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Intramolecular Charge Transfer Complexes

2. Poly(2-Naphtyl Methacrylate-Co-Picryl Methacrylate)

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SUMMARY

In chloroform solutions, 2-naphtyl methacrylate (M_1) and picryl methacrylate (M_2) give a charge transfer complex (CTC) having a 1:1 composition. The CTC plays a decisive part in the radical copolymerization of these monomers. The reactivity ratio values for this system are : $r_{12} = 30$; $r_{1C} = 0.14$; $r_{1C1} = 0.19$; and $r_{1C2} = 0.53$.

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

INTRODUCTION

In a previous paper (SIMIONESCU et al.), the synthesis and the intramolecular charge transfer interactions of the intramolecular charge transfer complex (CTC) poly(N-(2-hydroxyethyl)carbazolyl methacrylate-co-picryl methacrylate) were studied. Also, a short review of literature data concerning intramolecular CTC was presented. The 2-naphtyl methacrylate and picryl methacrylate copolymerization was already reported (KADOMA et al. 1975). The authors have demonstrated that copolymerization takes place through intermonomeric CTC, but they have determined the reactivity ratio values using the simple terminal model. The aim of this note is to obtain the reactivity ratio values taking into account the terminal-charge transfer copolymerization model (SEINER and LITT 1971) and to point out the intramolecular charge transfer interactions in the obtained copolymers.

EXPERIMENTAL

2-Naphtyl methacrylate (PATAI et al. 1952) and picryl methacrylate (KADOMA et al. 1975) were synthesized and purified by already published methods. Spectral (IR, NMR) and elemental analysis and melting points correspond to those given in the literature. AIBN and chloroform were purified by usual methods. Copolymerizations were carried out in chloroform solutions under argon at 60° C in joint-cap bottles. In all cases, the total monomer concentration was 0.25 moles/l and the initiator (AIBN) was 1% of the monomers. The copolymers were precipitated in methanol, dried in vacuum at room temperature and then purified by reprecipitation with methanol from chloroform solution. Copolymer composition (Table 1) was determined from the NMR spectra registered in $CDCl_3$ at room temperature and $60^{\circ}C$ (using the aromatic signals ratio and the aliphatic-aromatic signals ratio)and verified by IR spectroscopy (using the optical densities ratio D1732/D1762; 1732 cm^{-1} $\nu C=O$ of M_1 structural units and 1762 cm^{-1} $\nu C=O$ of M_2 structural units). The ratio D1732/D1762 linearly depends on the M_1/M_2 structural units ratio (y).

TABLE 1

Copolymerization results

Exp. no.	Molar fraction of M_1 in the initial mixture (F_1)	Reaction time (hours)	Conversion (%)	Molar fraction of M_1 in the copolymer(f_1)
C1	0.85	49.25	10.0	0.908
C2	0.70	49.25	3.5	0.847
C3	0.55	76.30	7.6	0.805
C4	0.40	90.00	4.0	0.778
C5	0.25	120.00	1.4	0.757

The intermonomeric CTC equilibrium constant (K) was determined by measuring the chemical shift (in Hz) of the picryl methacrylate aromatic protons in the NMR spectra registered in $CDCl_3$ (TSUCHIDA et al. 1972). The concentration range was between 0.341 and 0.227 moles/l for M_1 and between 0.022 and 0.045 moles/l for M_2. In this range, the chemical shift of uncomplexed picryl methacrylate aromatic protons was 548.0 Hz ($22^{\circ}C$) and 545.8 Hz ($60^{\circ}C$) from TMS. The equilibrium constant had the values of 0.56 ($22^{\circ}C$) and 0.47 ($60^{\circ}C$) l/moles. The attempt to determine K-value in benzene failed, the chemical shift being around the value found for uncomplexed picryl methacrylate in C_6D_6(i.e. 480.0 Hz ($22^{\circ}C$) and 483.9 Hz ($60^{\circ}C$) from TMS) at distances smaller than 1 Hz, without any systematic evolution. This fact can be explained by the existence of two CTC types in benzene solution (M_2-benzene and M_1-M_2), which does not allow precise K-value determinations (TSUCHIDA et al. 1972).

RESULTS AND DISCUSSIONS

The two monomers copolymerization through the charge transfer mechanism is demonstrated by the curvature of the KELEN and TUDOS plot (1975) (Fig. 1). In Figure 1 $r_{21} = 0$ can be seen, as KADOMA et al. (1975) stated, and this fact permits the use of KARAD and SCHNEIDER (1978) equation :

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

where [C] - intermonomeric CTC concentration;
$r_{12} = k_{11}/k_{12}$; $r_{1C} = k_{11}/k_{1C}$; $r_{1C1} = k_{11}/k_{1C1}$.

