION

In the precedent papers (1-6), some intramolecular charge transfer complexes (CTC) synthesis was studied by radical copolymerization of electrono-donor (M_1) and electrono-acceptor (M_2) monomer pairs. The influence of some factors affecting the microstructure and the intramolecular complexation of the obtained copolymers was also evidenced.

Copolymerization of these monomer pairs takes place through a simple terminal mechanism (5), especially when the K-value of the intermonomeric CTC equilibrium constant is rather low, or through a mechanism which involves the intermonomeric CTC participation (1,2,4,6,7).

From the data presented in the previous papers, one can conclude that the copolymer microstructure is determined by different factors (8):

- through the value of K
- through the individual propagation reaction rates

Of these factors, the ionization potential (I_D) of the donor monomer and the electronic affinity (E_a) of the acceptor monomer, are the most important in intramolecular complexation.

This paper studies radical copolymerization of 2,4-dinitrophenyl methacrylate (DNPM) with N-(2-hydroxyethyl)-3,6-dichlorocarbazolyl methacrylate ($HECl_2CM$) and N-(2-hydroxyethyl)-3,6-dichlorocarbazolyl acrylate ($HECl_2CA$), respectively. The ionization potential values of 3,6-dihalogencarbazole monomers are higher than those for carbazole monomers (9,10).

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*6th part in this series: reference (6)

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EXPERIMENTAL

DNPM was synthesized according to the literature (11), HECl$_2$CM and HECl$_2$CA were prepared as previously described (10). Copolymerizations were carried out in dioxane, with 1% (based on monomers) AIBN, under argon at 60°C. Dioxane and AIBN were purified by usual methods (1). Total monomer concentration was in all cases 0.3125 M. The copolymers were separated from the reaction mixture by precipitation with a 1/1 (v/v) mixture methanol/acetone and purified by reprecipitation from tetrahydrofuran solutions with the same solvents mixture. Copolymer composition was determined from the ^{1}H-NMR spectra registered at 60°C and 25°C in DMSO-d$_6$ and dioxane solutions on a JEOL C-60 HL spectrometer. UV-visible spectra were obtained on a UNICAM SP 800 spectrophotometer at concentration of 0.3125 M in dioxane. Poly(DNPM) was obtained by radical polymerization of DNPM (5). Copolymerization results are given in table 1.

TABLE 1
Copolymerization data

Sample	F_1	HECl$_2$CM-DNPM			HECl$_2$CA-DNPM		
		Time (hr)	Conversion (%)	f_1	Time (hr)	Conversion (%)	f_1
1D	0.875	6.5	3.8	0.630	7.7	10.9	0.605
2D	0.750	10.1	3.8	0.500	7.8	6.8	0.510
3D	0.625	15.2	3.9	0.420	10.0	6.1	0.420
4D	0.500	17.0	3.6	0.350	10.1	4.2	0.340
5D	0.375	20.4	4.8	0.280	10.2	5.4	0.265
6D	0.250	21.9	3.1	0.200	10.2	5.9	0.185
7D	0.125	26.9	4.5	0.100	10.3	5.7	0.095

F_1= molar fraction of M_1 in the initial mixture; f_1=molar fraction of M_1 in the copolymer

RESULTS AND DISCUSSIONS

When mixing the solutions of the two monomer pairs, a yellow colour is obtained, due to intermonomeric complexation. Using Job's method (12), the complex composition is proved to be 1:1 from the absorption spectra.

For both monomer pairs, the Kelen-Tudos (13) plots are straight lines (figure 1), and this proves that the copolymerization mechanism can be approximated by a simple terminal model having the parameters:

HECl$_2$CM - DNPM $r_1 = 0.13$ $r_2 = 1.65$
HECl$_2$CA - DNPM $r_1 = 0.13$ $r_2 = 1.20$

Diad sequences fractions are calculated according to Harwood's algorithm (14): $f_{12}=2f_1P_{12}$ where P_{12} is the probability of M_2 addition at M_1-ended macroradical. $P_{12}=1/(1 + r_1x)$ and $x=F_1/F_2$.

As demonstrated in the previous papers (1-7) the intramolecular complexation can be evidenced by measuring the chemical shift of the aromatic protons of acceptor structural units. The actual chemical shift of this signal is a ponderate average of uncomplexed and complexed states. The higher is this chemical shift, the higher is the intramolecular complexation degree.

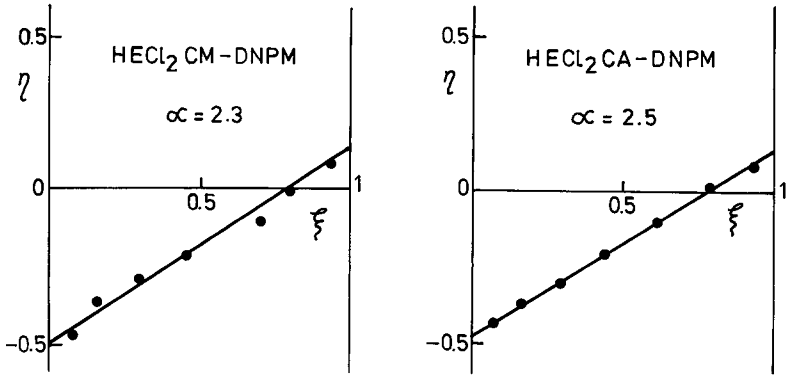

Figure 1. Kelen-Tudos plots for the two copolymerization systems.

