Intramolecular charge transfer complexes: 1. Poly [*N*-(2-hydroxyethyl) carbazolyl methacrylate-co-picryl methacrylate]

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The synthesis of an intramolecular charge transfer complex (CTC) was studied by radical copolymerization of *N*-(2-hydroxyethyl)carbazolyl methacrylate (M_1) with picryl methacrylate (M_2) in dioxane and benzene solutions. For the dioxane solution copolymerizations, the kinetic parameters of the reactions were determined to be: $r_{12} = 10.6$; $r_{1C} = 0.40$; $r_{1C1} = 3.08$; $r_{1C2} = 0.50$ using the intermonomeric CTC mechanism. The intramolecular charge transfer interaction in the copolymer chain and the copolymer configuration and conformation influence on the intramolecular CTC were evidenced.

INTRODUCTION

Interest in macromolecular charge transfer complexes (CTC) is constantly increasing[1], especially due to the use of poly[*N*-vinyl carbazolel] –2,4,7-trinitro-9-fluorenone CTC in electrophotography as a photoconductor[2]. However, only a few examples of intramolecular CTC existing in copolymers with both donor and acceptor groups can be found in the literature. The first published data refer to alternating copolymers of trinitrostyrene with vinyl pyridines or *p*-dimethylaminostyrene[3]. These results have been shown to be questionable[4]. Mulvaney *et al.*[5] reported the synthesis of intramolecular complexes having carbazolyl and dinitrobenzoyl or chloranil side groups. Schulz[1] synthesized copolyesters based on spirocyclopropanetetranitrofluorene/fluorene and showed the existence of intramolecular charge transfer interactions. Tsuchida *et al.*[6] prepared a Mannich-type polymer from dinitrotoluene, 1,3-di-4-piperidylpropane and formaldehyde and also observed intramolecular complexation interactions. Although Kadoma *et al.*[7] reported picryl methacrylate and 2-naphthyl methacrylate copolymerization, they did not study intramolecular complexation. Finally Turner and Stolka[8] synthesized an intramolecular CTC by copolymerization of 2,4,7-trinitro-9-fluorenyl methacrylate with 1-(2-anthryl)ethyl methacrylate.

The aim of this paper is to present the synthesis of a polymeric intramolecular CTC by radical copolymerization of *N*-(2-hydroxyethyl)carbazolyl methacrylate (M_1) with picryl methacrylate (M_2).

EXPERIMENTAL

Materials

N-(2-hydroxyethyl)carbazolyl methacrylate. A mixture of 14.63 g (0.14 mol) methacryloyl chloride and 20 ml benzene was added dropwise (in 30 min) under strong stirring to a solution (cooled at 8°C) consisting of 25 g (0.118 mol) *N*-hydroxyethylcarbazole, 250 ml benzene and 14.17 g (0.14 mol) triethylamine. The mixture was stirred for 1 hour at 10°C and 2 hours at room temperature. Then $Et_3N \cdot HCl$ was separated by filtration and the benzene solution was 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 23 g (69.5%) white crystals (m.p. 77--78°C). Calcd. for $C_{18}NO_2H_{17}$ (279): C, 77.42%; N, 5.02%; O, 11.47%; H, 6.09%. Found: C, 77.55%; N, 5.10%; H, 6.00%; I.r. (KBr): 722, 745 cm^{-1} (carbazolyl group), 1715 cm^{-1} ($\nu_{C=0}$). N.m.r. ($CDCl_3$, TMS, 25°C): $\delta_{CH_3} = 1.85$; $\delta_{-(CH_2)_2-} = 4.66$; $\delta_{=CH-} = 5.58$ (*cis* to CH_3); $\delta_{=CH-} = 5.96$ (*trans* to CH_3); $\delta =$ 7.2--7.85 (aromatic 1, 2, 3, 6, 7, 8 protons); $\delta = 8.28$ (aromatic 4, 5 protons).

