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Intramolecular Charge Transfer Complexes

13. Copolymers of Acryloyl-β-hydroxyethyl-3,5-dinitrobenzoate with N-(2-hydroxyethyl)Carbazolyl Acrylate and Methacrylate

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Dedicated to Professor G. Manecke's 65th anniversary

SUMMARY

The synthesis of acryloyl-β-hydroxyethyl-3,5-dinitrobenzoate (DNBA) and of its copolymers with N-(2-hydroxyethyl)carbazolyl acrylate (HECA) and methacrylate (HECM) is presented. A copolymerization mechanism implying intermonomeric charge transfer complexes (CTC) is evidenced, although according to the Kelen-Tüdös equation the terminal model seemed to be valid. The copolymers obtained are intramolecular CTC.

INTRODUCTION

Radical copolymerization of electrono-donor and electrono-acceptor monomer pairs can lead to intramolecular charge transfer complexes (CTC) (1-12). The intramolecular complexation degree is determined by the copolymer microstructure (13). Therefore, it is very important to know the copolymerization mechanism. Up to now, two mechanisms were evidenced :

1. When one of the monomers does not homopolymerize, the Kelen-Tüdös plot presents a curvature indicating a mechanism which implies intermonomeric CTC participation. This is the case of picryl methacrylate, copolymerized with N-(2-hydroxyethyl)carbazolyl methacrylate (HECM)(1,6), 2-naphthyl methacrylate (2), N-(2-hydroxyethyl)carbazolyl acrylate (HECA)(4), N-ethyl-3-hydroxymethyl carbazolyl methacrylate and α-(2-fluorenyl)ethyl methacrylate (14).
2. When both monomers can homopolymerize, the Kelen-Tüdös plots are straight lines permitting relative reactivities and sequence distribution calculation, using the terminal model. Such acceptor monomers are : 2,4-dinitrophenyl methacrylate, copolymerized with HECM (5), 3,6-dichloro-HECM and 3,6-dichloro-HECA (7) and HECA (8), 2,4-dinitrophenyl acrylate, copolymerized with HECA and HECM (9), methacryloyl-β-hydroxyethyl-3,5-dinitrobenzoate (DNBM), copolymerized with HECA and HECM (10,11) and 2'-ethylacryl-4,5,7-trinitro-9-fluorenon-2-carboxylate, copolymerized with HECA (12).

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Of the microstructural factors which affect the intramolecular complexation degree, the chain configuration is important when at least one of the structural units has the complexing group directly bonded to the main chain (picryl methacrylate, 2,4-dinitrophenyl acrylate and methacrylate). When the distance between the complexing group and the main chain is sufficient to permit the complexation even in cosyndiotactic diads, the copolymer configuration does not affect the intramolecular complexation degree (DNBM copolymers with HECA and HECM (10,11)).

This paper presents the synthesis of the acceptor monomer acryloyl-β-hydroxyethyl-3,5-dinitrobenzoate (DNBA, M_2) and of its copolymers with HECA and HECM, respectively (M_1), in order to confirm the independence of intramolecular complexation on chain configuration.

EXPERIMENTAL

HECA (4) and HECM (1) were synthesized according to already described methods. DNBA was synthesized like DNBM (10).

Acryloyl-β-hydroxyethyl-3,5-dinitrobenzoate. A mixture of 14.4 g (0.1587 moles) acryloyl chloride and 15 ml THF was added dropwise during 20 minutes under strong stirring to a solution of 30 g (0.1134 moles) β-hydroxyethyl-3,5-dinitrobenzoate and 22.2 ml (0.1587 moles) triethylamine in 400 ml THF (cooled at 8°C). The mixture was stirred one hour at 8°C and 6 hours at room temperature. The obtained precipitate ($NEt_3 \cdot HCl$) was filtered and washed several times with THF. The obtained solution was concentrated to ca. 75 ml in a rotovapour (under 30°C) and poured into water. The precipitate was filtered, washed with water to neutrality and dried. The product was twice recrystallized from methanol to afford 23 g (65.4%) white crystals with m.p. 61-62°C. IR (KBr): 1713 cm^{-1} ($\nu C{=}O$), 1622 cm^{-1} ($\nu C{=}C$), 1535 cm^{-1} (νNO_2 asym.), 1342 cm^{-1}(νNO_2 sym) NMR ($CDCl_3$): 4.61 ppm ($-CH_2CH_2-$), 5.6-6.7 ppm ($-CH{=}CH_2$) 9.08 ppm (aromatic protons).

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 reprecipitated with methanol from THF solutions. Copolymer compositions were determined from the ^1H-NMR spectra registered in DMSOd_6 at 150°C on a JEOL C-60HL spectrometer. The ratio of aromatic proton signal of HECA (or HECM) to the aromatic proton signal of DNBA was used, and also the ratio of all aromatic proton signals to the $-CH_2CH_2-$ proton signal.