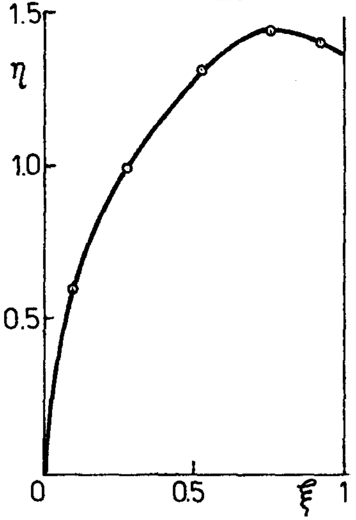

Figure 1. The Kelen-Tüdős plot

In the previous paper (SIMIONESCU et al.) the validity of eq.(1) for all copolymerization domains was demonstrated. The reactivity ratio values are determined by fitting the best straight line for some r_{12} values. The result is :

$r_{12} = 30$ $r_{1C1} = 0.19$ $r_{1C2} = 0.53$ $r_{1C} = 0.14$

where $r_{1C2} = k_{11}/k_{1C2} = k_{11}/(k_{1C} - k_{1C1})$.

These values indicate a strong preference of M_1 for homopropagation ($k_{11} = 30\ k_{12}$) as compared with cross addition. However, by comparing the CTC addition with M_1 homopropagation, the first is preferred (r_{1C}, r_{1C1}, $r_{1C2} < 1$) to the second. If the ratio $r_{12}/r_{1C} = k_{1C}/k_{12} = 215$ is considered, one can conclude that, as KADOMA et al. (1975) already suggested, the copolymerization takes place almost entirely through CTC addition at M_1-ended macroradical, the concurrent reaction being M_1 homopropagation. This is the reason for the relatively low M_2 content in the copolymer. It is also necessary to take into account the fact that the model used does not consider the chain transfer reactions. These reactions must influence the copolymer composition, especially in samples copolymerized for a long time in chloroform.

The copolymers obtained have an intramolecular CTC character. This can be demonstrated by the linear dependence of CTC absorption band on concentration for some wavelengths (Fig. 2).

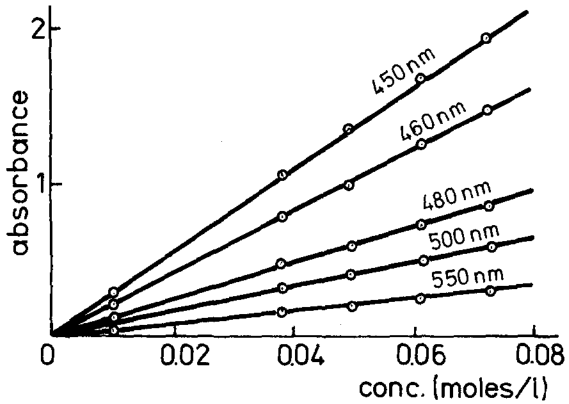

Figure 2. CTC absorption band linear dependence on concentration for C3 sample in $CHCl_3$, path length = 1 cm, 25°C

Also, as evidenced for poly(N-(2-hydroxyethyl)carbazolyl methacrylate-co-picryl methacrylate) CTC (SIMIONESCU et al.), the CTC absorption band linearly depends on copolymer composition (Fig. 3).

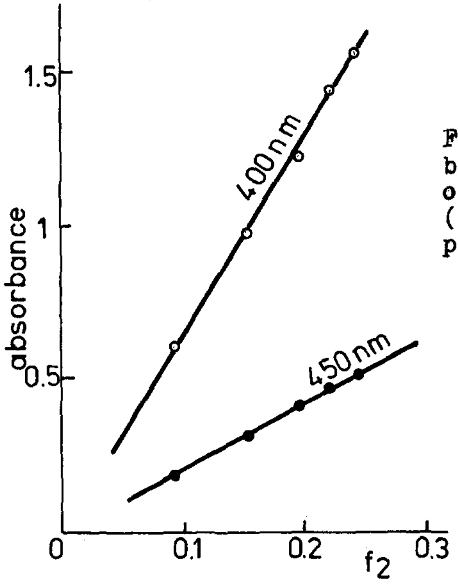

Figure 3. CTC absorption band linear dependence on copolymer composition (concentration 0.01 M, path length = 1 cm, 25°C)

The intramolecular complexation is observed also from the dependence of the chemical shift of the aromatic protons from picryl methacrylate structural units on copolymer composition and on the NMR spectrum registration temperature (Fig. 4). This chemical shift is higher at higher temperatures, indicating the decomplexation due to the increased segmental mobility (conformational changes) and at higher M_2 molar fractions in copolymer, indicating lower CTC apparent concentration.

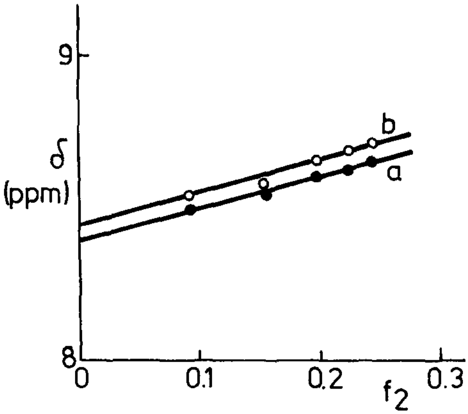

Figure 4. Chemical shift of M_2 structural unit aromatic protons against copolymer composition. Spectra registered at room temperature (a) and 60°C (b)

This fact can be explained by taking into account that the real chemical shift is a ponderate average of complexed and uncomplexed M_2 structural units.

CONCLUSIONS

Radical copolymerization of 2-naphtyl methacrylate with picryl methacrylate takes place mainly through the intermonomeric CTC. The intramolecular charge transfer interactions depend on copolymer composition and conformation.

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