

## **Intramolecular Charge Transfer Complexes**

### **14. Copolymers of N-ethyl-3-hydroxymethyl Carbazolyl Methacrylate with Acryloyl and Methacryloyl- $\beta$ -hydroxyethyl-3,5-dinitrobenzoate**

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*Dedicated to Professor B. Vollmert's 60th anniversary*

#### SUMMARY

Radical copolymerization of N-ethyl-3-hydroxymethyl carbazolyl methacrylate (EHMCM) with methacryloyl- $\beta$ -hydroxyethyl-3,5-dinitrobenzoate (DNBM) and acryloyl- $\beta$ -hydroxyethyl-3,5-dinitrobenzoate (DNBA), respectively, lead to intramolecular charge transfer complexes (CTC). In the case of EHMCM-DNBA copolymerization, a mechanism involving intermonomeric CTC participation is evidenced.

#### INTRODUCTION

Of the electrono-acceptor monomers used for intramolecular charge transfer complexes (CTC) synthesis by radical copolymerization with electrono-donor monomers, the most interesting were proven to be methacryloyl (DNBM) and acryloyl (DNBA)- $\beta$ -hydroxyethyl-3,5-dinitrobenzoate. DNBM and DNBA copolymers with N-(2-hydroxyethyl)carbazolyl acrylate (HECA) and methacrylate (HECM)(1,2) present a chemical shift of the aromatic protons from acceptor structural unit of 0.4-0.5 ppm between the uncomplexed and the most complexed states, even at high temperatures, indicating the formation of strong and stable complexes.

For DNBM it was demonstrated that the distance between the acceptor group and the double bond permits intramolecular complexation independent on chain configuration (1,3). For DNBA, a copolymerization mechanism involving intermonomeric CTC participation was evidenced, although from the Kelen-Tüdös plots a terminal model seemed to be reliable (2).

These two electrono-acceptor monomers are used in this paper in the synthesis of intramolecular CTC by copolymerization with another electrono-donor monomer: N-ethyl-3-hydroxymethyl carbazolyl methacrylate (EHMCM,  $M_1$ ).

#### EXPERIMENTAL

EHMCM (4), DNBM (1) and DNBA (2) were synthesized according to the described methods. Copolymerizations were performed in dioxane solutions under argon in

