Intramolecular Charge Transfer Complexes. 4. Poly(N-(2-hydroxyethyl)carbazolyl Acrylate-co-Picryl Methacrylate)

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ABSTRACT

Radical copolymerization of N-(2-hydroxyethyl)carbazolyl acry-
late with picryl methacrylate takes place mainly through the inter-
monomeric charge transfer complex (CTC) in dioxane solution.
When the solvent is 1,2-dichloroethane, concurrent chain transfer
reactions arise. The copolymers obtained are intramolecular CTC.
The charge transfer interaction depends on copolymer composition
and conformation, and on the copolymerization solvent.

INTRODUCTION

In the first paper of this series [1] the importance of charge trans-
fer complexes (CTC) was presented together with a short review of
literature data concerning intramolecular CTC. Also, the copolymeri-
zations of picryl methacrylate with N-(2-hydroxyethyl) carbazolyl
methacrylate (HECM) [1] and 2-naphthyl methacrylate [2] were re-
ported, special attention being paid to the intermonomeric CTC
behavior and to the dependence of intramolecular charge transfer
interactions on copolymer composition, configuration, and conforma-
tion.

405

The aim of this paper is to present the synthesis of a new intra-molecular CTC obtained by radical copolymerization of N-(2-hydroxy-ethyl) carbazolyl acrylate (M_1, HECA) with picryl methacrylate (M_2).

EXPERIMENTAL

Materials

N-(2-hydroxyethyl) Carbazolyl Acrylate

A mixture of 12.7 g (0.14 mol) acryloyl chloride and 25 mL ben-zene was added dropwise (in 30 min) under stirring on a solution (cooled at 8°C) consisting of 25 g (0.118 mol) N-hydroxyethyl carba-zole, 250 mL benzene (dried on Na), and 14.17 g (0.14 mol) triethyl-amine. The mixture was stirred 1 h at 10°C and 2 h at room tempera-ture. Then $Et_3N.HCl$ was separated by filtration and the benzene solution washed successively with NaOH (5% solution in water), water, and finally dried on $CaCl_2$. After benzene evaporation in vacuum at temperatures lower than 30°C, the product was recrystallized twice from methanol, giving 20 g (63.5%) white crystals, mp 74-75°C.

Analysis: Calculated for $C_{17}NO_2H_{15}$ (265.298): C, 76.959%; N, 5.280%; O, 12.062%; H, 5.699%. Found: C, 76.82%; N, 5.35%; H, 5.75%. IR (KBr): 720, 749 cm^{-1} (carbazolyl group), 1716 cm^{-1} ($\nu_{C=O}$). NMR ($CDCl_3$, TMS, 25°C): $\delta_{-(CH_2)_2-}$ = 4.40; δ = 5.50-6.10 (vinyl group); δ = 7.00-7.40 (aromatic 1,2,3,6,7,8 protons); δ = 7.95 (aromatic 4,5 protons).

N-Hydroxyethyl carbazole was synthesized from carbazole and ethylenoxide [3] and purified by three successive recrystallizations from a cyclohexane-benzene (1:1) mixture. Acryloyl chloride was synthesized according to the general method for obtaining acid chlo-rides from acrylic acid and benzoyl chloride [4]. After two distilla-tions, only the vinylic protons were observed in the NMR spectrum.

Picryl methacrylate was prepared according to published method [5] and purified as reported elsewhere [1].

Dioxane and 1,2-dichloroethane were dried by reflux on Na and CaH_2, respectively, distilled under argon, and kept on CaH_2 in an argon atmosphere.

AIBN was recrystallized twice from methanol.

Instrumental Analysis

The IR spectra were registered on a Perkin-Elmer 577 spectro-photometer (KBr pellets), the UV spectra on a Unicam SP 800, and the NMR spectra on a Jeol C-60HL (60 MHz) spectrometer in $CDCl_3$ solutions (reference TMS).

Copolymerization

Copolymerizations were carried out in dioxane or 1,2-dichloro-ethane solutions under argon at 60°C in joint-cap bottles. In all cases the total monomer concentration was 0.5 mol/L and the initiator (AIBN) was 1% from monomers. The copolymers were precipitated in methanol, dried in vacuum at room temperature, and then purified by reprecipitation with methanol from dioxane solutions.

