

## **Intramolecular Charge Transfer Complexes**

### **9. Radical Copolymers of 2,4-Dinitrophenyl Acrylate with N-(2-Hydroxyethyl)Carbazolyl Acrylate and Methacrylate**

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#### SUMMARY

Poly[N-(2-hydroxyethyl)carbazolyl methacrylate (HECM)-co-2,4-dinitrophenyl acrylate (DNPA)] and poly[N-(2-hydroxyethyl)carbazolyl acrylate (HECA)-co-DNPA] are intramolecular charge transfer complexes. The intramolecular complexation degree depends on the  $\alpha$ -substitution at the monomer double bond. The complex containing two acrylate structural units is the strongest, followed by a methacrylate-acrylate copolymer and a methacrylate-methacrylate one, due to the decrease of the coisotactic tendency.

#### INTRODUCTION

In a previous paper (PERCEC et al. 1980), a comparison was made between intramolecular complexation degrees of copolymers obtained from electron-donor and electron-acceptor monomers: acrylates and methacrylates. The conclusion was that the intramolecular charge transfer complexes (CTC) are stronger when obtained from an acrylate donor and a methacrylate acceptor than those from a methacrylate donor and a methacrylate acceptor. A more coisotactic configuration was supposed for the acrylate-methacrylate copolymer, by analogy with the copolymers having acrylic and vinyl-aromatic structural units (ITO et al. 1967).

In this paper, the synthesis of intramolecular CTC by copolymerization of an acrylic acceptor monomer (2,4-dinitrophenyl acrylate, DNPA,  $M_2$ ) with methacrylic and acrylic donors, respectively, (N-(2-hydroxyethyl)carbazolyl methacrylate (HECM), N-(2-hydroxyethyl)carbazolyl acrylate (HECA),  $M_1$ ) is presented in order to correlate the intramolecular complexation degree with the  $\alpha$ -substitution of the monomer double bond.

#### EXPERIMENTAL

HECM (SIMIONESCU et al. 1980a) and HECA (PERCEC et al. 1981) were synthesized according to the described methods. DNPA was synthesized like 2,4-dinitrophenyl methacrylate (DNPM) (KADOMA et al. 1975) by 2,4-dini-

trophenol reaction with acryloyl chloride in benzene solution in the presence of pyridine. The monomer was twice recrystallized from ethanol, giving white crystals, m.p. 43-44°C. IR(KBr) : 1745 ( $\nu_{C=O}$ ), 1525 ( $\nu_{NO_2}$  asym.), 1338  $cm^{-1}$  ( $\nu_{NO_2}$  sym.). NMR( $CDCl_3$ ) : 5.7-6.8 (CH=CH<sub>2</sub>), 7.34 (6th aromatic proton), 8.32 (5th aromatic proton), 8.70 ppm (3rd aromatic proton), J(ortho) = 9 Hz, J(meta) = 3 Hz.

Copolymerizations were carried out in dioxane solutions under argon at 60°C in sealed ampoules. In all cases the total monomer concentration was 0.5 mole/l and the initiator (AIBN) was 1% from monomers. Dioxane and AIBN were purified according to the described methods (SIMIONESCU et al. 1980a). DNPA homopolymerization, in the same conditions as the copolymerizations, gave 9.1% poly(DNPA) in 26 hours.

The copolymers were precipitated in methanol, dried in vacuum at room temperature and then purified by reprecipitation with methanol from dioxane solutions.

<sup>1</sup>H-NMR spectra were registered in DMSO-d<sub>6</sub> solutions on a JEOL C-60HL. Copolymer compositions were determined using different signal integral ratios. Copolymerization data are presented in table 1.

TABLE 1.  
Copolymerization data

HECA-DNPA					HECM-DNPA				
Sample	x	Time	Conv.	y	Sample	x	Time	Conv.	y
1	7.00	20.4	19.0	1.86	11	7.00	20.0	41.9	2.85
2	3.00	20.5	11.7	1.33	12	3.00	20.4	22.6	1.70
3	1.67	20.7	8.8	1.08	13	1.67	20.5	20.2	1.27
4	1.00	20.8	8.9	0.96	14	1.00	20.5	17.9	1.04
5	0.60	20.8	5.5	0.89	15	0.60	20.7	10.8	0.89
6	0.33	20.8	4.2	0.69	16	0.33	20.8	10.3	0.69
7	0.14	26.1	3.7	0.43	17	0.14	20.8	7.9	0.41

$\bar{x} = [M_1]/[M_2]$ ; Time = hours; Conversion = %;  $y = dM_1/dM_2$

#### RESULTS AND DISCUSSION

The copolymerization diagrams are presented in figure 1, and the Kelen-Tüdös plots for reactivity ratio determination in figure 2. Because the yields in HECM-DNPA system surpassed in almost all cases 10%, the reactivity ratio values were determined by the method valid at high conversions (TUDOS et al. 1976), whereas for HECA-DNPA system, the simple method was used (KELEN & TUDOS 1975).