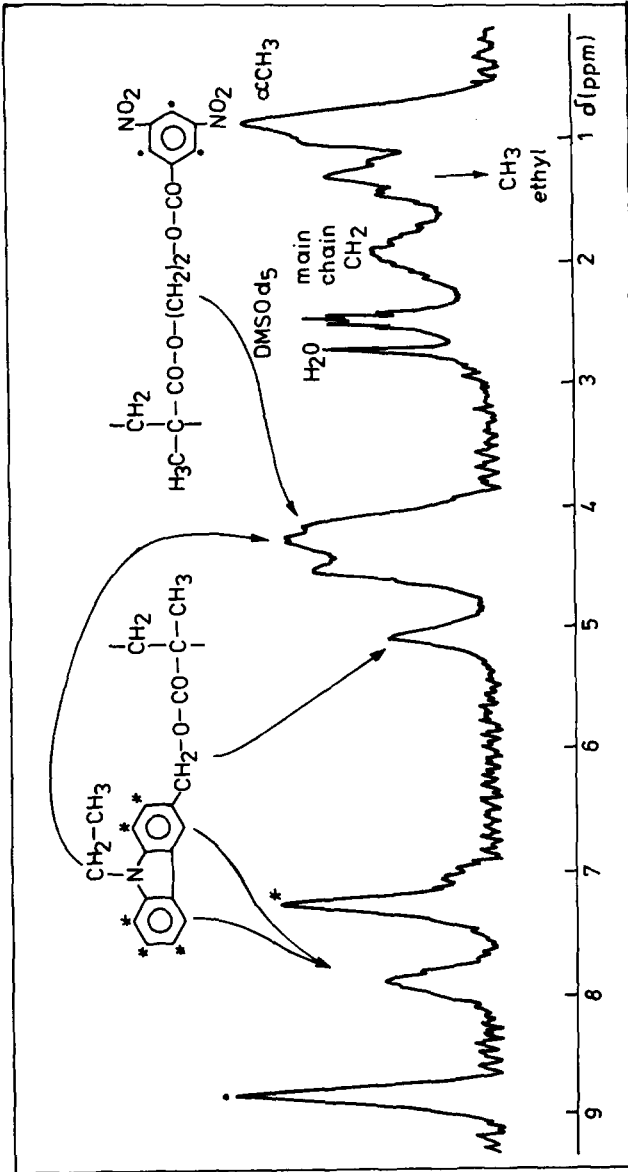


Figure 1.  $^1\text{H-NMR}$  spectrum of sample 6

sealed ampoules at 60°C. In all cases the total monomer concentration was 0.5 moles/l and the initiator (AIBN) was 1% from monomers. The copolymers were precipitated with methanol, dried and reprecipitated with methanol from THF solutions.

Copolymer compositions were determined from  $^1\text{H-NMR}$  spectra registered in  $\text{DM}_3\text{O}_d_6$  at 150°C on a JEOL C-60HL spectrometer. A typical  $^1\text{H-NMR}$  spectrum is presented in figure 1 together with the assignments. The aromatic signals ratio and the  $\text{CH}_2$  groups ratio were used. Copolymerization data are presented in table 1.

TABLE 1  
Copolymerization data

EHMCM-DNBM				EHMCM-DNBA					
Sample	x	Time (h)	Conv. (%)	y	Sample	x	Time (h)	Conv. (%)	y
1	7.00	1.0	6.5	5.67	8	7.00	6.8	64.5	11.50
2	3.00	2.0	13.8	2.70	9	3.00	23.3	46.8	4.88
3	1.67	2.7	8.4	1.63	10	1.67	23.5	57.4	3.17
4	1.00	3.7	13.7	1.13	11	1.00	23.5	35.9	2.13
5	0.60	4.5	12.8	0.75	12	0.60	23.5	19.5	1.56
6	0.33	5.0	16.8	0.47	13	0.33	23.7	13.0	1.13
7	0.14	5.5	19.9	0.20	14	0.14	23.7	5.8	0.72

$$x = [M_1] / [M_2] \quad y = d[M_1] / d[M_2]$$

#### RESULTS AND DISCUSSION

Mixing of the comonomer solutions produces an intense yellow color indicating the intermonomeric CTC formation. The copolymers are also intensely yellow-orange colored, unlike the homopolymers, which are white.

The copolymerization diagrams are presented in figure 2.

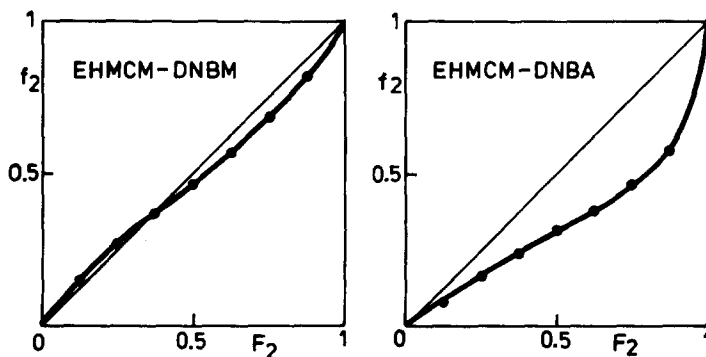


Figure 2. Copolymerization diagrams

As it can be seen, DNBM has a higher enchainment probability than DNBA on all compositional domain. Also, DNBA can generate copolymers with more than 50% acceptor structural units, as in the case of its copolymers with HECA and HECM (2). This is again a proof for the intermonomeric CTC participation in propagation (2).