Composition and Equilibrium Constant of Inter-monomeric CTC Determination

Mixing of the monomers in dioxane and 1,2-dichloroethane produced red-colored solutions accompanied by a continuous absorption (between 400 and 600 nm) in the visible domain of the absorption spectrum. By Job's method [6] the 1:1 composition of the intermonomeric CTC was proved. The equilibrium constant of CTC (K) was determined by measuring the chemical shift (in Hz) of the aromatic protons of picryl methacrylate in the ^{1}H-NMR spectrum [7]. In both solvents the concentrations ranged from 0.341 to 0.227 mol/L for M_1 and from 0.022 to 0.045 mol/L for M_2. The chemical shift of the aromatic protons of uncomplexed picryl methacrylate in this range of concentrations is 336.2 Hz (25°C) and 334.1 Hz (60°C) from the dioxane signal and 322.4 Hz (25°C) and 321.3 Hz (60°C) from the 1,2-dichloroethane signal. In these conditions the values found for the equilibrium constant (determined by the Hanna [8] and Foster [9] methods) are presented in Table 1. An example for K-value determination is given in Fig. 1, illustrating Hanna's method [8] for dioxane solutions.

Copolymer Composition Determination

Copolymer composition was determined from ^{1}H-NMR spectra registered at room temperature and 60°C. The ratio of signals corresponding to the aromatic protons of M_2 structural units, 4,5 aromatic protons of M_1 structural units, and $-(CH_2)_2-$ protons were used. A typical ^{1}H-NMR spectrum is presented in Fig. 2 together with the assignments. In all cases the ratio of the 4,5 aromatic protons signal from carbazole was constant.

The composition determined by NMR was also verified by IR spectroscopy by using the optical densities ratio D_{1720}/D_{1760} (1720 cm^{-1} $\nu_{C=O}$ from M_1 structural units and 1760 cm^{-1} $\nu_{C=O}$ from M_2 structural units). This ratio depends linearly on the structural units ratio in the copolymer (y).

TABLE 1. Intermonomeric CTC Equilibrium Constants (L/mol)

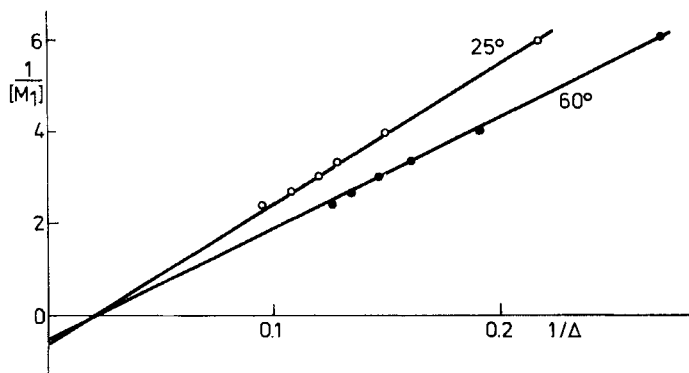| Solvent	K (25°C)	K (60°C)
Dioxane (D)	0.60	0.50
1,2-Dichloroethane (E)	0.65	0.61

FIG. 1. K value determination of intermonomeric CTC in dioxane ($\triangle$ = chemical shift difference between complexed and uncomplexed M_2).

RESULTS AND DISCUSSION

From Table 1 it is clear that, as expected, in 1,2-dichloroethane the intermonomeric CTC concentration is higher than in dioxane. Dioxane gives concurrent complexation because its ionization potential is lower [10].

The copolymers obtained are brick-colored and the color becomes darker when the copolymer picryl methacrylate content is increased. The solubility in chloroform, benzene, dioxane, 1,2-dichloroethane, and tetrahydrofuran decreases with increasing picryl methacrylate content. Table 2 gives the initial compositions, copolymerization times, conversions, and copolymer compositions for the two series of copolymerizations.

The Kelen-Tüdös plot [11] presents a slight curvature in the picryl methacrylate-rich samples domain (Fig. 3), and that suggests a charge transfer copolymerization mechanism. For $\xi = 0$, one obtains $\eta = 0$, which confirms the fact that picryl methacrylate does not homopolymerize [5].

The kinetic parameters for these copolymerizations are determined according to the Seiner and Litt's model [12] in the particular
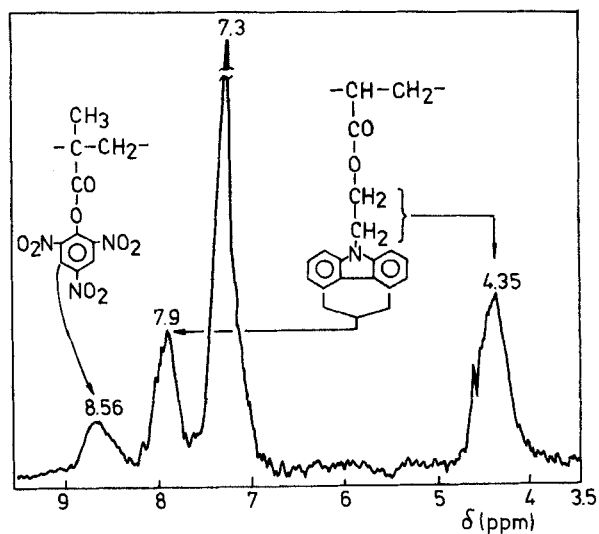
FIG. 2. ^{1}H-NMR spectrum of sample D_2 in $CDCl_3$ at 60°C.