N-Hydroxyethylcarbazole was synthesized from carbazole and ethylene oxide[9] and purified by three successive recrystallizations from a cyclohexane–benzene (1:1) mixture. The methacryloyl chloride was synthesized according to the general method for acid chlorides obtaining from acids with benzoyl chloride[10]. After two distillations, only the vinylic and α-methylvinylic protons were observed in the n.m.r. spectrum.

Picryl methacrylate was prepared according to the published method[7] and recrystallized twice from ethanol. The recrystallization from ethanol proved not to be sufficient, because by heating in solvents with minor water content, the picryl methacrylate decomposes to picric acid (yellow coloured) and methacrylic acid. A very high purification of picryl methacrylate was realized by washing with water at temperatures lower than 20°C and drying in vacuum at the same temperatures. The product is white crystalline (m.p. 114–118°C) (ref 7: m.p. 115–119°C). I.r.: 720, 735, 800 cm^{-1} (ν_{-CH} out of plane) 1340, 1345 cm^{-1} (ν_{-NO_2}) 1750 cm^{-1} ($\nu_{-C=O}$). N.m.r: $\delta_{CH_3} = 2.11$; $\delta_{=CH-} = 5.95$ (*cis*) and 6.40 (*trans*); $\delta_{aromatic} = 9.10$.

Benzene and dioxane were purified by reflux on Na, distillation under argon and then kept on CaH_2. AIBN was twice recrystallized from methanol.

Poly[*N*-(2-hydroxyethyl)carbazolyl methacrylate] was

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Table 1 Copolymerization results

Exp. no.	Molar fraction of M_1 in the initial mixture (F_1)	Reaction time (h)	Conversion (%)	Molar fraction of M_1 in the copolymer (f_1)
D1	0.85	26.0	13.70	0.894
D2	0.70	44.5	8.19	0.814
D3	0.55	44.5	5.31	0.756
D4	0.40	30.0	2.00	0.695
D5	0.25	30.0	1.28	0.669
B1	0.85	21.0	12.06	0.874
B2	0.70	21.0	7.94	0.800
B3	0.55	20.5	5.08	0.744
B4	0.40	30.0	4.74	0.693
B5	0.25	44.5	3.23	0.625

D-samples were copolymerized in dioxane and B-samples in benzene

obtained by radical polymerization (10% solution in benzene, AIBN 1%, 60°C, 8 h) and purified by precipitation in methanol.

Instrumental analysis

The i.r. spectra were registered on a Perkin-Elmer 577 spectrophotometer (KBr pellets), the u.v. spectra on a Unicam SP 800, and the n.m.r. spectra on a JEOL C-60HL (60 MHz) spectrometer in $CDCl_3$ solutions (ref. TMS).

Copolymerization

Copolymerizations were carried out in dioxane or benzene 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.

RESULTS AND DISCUSSION

Composition and equilibrium constant of intermonomeric CTC determination

Mixing of the monomers, *N*-(2-hydroxyethyl)carbazolyl methacrylate and picryl methacrylate, in dioxane or benzene, produced rosy and red coloured solutions, respectively, accompanied by a continuous absorption (between 400 and 600 nm) in the visible domain of the absorption spectrum.

The CTC formed has a 1:1 composition, as proved by Job's method[11]. Plotting absorption against molar fraction of one monomer, a maximum is obtained at 1:1 composition.

The equilibrium constant of CTC (K) was determined measuring the chemical shift (in Hz) of the aromatic protons of picryl methacrylate in the n.m.r. spectrum[12]. 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. In these conditions, the values found for equilibrium constants are 1.05 (at 25°C) and, respectively, 0.96 (at 60°C) (l/mol).

In C_6D_6 solutions, the equilibrium constants could not be determined, because the signal to be measured is overlapped by the aromatic resonances of M_1. This shift to higher fields suggests a stronger complexation in benzene solutions.

The attempt to determine K by the Benesi–Hildebrand method from the u.v. spectra[13] failed, the results obtained being different from the n.m.r. results, although the same dioxane solutions were used. This can be explained by the marked influence of the uncomplexed monomers absorptions (the carbazole monomer absorbs up to 420 nm) on the CTC absorption[14]. However, if we consider the higher electron-donating character of dioxane as compared with benzene[15], a bigger value of K for benzene than dioxane solutions can be assumed.