As it can be seen in figure 2, these two copolymerization systems can be treated by the simple terminal model having the parameters :

HECA-DNPA :  $r_1 = 0.13 \pm 0.03$      $r_2 = 0.18 \pm 0.03$

HECM-DNPA :  $r_1 = 0.24 \pm 0.07$      $r_2 = 0.20 \pm 0.07$

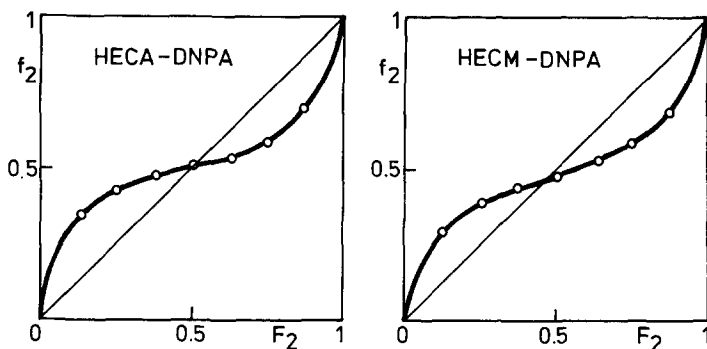


Figure 1. Copolymerization diagrams

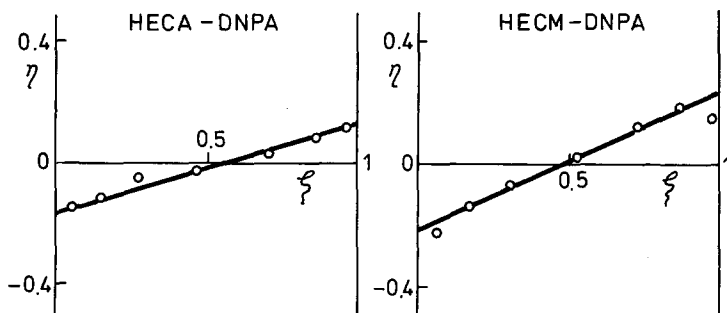


Figure 2. Kelen-Tüdös plots

The error was calculated for 95% confidence interval (KELEN et al. 1980). The terminal model of copolymerization holds as for HECA and HECM copolymerizations with DNPM (SIMIONESCU et al. 1980b; submitted). The intramolecular complexation degree is estimated by measuring the chemical shift of the 3rd aromatic proton of DNPA structural unit for  $^1\text{H-NMR}$  spectra registered in  $\text{DMSO-d}_6$  at  $60^\circ\text{C}$ . This chemical shift in poly (DNPA) is 8.74 ppm from TMS. It is preferable to measure the chemical shift of the 3rd aromatic proton, because it is the most deshielded and resonates separately. All other protons give overlapping resonances. Figure 3 gives the plot of this chemical shift against the DNPA structural unit fraction being in alternating diads. This kind of correlation eliminates the copoly-

mer composition and sequence distribution influence on the intramolecular complexation. Therefore, the complexation differences between the two copolymers appearing in figure 3, (poly(HECA-co-DNPA) is a stronger complex than poly(HECM-co-DNPA), because the shift to higher fields at the same sequence distribution is higher for the first copolymer) can be explained by configurational and/or conformational effects.

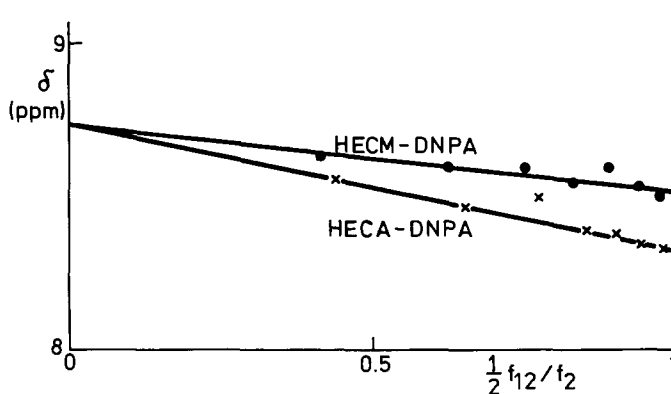


Figure 3. Chemical shift of the 3rd aromatic proton of DNPA structural unit against DNPA structural unit fraction being in alternating sequences

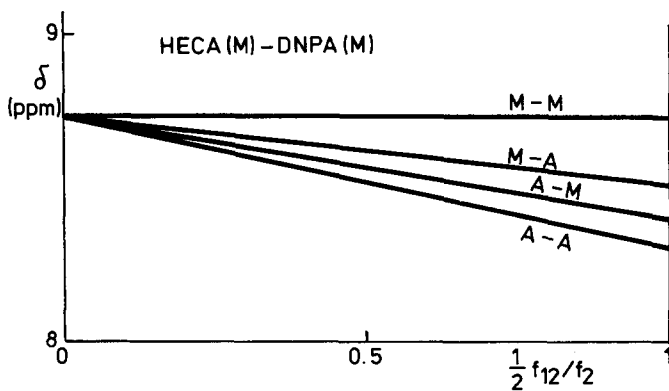


Figure 4. Chemical shift of the 3rd aromatic proton of acceptor structural unit against acceptor structural unit fraction being in alternating sequences

Figure 4 represents the comparison of systems :  
 poly(HECM-co-DNPM), (SIMIONESCU et al. 1980b)  
 poly(HECA-co-DNPM), (SIMIONESCU et al. submitted)  
 poly(HECM-co-DNPA) and poly(HECA-co-DNPA) (this paper),  
 all spectra being registered in DMSO<sub>d6</sub> at 60°C. For  
 the copolymer having only methacrylic structural units,  
 in this solvent, there is no evidence of intramolecu-  
 lar complexation. The acrylate-methacrylate structu-  
 ral units generate stronger complexes, and the highest  
 charge transfer interaction is observed in the copoly-  
 mer having only acrylic structural units, as it was  
 supposed in the previous paper (PERCEC et al. 1980).  
 Therefore, the increase of coisotactic alternating  
 sequence fraction, which is a consequence of the non-  
 substitution of the comonomer double bond (ITO et al.  
 1967), determines an increase of the intramolecular  
 complexation degree, at least for copolymers having  
 the electrono-donor or electrono-acceptor groups di-  
 rectly bonded to the polymer main chain.

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