

Intramolecular Charge Transfer Complexes 6.

Temperature Influence on the Copolymerization of N-(2-Hydroxyethyl) Carbazolyl Methacrylate with Picryl Methacrylate

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Summary

By modifying the copolymerization temperature for the system N-(2-hydroxyethyl) carbazolyl methacrylate and picryl methacrylate in dioxane, the reactivity ratio values were shown to be determined mainly through the entropic factor. The obtained intramolecular charge transfer complexes copolymers presented a different intramolecular complexation degree.

Introduction

The synthesis of intramolecular charge transfer complexes (CTC) by copolymerization of some electron-donor and electrono-acceptor monomer pairs was studied in the previous papers (1-6). When one monomer has small ionization potential (electrono-donor monomer, for example N-(2-hydroxyethyl) carbazolyl methacrylate, HECM) and the other high electronic affinity (electrono-acceptor monomer, for example picryl methacrylate, PM) the intermonomeric CTC plays an important part in copolymerization. Then, the copolymer composition and microstructure are determined by the intermonomeric CTC concentration, which is determined not only by the comonomer nature, but also by the total monomer concentration, and by the solvent polarity.

Radical copolymerization of HECM (M_1) with PM (M_2) was studied in benzene and dioxane at 60°C (1). The solvent having higher ionization potential (benzene) gave copolymers with higher PM content. For benzene-resolution copolymerizations, the reactivity ratios could not be determined, because it was impossible to measure K-value (the equilibrium constant of intermonomeric CTC formation) in this solvent, due to the signal overlapping in the $^1\text{H-NMR}$ spectrum.

Because K-value also depend on temperature, the intramolecular CTC microstructure must be determined by the temperature more than in the simple terminal systems.

Experimental

HECM, PM, dioxane and AIBN were synthesized and purified as previously described (1). Copolymerizati-

ons were performed in dioxane under argon with 1% AIBN (from monomers) at a total monomer concentration of 0.5 M. Copolymers were separated by precipitation with methanol and purified by reprecipitation from dioxane solutions with methanol. Copolymer composition was determined from the $^1\text{H-NMR}$ spectra registered in CDCl_3 on a JEOL C-60HL spectrometer. The copolymerization results are given in Table 1, those of 60°C were taken from the precedent paper (1).

Table 1
Copolymerization data

Sample	F_1	Copolymerization at 80°C			Copolymerization at 100°C		
		Time (hr)	Conv. (%)	f_1	Time (hr)	Conv. (%)	f_1
1	0.85	4.0	10.9	0.905	1.0	10.4	0.933
2	0.70	6.0	4.7	0.828	1.8	1.2	0.869
3	0.55	8.5	2.3	0.769	3.5	1.5	0.810
4	0.40	22.5	1.3	0.722	22.5	0.6	0.765
5	0.25	24.0	0.9	0.691	24.0	0.5	0.738

F_1 = molar fraction of HECM in the initial mixture
 f_1 = molar fraction of HECM in copolymer

The intermonomeric CTC equilibrium constant was determined as in the precedent papers (1,2,4) by NMR spectroscopy, and its temperature dependence, together with the thermodynamic parameters are given in Table 2.

Table 2
Intermonomeric complexation parameters

Temperature ($^\circ\text{C}$)	K (1/mole)	E (kcal/mole)	ΔS (cal/mole.dgr)
25	1.05		
60	0.96		
80	0.92	- 0.4	- 1.45
100	0.90		

Results and Discussions

The copolymerization diagrams for 60° , 80° and 100°C are given in figure 1. The PM content in copolymer decreases as the copolymerization temperature increases. This could be explained by the intermonomeric CTC concentration decrease. But, from table 3, it is obvious that the K-value differences are too small to influence the intermonomeric CTC concentration. Therefore, the only explanation for the copolymer PM content decrease remains the change of the individual propagation rates, and this can be seen from the reactivity ratio values.

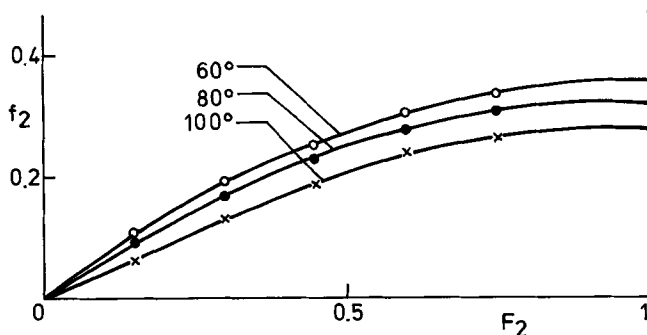
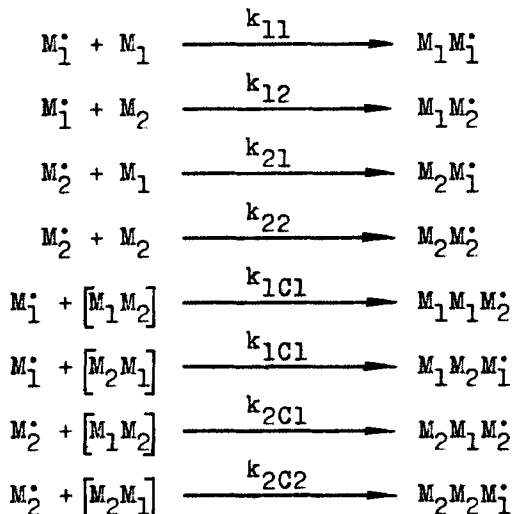