Copolymerization results

Copolymerization results are presented in *Table 1*. The copolymers are soluble in chloroform, benzene, dioxane, tetrahydrofuran. The solubility decreases when increasing the picryl methacrylate content in the copolymer.

From *Table 1* it is clear that both the reaction rate and the picryl methacrylate content are higher for benzene solution copolymerizations. This is a consequence of the larger intermonomeric CTC concentration given by the higher value of K in benzene.

Copolymer composition was determined from the ^1H n.m.r. spectra registered at room temperature using the relation:

$$\frac{A_{\text{aromatic}}}{A_{-(\text{CH}_2)_2-}} = \frac{8f_1 + 2(1-f_1)}{4f_1}$$

where A = corresponding signal area, f_1 = molar fraction of M_1 structural unit. From the aromatic region of the spectra registered at 60°C the composition was verified with the formula:

$$\frac{A_{\text{aromatic } M_1}}{A_{\text{aromatic } M_2}} = \frac{8f_1}{2(1-f_1)}$$

Only at 60°C could the aromatic signals for the two structural units be separated. A typical n.m.r. spectrum is presented in *Figure 1*. For all copolymer composition domains the ratio of signals at 7.3 ppm and 7.9 ppm is 6 protons: 2 protons, indicating the correctness of the assignments.

The compositions determined by n.m.r. were verified also by i.r. spectroscopy, using the optical densities ratio D_{1723}/D_{1770} (1723 cm^{-1} $\nu_{C=O}$ from M_1 structural units, 1770 cm^{-1} $\nu_{C=O}$ from M_2 structural units). This ratio linearly depends on the structural units ratio in copolymer, and the straight line obtained passes through the axis origin. A typical i.r. spectrum is presented in *Figure 2*. The attempt to correlate the absorptions of 722 and 750 cm^{-1} bands (from carbazole) and the 823 cm^{-1} band (from 1,3,4,5-tetrasubstituted benzene) failed, because the 722 cm^{-1} band from picryl methacrylate overlaps the carbazole band.

Copolymerization mechanism

This system cannot be characterized by a simple terminal mechanism, because the Tüdös plots[16,17] calculated for dioxane and benzene solutions copolymerizations (*Figure 3*) are curves and not straight lines.

The intermonomeric CTC has to be taken into account, using the eight equations described by Seiner and Litt[18]:

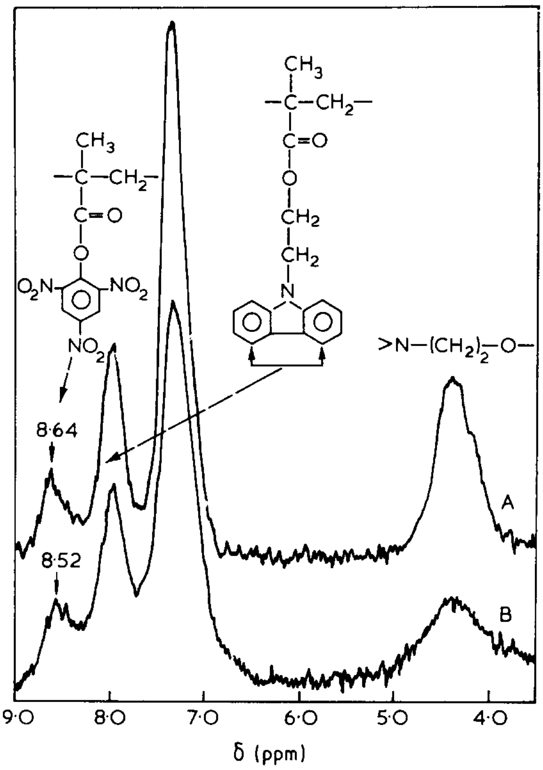

Figure 1 ^{1}H n.m.r. spectrum of D3 copolymer sample at (A) 60°C and (B) room temperature

