

## **Intramolecular Charge Transfer Complexes**

### **10. Radical Copolymers of Methacryloyl $\beta$ -Hydroxyethyl-3,5-Dinitrobenzoate with N-(2-Hydroxyethyl)Carbazolyl Acrylate and Methacrylate**

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#### SUMMARY

A new acceptor monomer (methacryloyl  $\beta$ -hydroxyethyl 3,5-dinitrobenzoate), having an increased distance between the acceptor group and the double bond, was copolymerized with N-(2-hydroxyethyl)carbazolyl methacrylate and acrylate, respectively. The copolymers are strong intramolecular charge transfer complexes, even at high temperatures. Because the increased distance between the acceptor group and the main chain permits a favourable steric arrangement of the donor and acceptor groups, the intramolecular complexation is independent on copolymer configuration.

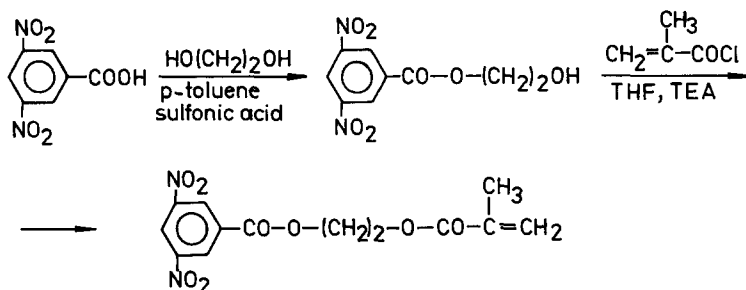
#### INTRODUCTION

In a series of previous papers (1-11), intramolecular charge transfer complexes (CTC) were obtained by radical copolymerization of electrono-donor and electrono-acceptor monomer pairs. As electrono-acceptor monomers, picryl methacrylate (PM) (1,2,4,5,10,11), 2,4-dinitrophenyl methacrylate (DNPM) (6-8,11) and 2,4-dinitrophenyl acrylate (DNPA) (9) were used. When at least one of the comonomers does not homopolymerize, the copolymerization must be described by a mechanism which implies the intermonomeric CTC participation. Then, copolymer sequence distribution and configuration are strongly affected by the intermonomeric CTC concentration (11). By increasing the intermonomeric CTC concentration, both alternating diad fractions and coisotactic alternating sequences are increased as a consequence of the increased CTC addition probability. When both monomers can homopolymerize, the copolymerization may be described approximately by the simple terminal model, and the copolymer constitutional and configurational sequence distribution will not be modified significantly by the intermonomeric CTC concentration. When the acceptor group is directly bonded to the copolymer main chain (as for PM, DNPM and DNPA structural units), the decrease of the coisotactic alternating sequences can lead to a copolymer which has no intramolecular CTC character (7).

It can be supposed that the configuration influence on intramolecular complexation could be avoided by increasing the distance between the donor (or acceptor) group and the main chain. When the chain between this group and the double bond of the monomer is rather long and flexible, the intramolecular complexation in alternating diads should be realized for both meso and racemic (coiso and cosyndio) configurations. The aim of this paper is to verify this hypothesis on intramolecular CTC obtained by copolymerization of monomers having the donor and acceptor groups at longer distances from the double bonds, as compared with those studied previously. The monomers are : methacryloyl  $\beta$ -hydroxyethyl-3,5-dinitrobenzoate (DNBM,  $M_2$ ) and N-(2-hydroxyethyl)carbazolyl acrylate (HECA) or N-(2-hydroxyethyl)carbazolyl methacrylate (HECM), ( $M_1$ ), respectively.

#### EXPERIMENTAL

HECM (1) and HECA (4) were synthesized according to the already described methods. DNBM was synthesized by the following reaction sequence :



$\beta$ -hydroxyethyl-3,5-dinitrobenzoate was synthesized by 3,5-dinitrobenzoic acid esterification with ethylene glycol according to a published method (12). The m.p. and IR and NMR spectra correspond to those in literature.