The attempt to homopolymerize DNBA in the same conditions failed, even after 96 hours of reaction. Therefore, DNBA does not homopolymerize in these conditions, perhaps due to the inhibiting effect of the nitro groups. This effect cannot be evidenced for DNBM, probably due to configurational differences. Table 1 summarizes the copolymerization data.

TABLE 1
Copolymerization data

HECA-DNBA					HECM-DNBA				
Sample	x	Time (h)	Conv. (%)	y	Sample	x	Time (h)	Conv. (%)	y
1	7.00	52.4	18.8	5.25	8	7.00	11.6	10.2	7.33
2	3.00	52.4	6.4	2.57	9	3.00	20.6	32.3	4.00
3	1.67	56.6	6.0	1.70	10	1.67	28.2	22.3	2.57
4	1.00	56.6	5.2	1.17	11	1.00	28.2	25.9	1.94
5	0.60	96.4	6.7	0.85	12	0.60	28.2	16.1	1.44
6	0.33	96.5	3.0	0.54	13	0.33	28.3	8.2	1.00
7	0.14	119.8	2.4	0.32	14	0.14	62.0	8.7	0.61

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

RESULTS AND DISCUSSION

Mixing the two comonomer solutions produces an intense yellow color, indicating an intermonomeric CTC formation. The copolymers are also intensely yellow-orange colored.

The copolymerization diagrams for the two systems are given in figure 1.

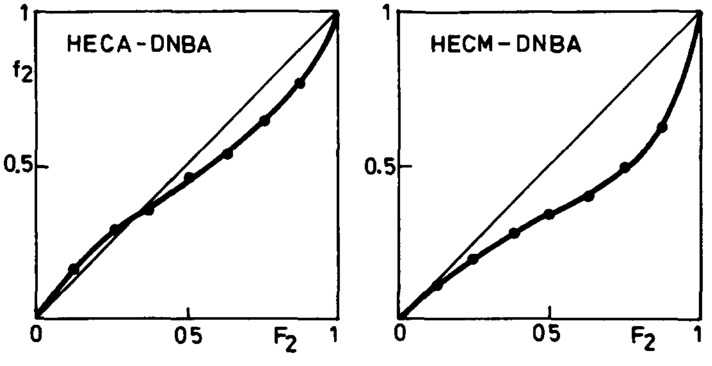

Figure 1. Copolymerization diagrams

Surprisingly, although DNBA does not homopolymerize, the copolymer composition surpasses in some cases 50% DNBA structural units, which means that the probability of 22 sequences formation is not null.

Copolymerization data processing according to Kelen and Tüdös method at low conversions (15) for HECA-DNBA and at high conversions for HECM-DNBA (16) gives the plots presented in figure 2, straight lines from which the relative reactivities are obtained :

HECA-DNBA $r_1 = 0.62$ $r_2 = 0.37$
HECM-DNBA $r_1 = 1.04$ $r_2 = 0.10$

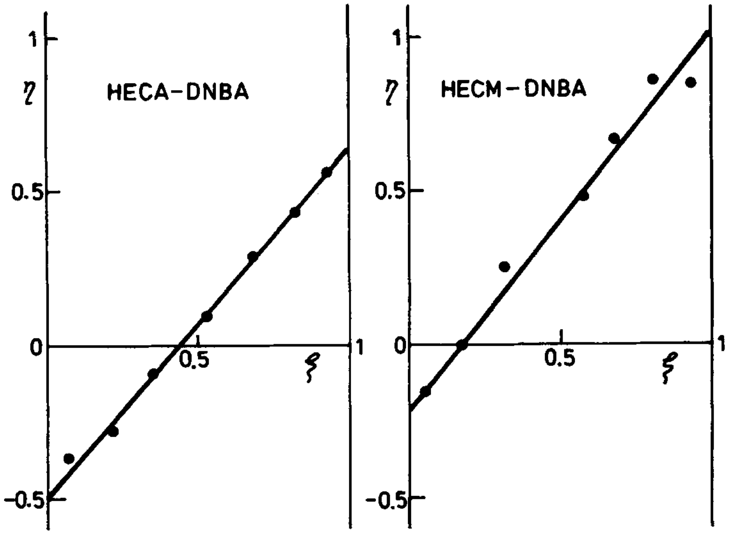

Figure 2. The Kelen-Tüdös plots

In both cases, therefore, $r_2 \neq 0$, although, according to its definition, $r_2 = k_{22}/k_{21}$ and $k_{22} = 0$ (DNBA does not homopolymerize).

In order to explain this unconcordance, another copolymerization mechanism has to be taken into account, even if, apparently, the terminal model seems to be valid. Consequently, the homopolymerization of DNBA was performed in dioxane at 60°C with 1% AIBN under argon in a sealed ampoule in the presence of an inert electrono-donating compound - N-ethyl carbazole (mole: mole with respect to DNBA). In these conditions, poly(DNBA) was indeed obtained as a white powder with an yield of 5.94% in 20.25 hours (and after two reprecipitations). This demonstrates that DNBA homopolymerization and, consequently, 22 sequence formation in copolymerization, takes place through CTC according to the equation :

$$M_2^{\bullet} + [M_2M_1] \xrightarrow{k_{2c2}} M_2M_2^{\bullet} + M_1$$

where M_1 is the electrono-donor monomer or the inert electrono-donating compound.