The aromatic region of some $HECl_2CA$-co-DNPM samples (spectra registered in DMSO-d_6 at 60°C) is presented in figure 2. The shift of 3-rd and 5-th aromatic protons of DNPM structural units to higher fields when decreasing DNPM content in the copolymer is observed. The $HECl_2CM$-co-DNPM samples spectra do not present observable shifts in similar conditions. For this last system, in the spectra registered in dioxane (more inert solvent than DMSO) a slight shift of 3-rd and 5-th protons signals from DNPM structural units can be observed at 25°C.

Because the 3-rd aromatic proton of DNPM structural units is the most deshielded (and therefore easier to be measured), its chemical shift is represented against DNPM structural units fraction laying in alternating diad sequences ($\frac{1}{2}f_{12}/f_2$) (figure 3).

Intramolecular complexation is determined by the possibility to have a favourable steric arrangement of electrono-donor and electrono-acceptor groups, therefore depends on sequence distribution, configuration and conformation of the side-chain and the chain segments (1). It seems reasonable that the conformation, at least for the side-chains, in the same solvent at the same temperature, can be considered the same. Consequently, the differences of intramolecular complexation evidenced in figure 3 must be explained by the different configuration of the two systems. As it can be seen in figure 3, $HECl_2CA$-co-DNPM is a stronger intramolecular CTC than $HECl_2CM$-co-DNPM, where the intramolecular complexation is very weak. The same phenomenon is evidenced when analysing the systems N-(2-hydroxyethyl) carbazolyl methacrylate (HECM)-co-picryl methacry-

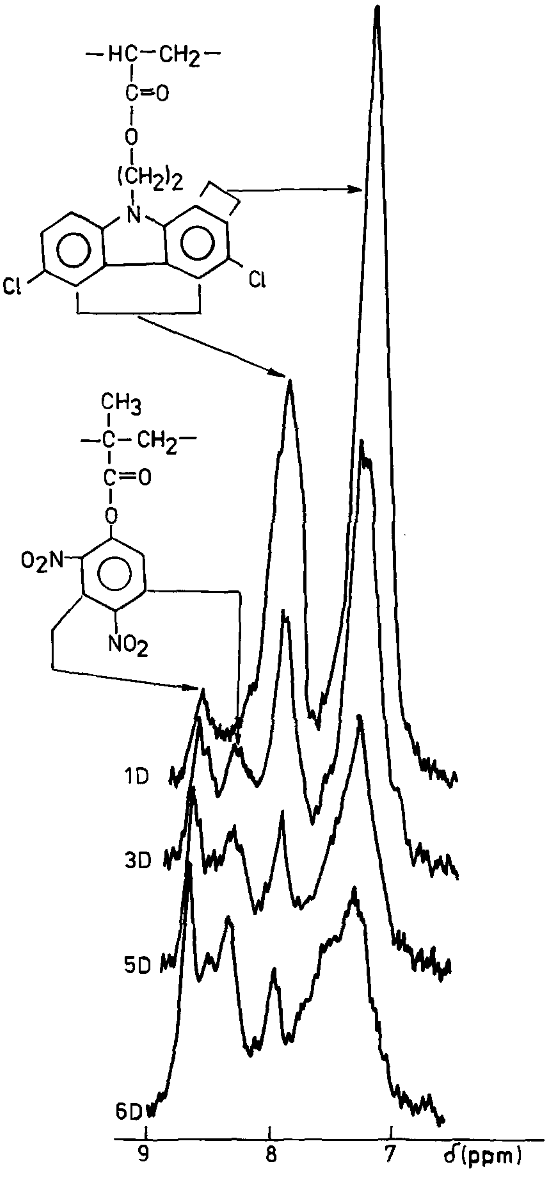

Figure 2. Aromatic region of some $HECl_2CA$-co-DNPM samples.

late (PM) (1) in comparision with N-(2-hydroxyethyl) carbazolyl acrylate (HECA)-co-PM (4) and HECM-co-DNPM (5) with HECA-co-DNPM (15).

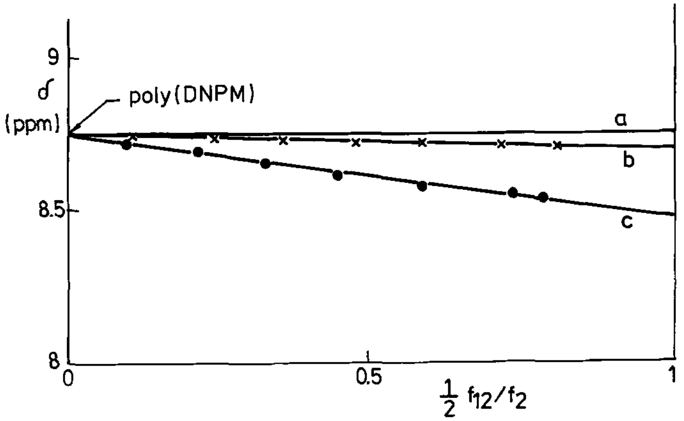

Figure 3. Chemical shift of the 3-rd aromatic proton of DNPM structural units against DNPM fraction being in alternating diad sequences: a) $HECl_2CM$-co-DNPM in DMSO-d_6 at 60°C; b) $HECl_2CM$-co-DNPM in dioxane at 25°C; c) $HECl_2CA$-co-DNPM in DMSO-d_6 at 60°C.