Methacryloyl  $\beta$ -hydroxyethyl-3,5-dinitrobenzoate. A mixture of 5.52 g (0.0529 mole) methacryloyl chloride and 10 ml tetrahydrofuran (THF) was added dropwise (during 20 minutes) under vigorous stirring to a solution of 10 g (0.0378 mole)  $\beta$ -hydroxyethyl-3,5-dinitrobenzoate and 7.4 ml (0.0529 mole) triethylamine in 150 ml THF (cooled at 8°C). The mixture was stirred for 1 hour at 8°C and 6 hours at room temperature, then was poured into water. The obtained precipitate was filtered, washed with water to neutrality and dried. The product was twice recrystallized from methanol to afford 9.20 g (75%) white crystals. M.P. 65-66°C. IR (KBr) : 1725, 1705 ( $\nu$  C=O), 1619 ( $\nu$  C=C), 1535 ( $\nu$  NO<sub>2</sub> asym.), 1342 cm<sup>-1</sup> ( $\nu$  NO<sub>2</sub> sym.). NMR (CDCl<sub>3</sub>) : 2.03 (CH<sub>3</sub>), 4.69 (CH<sub>2</sub>CH<sub>2</sub>), 5.68 and 6.20 (=CH<sub>2</sub>), 9.13 ppm (aromatic protons).

Elemental analysis corresponds to the calculated one. Copolymerizations were performed in dioxane solutions under argon in sealed ampoules at 60°C. In all cases the total monomer concentration was 0.5 mole/l and the initiator (AIBN) was 1% from the monomers. Copolymers were precipitated with methanol from THF solutions. DNBM homopolymerization yielded, in the same conditions, 28.42% poly(DNBM) in 31.5 hours. Copolymer compositions were determined from the  $^1\text{H-NMR}$  spectra registered in  $\text{DMSO-d}_6$  between 130 and 170°C on a JEOL C-60HL spectrometer. The ratio of aromatic proton signal of HECA (or HECM) to the aromatic proton signal of DNBM was used, and also the ratio of all aromatic proton signals to the  $\text{CH}_2\text{CH}_2$  proton signal.

### RESULTS AND DISCUSSION

The obtained copolymers have an intense orange color, unlike the homopolymers, which are white. The copolymers are soluble in dioxane, THF, DMF and DMSO, especially at high temperatures. The homopolymers are also soluble in  $\text{CHCl}_3$ , poly(DNBM) at low concentrations. When increasing the alternant sequence concentration in copolymer, the color intensifies and the solubility decreases. The copolymerization data are given in table 1.

TABLE 1.  
Copolymerization data

HECA-DNBM				HECM-DNBM					
Sample	x	Time (h)	Conv. (%)	y	Sample	x	Time (h)	Conv. (%)	y
1M	7.00	4.67	4.93	2.85	8M	7.00	2.42	26.55	7.00
2M	3.00	7.67	5.11	1.44	9M	3.00	2.42	16.11	3.00
3M	1.67	9.42	8.43	0.85	10M	1.67	2.58	7.02	1.67
4M	1.00	9.50	11.21	0.59	11M	1.00	4.67	23.06	1.00
5M	0.60	9.53	9.62	0.37	12M	0.60	4.75	17.20	0.60
6M	0.33	9.58	10.36	0.22	13M	0.33	4.83	10.88	0.33
7M	0.14	9.67	13.59	0.10	14M	0.14	6.17	12.30	0.14

$$x = [M_1]/[M_2] ; y = d[M_1]/d[M_2]$$

As it can be seen in table 1, HECM and DNBM copolymerization is azeotropic, i.e. can be characterized by the values  $r_1 = r_2 = 1$ , and the copolymerization equation becomes  $y = x$ . Therefore, independent on conversion, these two monomers will keep the initial ratio. The copolymerization diagrams for the two systems are given in figure 1, and data processing by Kelen-Tüdös equation for HECA-DNBM system gives the plot in figure 2 ( $\alpha = 1.85$ ). The reactivity ratio values are obtained as :

$$r_1 = 0.35 \pm 0.03 \quad r_2 = 1.37 \pm 0.06$$

Therefore, for this electrono-acceptor monomer, as for DNPM and DNPA (5-7,9), the simple terminal model of copolymerization holds.