$$M_1\cdot + M_1 \xrightarrow{k_{11}} M_1M_1\cdot \tag{1}$$

$$M_1\cdot + M_2 \xrightarrow{k_{12}} M_1M_2\cdot \tag{2}$$

$$M_2\cdot + M_1 \xrightarrow{k_{21}} M_2M_1\cdot \tag{3}$$

$$M_2\cdot + M_2 \xrightarrow{k_{22}} M_2M_2\cdot \tag{4}$$

$$M_1\cdot + M_1M_2 \xrightarrow{k_{1C1}} M_1M_1M_2\cdot \tag{5}$$

$$M_1\cdot + M_2M_1 \xrightarrow{k_{1C2}} M_1M_2M_1\cdot \tag{6}$$

$$M_2\cdot + M_1M_2 \xrightarrow{k_{2C1}} M_2M_1M_2\cdot \tag{7}$$

$$M_2\cdot + M_2M_1 \xrightarrow{k_{2C2}} M_2M_2M_1\cdot \tag{8}$$

The copolymerization equation can be written as a two probabilities ratio[20]:

$$y = P_{21}/P_{12}$$

where $y = f_1/f_2$ (copolymer composition) and P_{ij} is the probability that j monomer adds at the i-ended growing chain. These probabilities can be calculated considering equations (1)–(8). One obtains the relation[18]:

$$y = \frac{\dfrac{1 + \left(\dfrac{r_{21}}{r_{2C2}} + \dfrac{r_{21}}{r_{2C1}}\right)\dfrac{[C]}{[M_1]} + \dfrac{r_{12}}{r_{1C2}}\dfrac{[C]}{[M_2]}\dfrac{1 + \dfrac{r_{21}}{r_{2C2}}\dfrac{[C]}{[M_1]}}{1 + \dfrac{r_{12}}{r_{1C1}}\dfrac{[C]}{[M_2]}}}{r_{21}\dfrac{[M_2]}{[M_1]} + 1 + \left(\dfrac{2r_{21}}{r_{2C2}} + \dfrac{r_{21}}{r_{2C1}}\right)\dfrac{[C]}{[M_1]} + \dfrac{r_{12}}{r_{1C2}}\dfrac{[C]}{[M_2]}\dfrac{1 + \dfrac{r_{21}}{r_{2C2}}\dfrac{[C]}{[M_1]}}{1 + \dfrac{r_{12}}{r_{1C1}}\dfrac{[C]}{[M_2]}}}}{\dfrac{1 + \left(\dfrac{r_{12}}{r_{1C1}} + \dfrac{r_{12}}{r_{1C2}}\right)\dfrac{[C]}{[M_2]} + \dfrac{r_{21}}{r_{2C1}}\dfrac{[C]}{[M_1]}\dfrac{1 + \dfrac{r_{12}}{r_{1C1}}\dfrac{[C]}{[M_2]}}{1 + \dfrac{r_{21}}{r_{2C2}}\dfrac{[C]}{[M_1]}}}{r_{12}\dfrac{[M_1]}{[M_2]} + 1 + \left(\dfrac{2r_{12}}{r_{1C1}} + \dfrac{r_{12}}{r_{1C2}}\right)\dfrac{[C]}{[M_2]} + \dfrac{r_{21}}{r_{2C1}}\dfrac{[C]}{[M_1]}\dfrac{1 + \dfrac{r_{12}}{r_{1C1}}\dfrac{[C]}{[M_2]}}{1 + \dfrac{r_{21}}{r_{2C2}}\dfrac{[C]}{[M_1]}}}} \tag{9}$$

where $[C] = [M_1M_2]$ = complex concentration in the initial monomer mixture, calculated from:

$$K = \frac{[C]}{[M_1][M_2]} = \frac{[C]}{([M_1]_0 - [C])([M_2]_0 - [C])}$$

$[M_1]_0$ and $[M_2]_0$ are the initial molar concentrations for the two comonomers and can be calculated from the data in *Table 1*;