TABLE 2.   Copolymerization Results

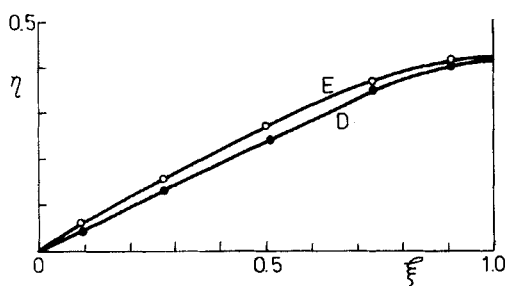| Exp. no.	Molar fraction of M_1 in the initial mixture (F_1)	Reaction time (h)	Conversion (%)	Molar fraction of M_2 in the copolymer (f_2)
D_1	0.85	24.0	1.88	0.221
D_2	0.70	72.0	2.74	0.321
D_3	0.55	144.0	2.78	0.392
D_4	0.40	240.0	2.24	0.441
D_5	0.25	336.0	1.06	0.465
E_1	0.85	75.0	5.49	0.216
E_2	0.70	78.5	4.88	0.314
E_3	0.55	147.5	4.54	0.375
E_4	0.40	241.5	3.16	0.433
E_5	0.25	336.0	2.16	0.450

FIG. 3. Kelen-Tüdös plots.

case $k_{22} = 0$ and $K > 0.03$ as analyzed by Karad and Schneider [13]. The equation is

$$y - 1 = \frac{r_{1C}}{r_{1C1}} + r_{1C}\left(\frac{[M_1]}{[C]} - \frac{y-1}{r_{12}} \frac{[M_2]}{[C]} \right) \tag{1}$$

where $y = f_1/f_2$ and $[M_1]$, $[M_2]$, and $[C]$ are the comonomers and CTC concentrations in the initial feed. Plots of $y - 1$ against $\{[M_1]/[C] - (y-1)[M_2]/r_{12}[C]\}$ are given in Fig. 4. The reactivity ratio values obtained are presented in Table 3.

Because the solution of Eq. (1) is somewhat "constrained" for dioxane solutions copolymerizations (better straight lines can be obtained for other r_{12} values, but they give negative r_{1C} values, which is absurd), the other copolymerization equation [14] is taken into account:

$$y = \frac{1 + r_{12}\dfrac{[M_1]}{[M_2]} + K[C](\alpha_{11}\alpha_{2C} + \alpha_{22}\alpha_{1C}) + \alpha_{2C}\dfrac{[C]}{[M_1]} + (\alpha_{11} + \alpha_{1C} + \alpha_{22}r_{12})\dfrac{[C]}{[M_2)}}{1 + r_{21}\dfrac{[M_2]}{[M_1]} + K[C](\alpha_{11}\alpha_{2C} + \alpha_{22}\alpha_{1C}) + \alpha_{2C}\dfrac{[C]}{[M_1]} + (\alpha_{22} + \alpha_{1C} + \alpha_{11}r_{21})\dfrac{[C]}{[M_2]}} \tag{2}$$

where

$$\alpha_{11} = k_{1C1}/k_{12}; \quad \alpha_{12} = k_{1C2}/k_{12}; \quad \alpha_{1C} = \alpha_{11} + \alpha_{12}$$

$$\alpha_{21} = k_{2C1}/k_{21}; \quad \alpha_{22} = k_{2C2}/k_{21}; \quad \alpha_{2C} = \alpha_{21} + \alpha_{22}$$
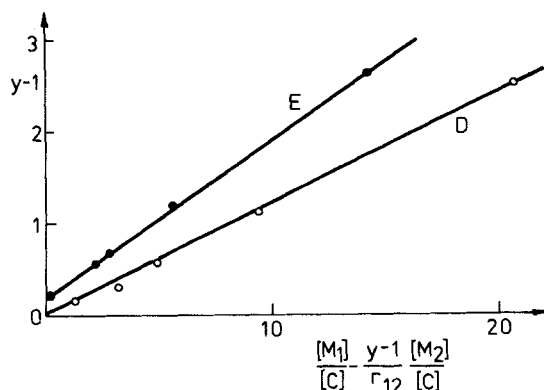
FIG. 4. Reactivity ratios determination by Eq. (1).