Copolymerization data processing is made according to Kelen-Tüdös procedure at high conversions (5). The plots (figure 3) are straight lines giving the results

EHMCM-DNBM	$r_1 = 0.71$	$r_2 = 0.55$
EHMCM-DNBA	$r_1 = 1.73$	$r_2 = 0.09$

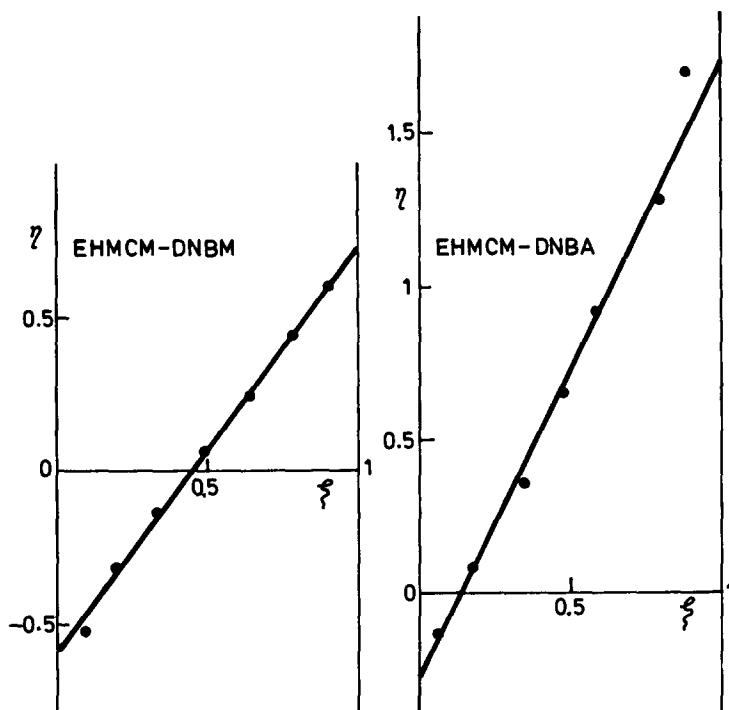


Figure 3. The Kelen-Tüdös plots

In these cases, also, the copolymerization mechanism can be approximated by the terminal model, in spite of the evidence for CTC participation, at least for DNBA. The conclusion is, that for model discrimination, compositional data can be insufficient.

The plot of the chemical shift of the aromatic protons from acceptor structural units against the fraction of acceptor structural units being in alternating sequences (figure 4) leads to the following conclusions :

-poly(EHMCM-co-DNBM) samples lie on a straight line

having the shift between the ends of ca. 0.4 ppm - poly(EHMCM-co-DNBA) samples do not follow a straight line, and the shift between the ends is higher (ca. 0.5 ppm). This can be explained by the fact that calculated sequence distribution for the terminal model cannot be correct. This is the case, also, for the other DNBA copolymerizations (2). It is not to be excluded an eventual influence of 121 or 211 triads on the intramolecular complexation degree. The real sequence distribution determination will elucidate this problem.

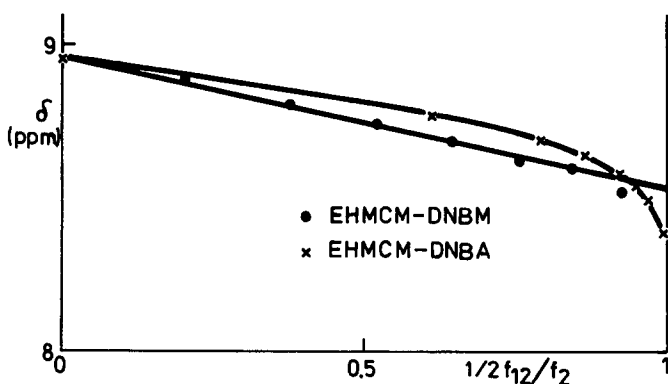


Figure 4. Chemical shift of the aromatic protons from acceptor structural units

It is very probable that, for DNBM also, the copolymerization mechanism should imply intermonomeric CTC participation, but its relatively high homopropagation rate overlaps the complex propagation.

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