$$r_{12} = k_{11}/k_{12}; r_{1C1} = k_{11}/k_{1C1}; r_{1C2} = k_{11}/k_{1C2}$$

$$r_{1C} = k_{11}/k_{1C}; k_{1C} = k_{1C1} + k_{1C2}; r_{21} = k_{22}/k_{21}$$

$$r_{2C1} = k_{22}/k_{2C1}; r_{2C2} = k_{22}/k_{2C2}$$

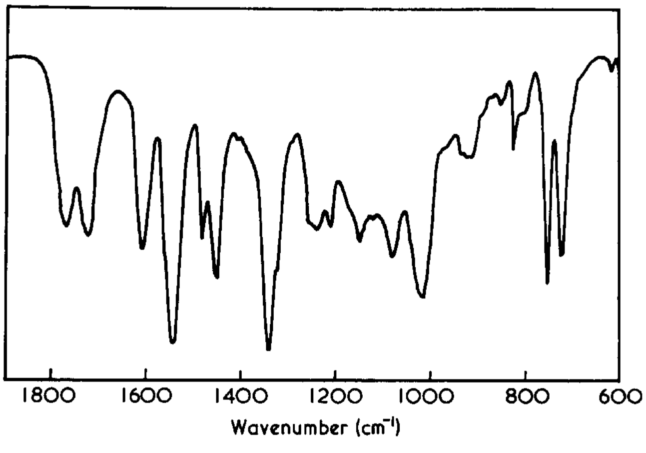

Figure 2 I.r. spectrum of B5 copolymer sample

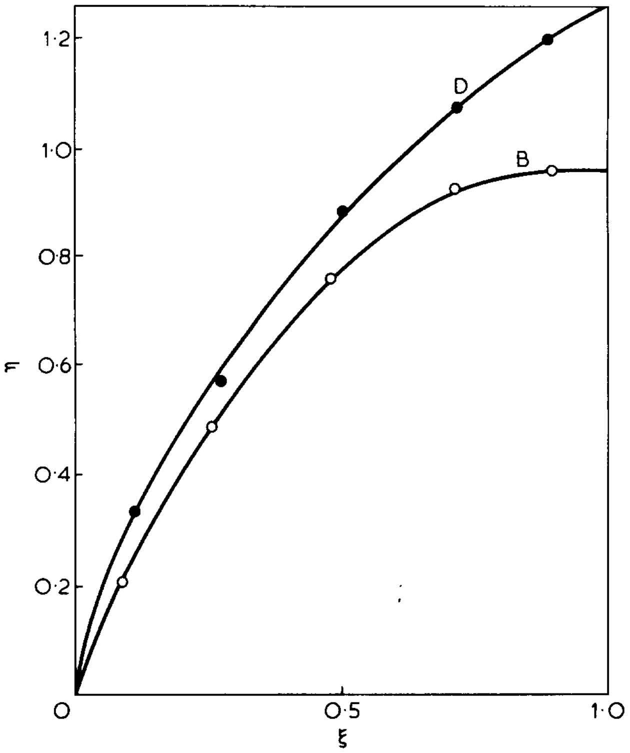

Figure 3 Tüdös plots for copolymerizations in benzene (B) and dioxane (D)

Replacing $r_{21} = 0$ (M_2 does not homopolymerize[7]) in equation (9), one obtains equation (10), derived also by Karad and Schneider[19] in another way:

$$y - 1 = \frac{r_{1C}}{r_{1C1}} + r_{1C}\left(\frac{[M_1]}{[C]} - \frac{y-1}{r_{12}}\,\frac{[M_2]}{[C]}\right) \qquad (10)$$

The plot of equation (10) for dioxane solutions copolymerization is given in *Figure 4*. The straight line in *Figure 4* was obtained by fitting some r_{12} values. The best straight line was obtained for $r_{12} = 10.6$. From the slope and intercept, one can obtain:

$r_{1C} = 0.40$ $r_{1C1} = 3.08$ $r_{1C2} = 0.50$

The reactivity ratios values indicate a strong preference of M_1 monomer to add to M_1-ended growing chains ($r_{12} \gg 1$). Comparing the homopropagation of M_1 with the complex addition to M_1 chain ends, this last is two and a half times larger ($r_{1C} = 0.40$). Also, the complex addition takes place mainly on the side that generates alternating sequences ($r_{1C1} > 1; r_{1C2} < 1$).