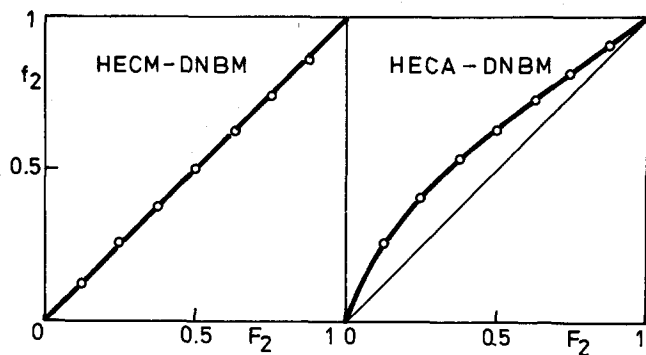


Figure 1. Copolymerization diagrams

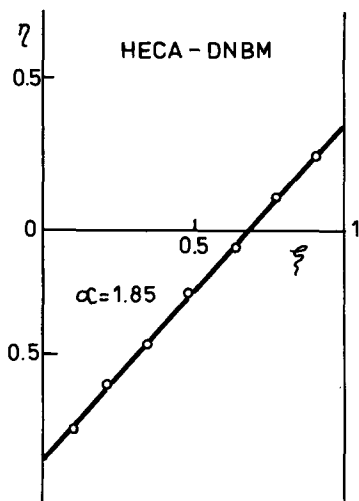


Figure 2. Kelen-Tüdös plot for HECA-DNBM

The intramolecular complexation degree can be estimated, as for the other intramolecular CTC, by measuring the chemical shift of the aromatic protons of DNBM. Their resonance is a quasi-singlet at 8.95 ppm in poly(DNBM). In copolymers, the intramolecular complexation induces a high-field shift. Figure 3 gives this shift, for both systems, against acceptor structural unit fraction being in alternating sequences ( $\frac{1}{2}f_{12}/f_2$ ) (spectra registered at 150°C. This figure suggests two conclusions:

1. The total shift is of 0.35 ppm, higher than in the precedent systems, therefore these complexes are stronger even at 150°C;
2. There is no complexation difference between the two

systems. Practically, independent on the  $\alpha$ -substitution of the monomer (methacrylate or acrylate), complexes equally strong are obtained, unlike DNPA and DNPM (5,8,9), when the complexation is higher for acrylic structural units.

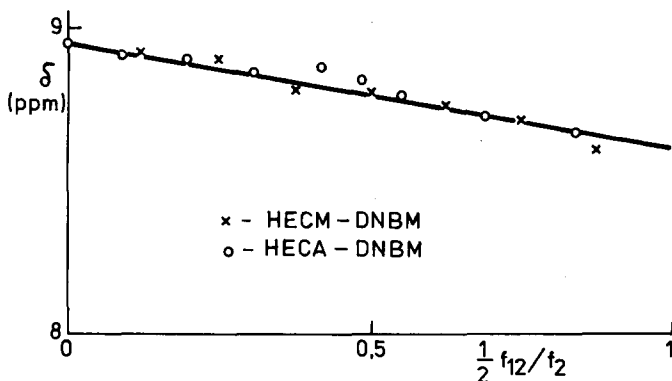


Figure 3. Chemical shift of the aromatic protons of DNBM structural units against DNEM units being in alternating diads

This can be explained by the significant increase of the distance between the aromatic ring, which realizes the complexation, and the rigid main chain. With DNBM, a favourable steric arrangement for the intramolecular complexation can be realized even in a racemic alternating diad (cosyndiotactic configuration) (figure 4), which is impossible with DNPM or DNPA. To confirm this hypothesis, a detailed configurational study was made on poly(HECM-co-DNBM) and poly(HECA-co-DNBM) (13).

Temperature influence on intramolecular complexation can be followed in figure 5, which represents the aromatic region of  $^1\text{H-NMR}$  spectrum of sample 11M registered at three different temperatures, together with the spectrum of poly(DNBM). The shift to higher fields when decreasing the registration temperature is explained by the decrease of the segmental and side-group mobility and the preference for complexation. Unfortunately, the solubility of samples in DMSO under  $130^\circ\text{C}$  is too low to permit the obtaining of a good spectrum.

In conclusion, the increase of the distance between the complexing groups (acceptor or donor) and the main chain for the intramolecular CTC obtained by copolymerization leads to stronger complexes, even at high temperatures. The intramolecular complexation degree is the same for the same sequence distribution, independent on the  $\alpha$ -substitution of the donor monomer, due to the increased side-group mobility and the

possibility to realize the complexation independent on configuration.