The general copolymerization model implying intermonomeric CTC and decomplexation during propagation was considered by Tsuchida and Tomono (17) and by Karad and Schneider (18) and consists in the next eight equations :

$$
\begin{array}{lll}
M_1^{\bullet} + M_1 & \xrightarrow{k_{11}} & M_1M_1^{\bullet} \\
M_1^{\bullet} + M_2 & \xrightarrow{k_{12}} & M_1M_2^{\bullet} \\
M_2^{\bullet} + M_1 & \xrightarrow{k_{21}} & M_2M_1^{\bullet} \\
M_2^{\bullet} + M_2 & \xrightarrow{k_{22}} & M_2M_2^{\bullet} \\
M_1^{\bullet} + [M_1M_2] & \xrightarrow{k_{1c1}} & M_1M_1^{\bullet} + M_2 \\
M_1^{\bullet} + [M_2M_1] & \xrightarrow{k_{1c2}} & M_1M_2^{\bullet} + M_1 \\
M_2^{\bullet} + [M_1M_2] & \xrightarrow{k_{2c1}} & M_2M_1^{\bullet} + M_2 \\
M_2^{\bullet} + [M_2M_1] & \xrightarrow{k_{2c2}} & M_2M_2^{\bullet} + M_1
\end{array}
$$

The first four equations characterize the terminal model, but cannot explain the systems analysed in this paper. The last four equations describe the intermonomeric CTC participation, but cannot be independently considered, because the copolymerization equation resulting from them is :

$$y = \text{const.}$$

the constant depending on individual k_{ici} values, but in our case y depends on comonomer feed.

Consequently, for HECA-DNBA and HECM-DNBA systems, the copolymerization model must include all eight propagation equations, having only one simplification ($k_{22} = 0$). Work is now in progress to obtain the general copolymerization equation, to define more conveniently the relative reactivities in order to calculate the sequence distribution. The general equation is different from that deriving of Seiner and Litt (19) model.

Having in mind the previously proposed (3) relative reactivities definition :

$$\alpha_{11} = k_{1c1}/k_{12},\ \alpha_{12} = k_{1c2}/k_{12},\ \alpha_{21} = k_{2c1}/k_{21},$$
$$\alpha_{22} = k_{2c2}/k_{21},\ r_{12} = k_{11}/k_{12},\ r_{21} = k_{22}/k_{21}$$

one can remark that r_{21} can be null without requiring α_{22} to be null. Such values have been obtained for HECA copolymers with picryl methacrylate (4). The present data support the fact that one cannot completely exclude 22 sequences existence. The simplified equation established by Karad and Schneider (18) on the basis that, if $k_{22} = 0$, then probably $k_{2c2} = 0$, must be, therefore, reconsidered.

Figure 3 represents the chemical shift of the aromatic protons from DNBA structural unit against DNBA structural unit fraction being in alternating sequences ($\frac{1}{2}f_{12}/f_2$). In poly(DNBA) this chemical shift is 8.95 ppm (spectrum registered in DMSOd_6 at 150°C). As expected, the plot in figure 3 is not a straight line, because sequence fractions calculated from the terminal model cannot be correct. In these conditions, it is impossible to analyse the role played by copolymer configuration in the intramolecular complexation.

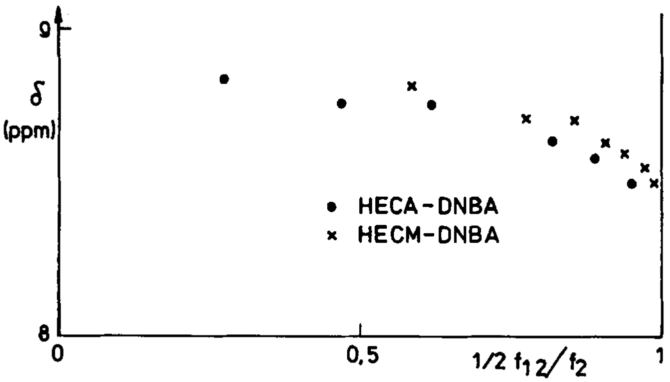

Figure 3. Chemical shift of the DNBA aromatic protons

In conclusion, the first evidence of the propagation through CTC addition on the same side for a monomer which does not homopolymerize, requires the reconsideration of all copolymerization data in which the terminal model seemed to be valid, according to the Kelen-Tüdős plot. Only compositional data probably overlap the intermonomeric CTC participation in copolymerization. Sequence distribution analysis for these copolymers will elucidate the copolymerization mechanism.

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