The kinetic constants for benzene solution copolymerization could not be determined, because the K value in benzene is not known.

Intramolecular charge transfer interactions

All obtained copolymers are brick-coloured in the solid state and the colour gets darker when increasing the copolymer picryl methacrylate content. Unlike poly[*N*-(2-hydroxyethyl)carbazolyl methacrylate], which absorbs only up to 420 nm, the copolymer spectra present a continuous absorption up to 650 nm. The intramolecular character of the charge transfer interaction between the side groups carbazolyl and picryl was proved by the linear dependence of the charge transfer absorption band on concentration for some wavelengths (*Figure 5*)[6,8]. An intermolecular interaction must vary non-linearly with concentration, due to the equilibrium between the donor and acceptor components. Also, for the same copolymer molar concentration (the copolymer molar mass $M = f_1M_1 + f_2M_2$, where M_1 and M_2 are the structural unit masses), the charge transfer absorption band, for some wavelengths (spectra registered in $CHCl_3$), varies linearly and growingly when increasing the picryl methacrylate content in the copolymer (*Figure 6*). From *Figure 6* it can be observed that the slope of this dependence is larger for the benzene-synthesized copolymers as compared with the dioxane-obtained samples. This fact is a consequence of the higher charge transfer interactions for the copolymers synthesized in benzene.

The same fact was observed representing the chemical shift of the aromatic protons signal of the picryl methacrylate structural units against molar fraction of M_2 in copolymer (*Figure 7*). This chemical shift increases when increasing the registration temperature (*Figure 1* and compare *Figures 7a* and *7b*). The chemical shift growing can be assigned to the apparent intramolecular CTC equilibrium displacement to decomplexation, which takes place when

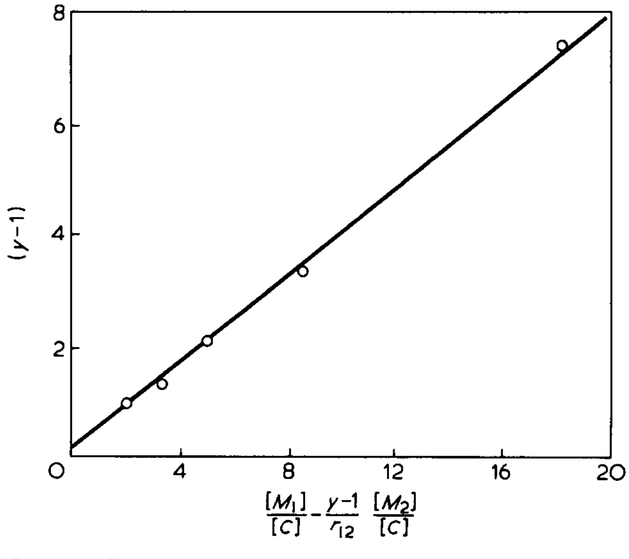

Figure 4 Reactivity ratios determination: r_{1C1}, r_{1C} and r_{1C2} according to equation (10)