TABLE 3. Reactivity Ratios Obtained by Eq. (1)

Solvent	r_{12}	r_{1C}	r_{1C1}	r_{1C2}
D	1.1	0.15	7.5	0.18
E	0.8	0.18	1.01	0.20

The principal argument for the need of Eq. (2) is the fact that, in similar conditions, HECA generates copolymers with higher picryl methacrylate content than does HECM [1]. Therefore, one can suppose that HECA has a much smaller homopropagation tendency than HECM in the given conditions; the reactivity ratios in Eq. (1) become close to zero, and Eq. (1) itself becomes inoperative.

The reactivity ratios in Eq. (2) are determined by using the ESTIM and VERIF programs described in the previous paper [14]. They are based on Marquardt's algorithm of nonlinear estimation with minimum square error [15]. The results are given in Table 4. Comparison of the two sets of results can be made by converting the two reactivity types (Table 5). As is clear from Table 5, in keeping with the results presented in the previous paper, the most affected parameter given by Eq. (1) is r_{1C1}, otherwise the two methods are in fairly good agreement. One can obtain more information from Eq. (2) about the M_2-ended macroradical. Table 4 reveals that intermonomeric CTC addition at this macroradical is much preferred compared with M_1 addition for dioxane solution copolymerizations ($\alpha_{2C} = 5.2$). These two reactions seem to be equally probable ($\alpha_{2C} = 1.0$) in 1,2-dichloroethane. Somewhat unexpected is the value $\alpha_{22} = 0.3$ for dioxane solution

TABLE 4. Reactivity Ratios Obtained by Eq. (2)

Solvent	α_{11}	α_{12}	α_{21}	α_{22}	r_{12}	r_{21}
D	0.3	6.6	4.9	0.3	1.1	0
E	0.5	3.4	1.0	0.0	0.9	0

TABLE 5. Comparison of Reactivity Ratio Values

Solvent	Equation	r_{12}	r_{1C}	r_{1C1}	r_{1C2}
D	1	1.1	0.15	7.5	0.18
D	2	1.1	0.16	3.7	0.17
E	1	0.8	0.18	1.01	0.20
E	2	0.9	0.23	1.8	0.26

copolymerization, because until now all authors have supposed k_{2C2} = 0 if k_{22} = 0 (consequently α_{22} = 0). The correctness of the value obtained can be verified by sequence distribution determinations which are now in progress. The value $\alpha_{22} \neq 0$ should generate a certain amount of diads of picryl methacrylate.

However, by analyzing the data in Table 4 for dioxane solution copolymerization, one can conclude that the intermonomeric CTC is highly active in copolymerization as compared with cross-addition (α_{1C} and $\alpha_{2C} \gg 1$) and with M_1 homopropagation because this latter value is almost equal to M_2 addition at an M_1-ended macroradical (r_{12} = 1.1). The complex reacts mainly on the side that generates alternating sequences ($\alpha_{12} > \alpha_{11}$ and $\alpha_{21} > \alpha_{22}$).

Unexpected results are obtained when comparing the data from Tables 2 and 4 for dioxane with 1,2-dichloroethane. Taking into account that in 1,2-dichloroethane the intermonomeric CTC concentration is higher, the copolymers obtained should have more M_2 units and the CTC addition preference should be at least comparable with that observed in dioxane. The explanation of this anomaly is given by the ^{1}H-NMR spectra of E3-E5 samples, where a signal at 3.7 ppm appears and grows. This signal can be assigned to $-CH_2Cl$ type groups, and it is present in samples maintained a long time in 1,2-dichloroethane. Thus one can suppose that chain transfer reactions to solvent are concurrent with the propagation reactions in 1,2-dichloroethane.
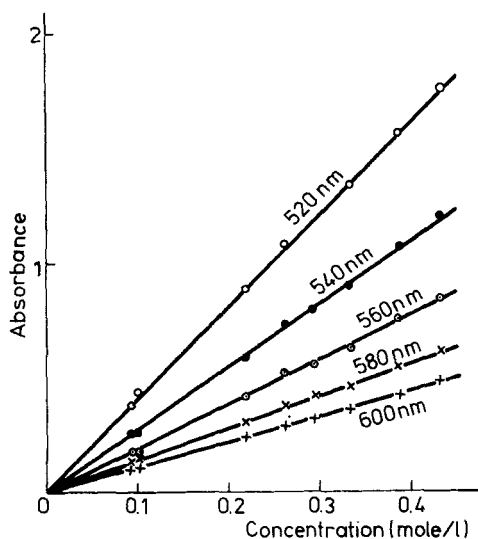
FIG. 5. CTC absorption band linear dependence on concentration
(sample E_1, $CHCl_3$, path length = 1 cm, $25°C$).