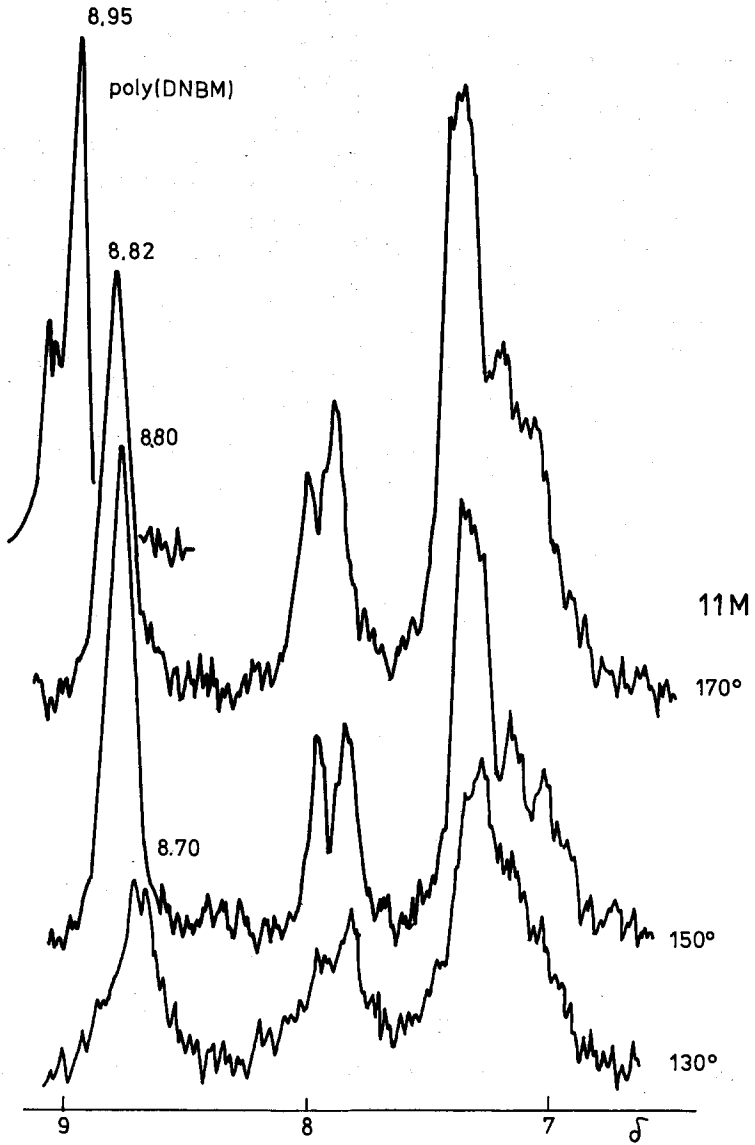


Figure 5. Aromatic region of the 11M sample  $^1\text{H-NMR}$  spectrum (also poly(DNBM))

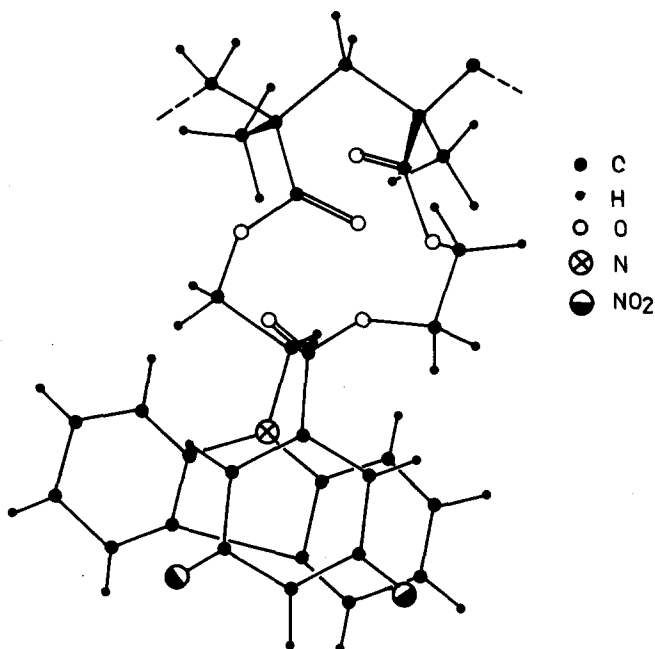


Figure 4. The steric model of a  $1r_2$  diad (alternating cosyndiotactic) which realizes the completion.

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