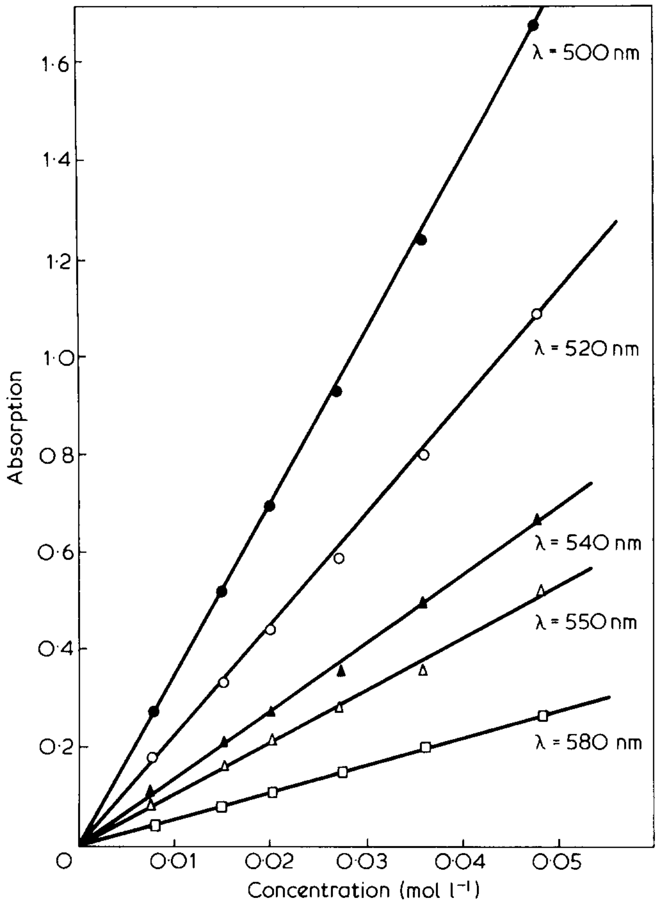

Figure 5 CTC absorption band linear dependence on concentration for D3 copolymer in CHCl$_3$, path length = 1 cm, 25°C

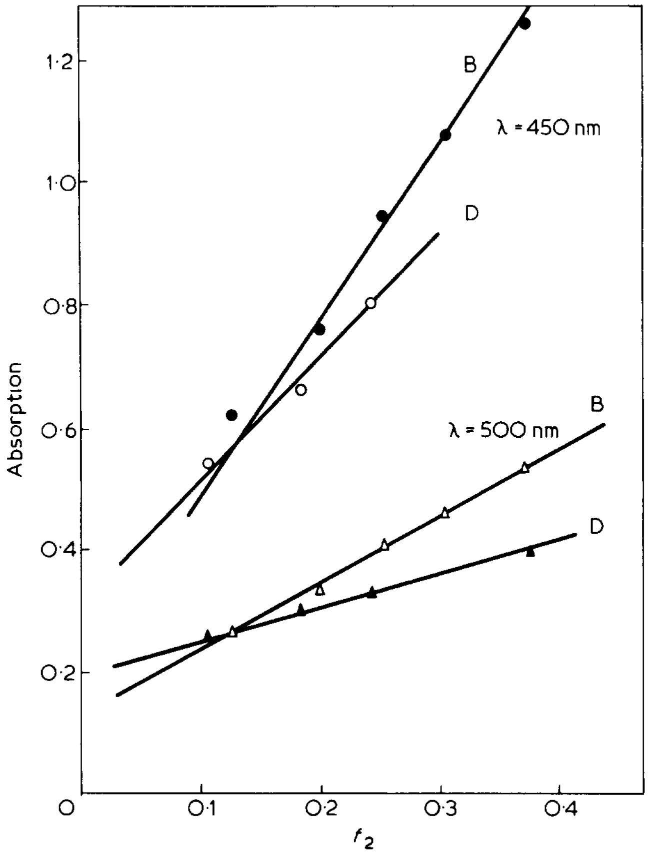

Figure 6 CTC absorption band linear dependence on copolymer composition for benzene (B) and dioxane (D) solutions copolymerizations. Concentration = 10^{-2} mol/l, CHCl$_3$, path length = 1 cm, 25°C

increasing the temperature and, consequently, the chain mobility. Thus, chain conformation influences the intramolecular charge transfer interaction.

Figures 6 and 7 indicate that, for the same composition (f_2), the intramolecular complex apparent concentration for samples obtained in different solvents is not the same. This phenomenon can be a consequence of the different sequence distribution of donor and acceptor units for the two series of copolymers. The differences in sequence distribution imply different intramolecular CTC concentrations for the same composition. Or, if the sequence distribution is the same, the differences in the intramolecular CTC apparent concentrations could be explained on the basis of different configurations for the two series of copolymers, configurations that generate stronger or weaker interactions.