The intramolecular character of the CTC copolymers obtained is
demonstrated by the linear dependence of the CTC absorption band
on the copolymer molar concentration. For a sample synthesized in
1,2-dichloroethane, this dependence, for some wavelengths, is given
in Fig. 5. The CTC absorption band linearly depends also on the
copolymer composition, as can be seen in Fig. 6. The slope of this
dependence is higher for stronger intramolecular charge transfer
interactions. As the reactivity ratio values demonstrate, the co-
polymers obtained in dioxane are intramolecular CTC stronger than
those obtained in 1,2-dichloroethane.

The chemical shift of the aromatic protons from picryl methacry-
late structural units also depends on copolymer composition, on the
registration temperature of the ^1H-NMR spectra, and on the solvent
used in synthesis [1, 2]. This is new evidence for the presence of
intramolecular charge transfer interactions. From Fig. 7, one can
conclude that the chemical shift is smaller for samples obtained in
dioxane than in 1,2-dichloroethane, confirming the stronger charge
transfer interactions in this series; and that by increasing the spec-
trum registration temperature, the chemical shift grows, and this
growth is explained by the apparent decomplexation generated by the
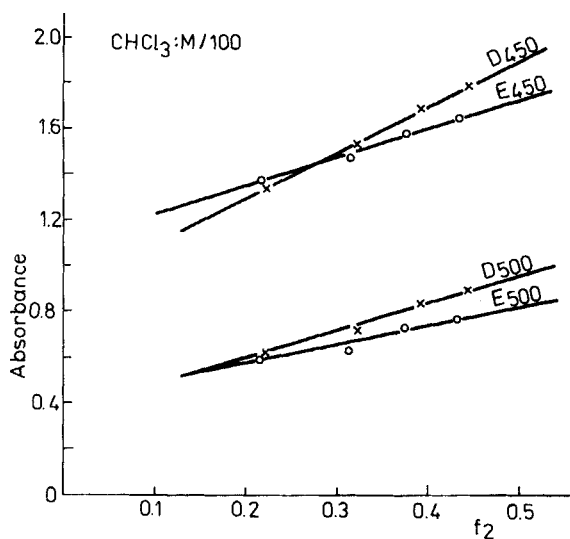increased segmental mobility (conformational change).

FIG. 6. CTC absorption band linear dependence on copolymer com-
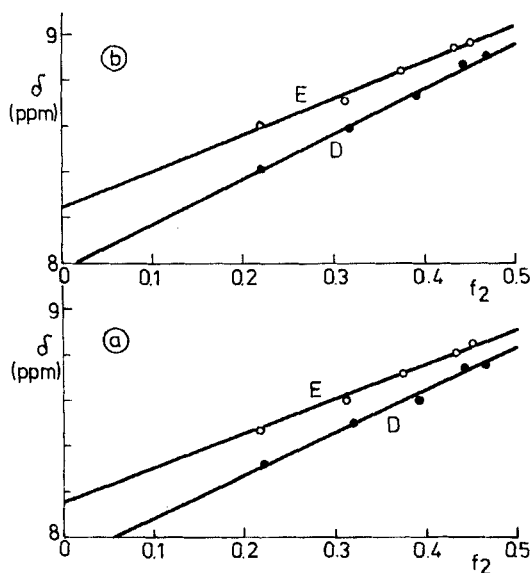position (concentration = 0.01 $\underline{M}$, CHCl$_3$, path length = 1 cm, 25°C).

FIG. 7. Chemical shift of M$_2$ structural unit aromatic protons
against copolymer composition. ^{1}H-NMR spectra registered in CDCl$_3$
at room temperature (a) and 60°C (b).

414

CONCLUSIONS

Radical copolymerization of HECA with picryl methacrylate takes place by the charge transfer mechanism. The copolymers obtained contain many more picryl methacrylate structural units than those obtained from HECM and picryl methacrylate. The reactivity ratios determined for dioxane solution copolymerization show a high preference for intermonomeric CTC addition at both macroradicals. Chain transfer reactions also occur in 1,2-dichloroethane, and the reactivity ratios obtained are less reliable. For this reason the intramolecular CTC character of the copolymers obtained in 1,2-dichloroethane is diminished as compared with those obtained in dioxane. The intramolecular charge transfer interactions depend on copolymer composition, on the solvent used in synthesis (which determines the copolymer microstructure, i.e., sequence distribution and configuration), and on chain conformation.

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