Figure 4 represents the chemical shift of the aromatic protons from PM structural unit in HECM-co-PM and HECA-co-PM systems (spectra registered in $CDCl_3$ at 60°C), and figure 5 the chemical shift of 3-rd aromatic proton from DNPM structural unit in HECM-co-DNPM and HECA-co-DNPM (spectra registered in DMSO-d_6 at 60°C).

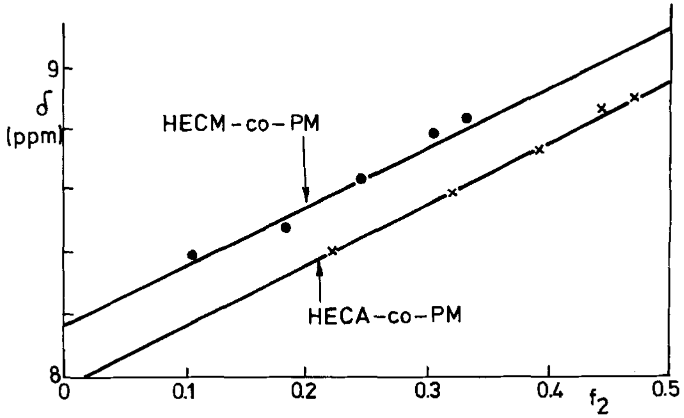

Figure 4. Chemical shift of the aromatic protons from PM structural unit against PM fraction.

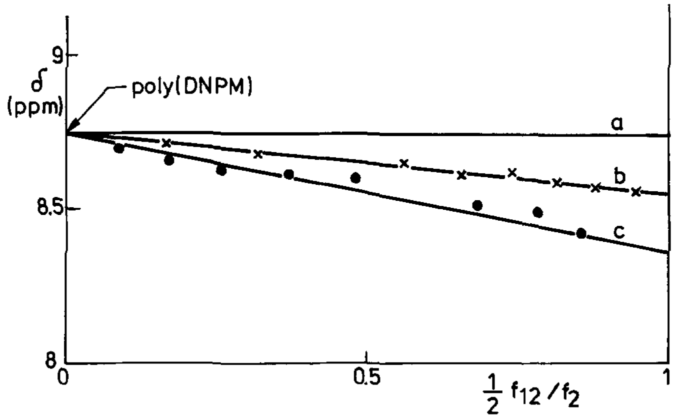

Figure 5. Chemical shift of the 3-rd aromatic proton of DNPM structural units against DNPM fraction being in alternating diad sequences: a) HECM-co-DNPM in DMSO-d_6 at 60°C; b) HECM-co-DNPM in dioxane at 25°C; c) HECA-co-DNPM in DMSO-d_6 at 60°C.

In all cases, the intramolecular complexes of acrylate-type donor monomer are stronger than those from methacrylate-type donor monomer.

The configurational differences of the two types of systems are supposed to be due to the sterical determination (through the α-methyl substituent) of substituents arrangement with respect to the main chain. Ito et al (16) proved this for some copolymerization systems where the intermonomeric interaction is rather poor. The unsubstituted monomers in α-position lead to a predominantly coisotactic configuration (i); if both monomers are α-substituted, a cosindiotactic preference results (ii); only one α-substitution produces an atactic chain (iii). The systems having HECA or $HECl_2CA$ as donors are of iii-type, and those having HECM or $HECl_2CM$ as donors are of ii-type. This explains the stronger complexation of iii-type systems.

When the intermonomeric complex plays an important part in copolymerization (1,4) it is reasonable to suppose that it markedly influences the steric course of the propagation reactions. In these systems, the configuration obtained from an intermonomeric CTC addition must be coisotactic and favoures the intramolecular complexation. This is the explanation why HECM-co-PM is a rather strong intramolecular complex, whilst HECM-co-DNPM presents a very poor intramolecular CTC character.

It is expected that acrylate-acrylate type systems will have the strongest intramolecular interaction. Work is now in progress on the systems HECA-co-2,4-dinitrophenyl acrylate and HECA-co-picryl acrylate.

CONCLUSIONS

Radical copolymerization of DNPM with $HECl_2CM$ and $HECl_2CA$, respectively, can be described by the simple terminal mechanism. Intramolecular complexation differences between the two systems are explained by configurational differences.

Abbreviations

The monomer mixture is indicated by the initials of the two monomers (for example HECA-PM) and their copolymer by the initials separated by -co- (for example HECA-co-PM).

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