It can be demonstrated that diad sequence fractions and, consequently, the sequence distribution, for the same copolymer composition do not depend on the solvent used, in the above described mechanism. For diad sequence fractions there are the relations:

$$f_{11}=f_1P_{11} \qquad f_{12}=2f_1P_{12}=2f_2P_{21} \qquad f_{22}=f_2P_{22}$$

When M$_2$ does not homopolymerize, $r_{21}=0$ and, replacing this in equation (9), one obtains $P_{21}=1$.

Thus, alternating diad fractions will be:

$$f_{12}=2f_2$$

i.e. all M$_2$ units are isolated on the chain and f_{12} depends

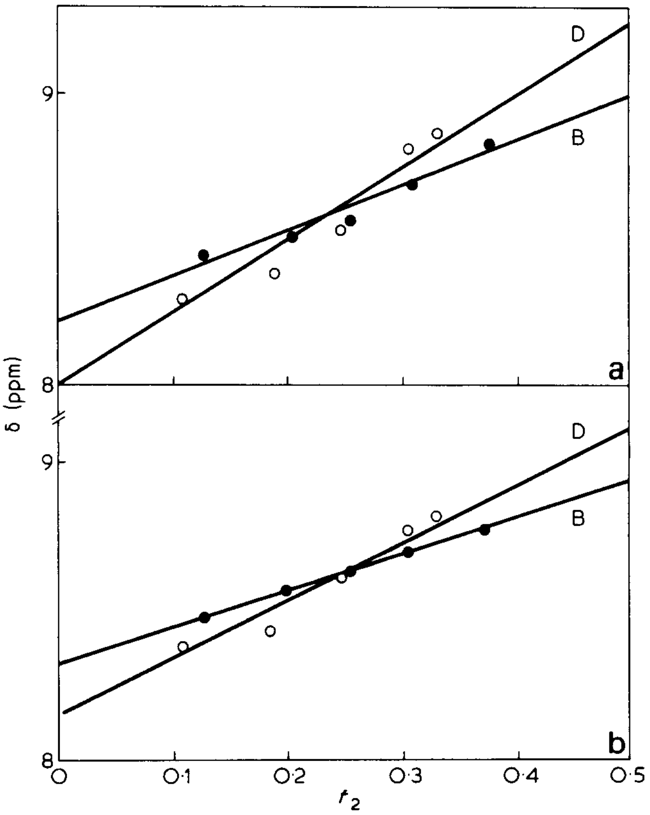

Figure 7 Chemical shift of M$_2$ structural unit aromatic protons against copolymer composition for benzene (B) and dioxane (D) solutions copolymerizations. Spectra registered in CDCl$_3$ at (a) room temperature and (b) 60°C

only on copolymer composition and not on the sample history. So, the explanation of the two straight lines in *Figures 6* and *7* for the two series of copolymers must be the different configurations at the same compositions.

12 diad sequences are formed when the chain grows according to equations (2), (3), (5)–(8). For equations (5)–(8) the 12 sequences exist preliminary in the adding complex, thus their configuration will most probably be co-isotactic. For equations (2) and (3), when the monomers add as separate entities, the steric repulsion rule is supposed to hold, as for most homopolymers[21], and the preferred configuration will be co-syndiotactic. At this moment, we do not have experimental proof to verify this hypothesis. It explains, however, the phenomenon observed in the absorption spectra (*Figure 6*) and in the n.m.r. spectra (*Figure 7*). Indeed, if the intermonomeric complex concentration is higher in benzene than in dioxane, one can suppose the configuration of samples copolymerized in benzene to be more co-isotactic than in dioxane, and, therefore, the steric conditions to have a stronger intramolecular complex to be realized for the copolymerizations in benzene.

CONCLUSIONS

Radical copolymerization of *N*-(2-hydroxyethyl)carbozolyl methacrylate and picryl methacrylate was studied in benzene and dioxane. Copolymerization takes place through the intermonomeric CTC. Solvent nature (the ionization potential) influences, through the intermonomeric CTC equilibrium constant, the copolymerization rate, the copolymer composition and configuration.

The copolymers obtained are intramolecular CTC. The intramolecular charge transfer interactions depend on the copolymer composition, configuration and conformation.

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