Figure 1. Copolymerization diagrams

Table 3
Intermonomeric CTC concentration

Sample	Concentration, [C], (mole/l)		
	60°C	80°C	100°C
1	0.021	0.021	0.020
2	0.035	0.034	0.034
3	0.041	0.041	0.040
4	0.040	0.039	0.039
5	0.031	0.031	0.030

Having in mind the eight propagation reactions for this copolymerization model (1,2,7,8):



one can determine the reactivity ratio values using the equation proposed by Seiner and Litt and particularized by Karad and Schneider for the case when one monomer does not homopolymerize:

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

where $r_{12} = k_{11}/k_{12}$; $r_{1C1} = k_{11}/k_{1C1}$; $r_{1C2} = k_{11}/k_{1C2}$
 $r_{1C} = k_{11}/k_{1C}$; $k_{1C} = k_{1C1} + k_{1C2}$.

The values given in table 4 are obtained.

Table 4
Reactivity ratio values

Temperature (°C)	r_{12}	r_{1C}	r_{1C1}	r_{1C2}
60	10.6	0.40	3.08	0.50
80	21	0.43	4.3	0.48
100	30	0.64	6.4	0.71

As it can be seen, all reactivity ratio values, higher or smaller than unity, increase with the copolymerization temperature. According to the O'Driscoll's equation (9):

$$\frac{d \ln r_i}{d 1/T} = T \ln r_i$$

the values $r_i < 1$ should increase and the values $r_i > 1$ decrease with the temperature. Therefore, one can conclude that the entropic factor cannot be neglected in radical copolymerization through complexes. The same phenomenon was evidenced in cationic copolymerization, where the frequency factor is decisive (10,11). Using Arrhenius equation:

$$\ln r_{1i} = (\Delta S_{11} - \Delta S_{1i})/R - (E_{11} - E_{1i})/RT$$

the activation energy values and activation entropy values were determined (figure 2) and presented in table 5.

Table 5
Activation energies and entropic factors

r_{1i}	$\Delta S_{11} - \Delta S_{1i}$ (cal/mole.dgr)	$E_{11} - E_{1i}$ (kcal/mole)
r_{12}	24.4	0.7
r_{1C}	8.7	0.4
r_{1C1}	17.3	0.5
r_{1C2}	5.8	0.2

The differences between the homopropagation activation energy and those of cross-propagation or complex addition are rather small, and cannot explain the reactivity ratios variation with the temperature. However, the entropic factor values are much higher, and this is an evidence of the fact that the reactivities in HECM and PM copolymerization are mainly determined by the frequency factor.

The homopropagation reactions are preferred to the cross-addition or to the complex addition, because,

although energetically the last ones are preferred, the entropic factor (which is the determinant one) favours the homopropagation.

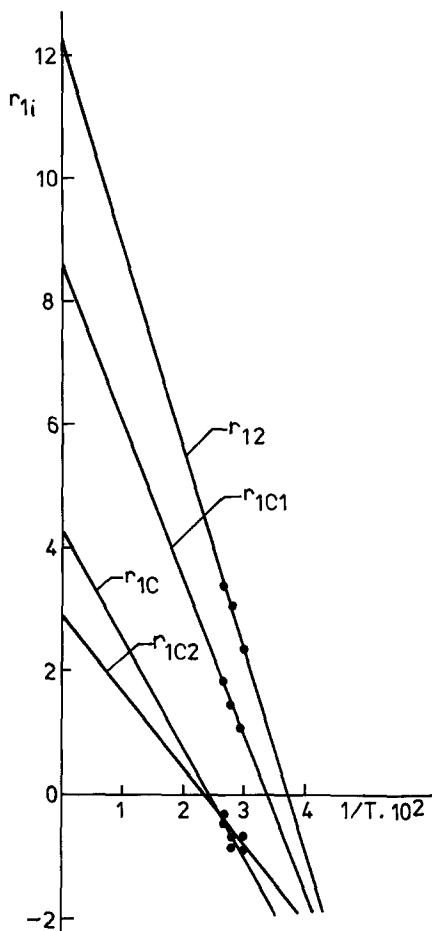


Figure 2. Arrhenius equation applied to the reactivity ratios

From the values given in table 5, the differences of activation energies and entropies between complex propagation and cross-propagation can be calculated:

$$\begin{array}{ll} E_{1C2} - E_{12} = 0.5 & \Delta S_{1C2} - \Delta S_{12} = 18.6 \\ E_{1C1} - E_{12} = 0.2 & \Delta S_{1C1} - \Delta S_{12} = 7.1 \\ E_{1C} - E_{12} = 0.3 & \Delta S_{1C} - \Delta S_{12} = 15.7 \end{array}$$

The above values indicate the entropic preference for complex addition as compared with cross-addition. The complex addition is entropically favoured on the side that generates alternant sequences.

All these data refer to the HECM-ended macroradical, because the reactivity ratios definition gives no data about the PM-ended macroradical. All r_{21} values are null, according to the copolymerization equation, therefore all PM structural units in copolymer have to be isolated, 22 sequences cannot exist. Consequently, for the same composition, the sequence distribution is the same (1). The chemical shift of aromatic protons from PM structural units ($^1\text{H-NMR}$ spectra registered in CDCl_3 at 23° and 60°C) represented against copolymer composition gives different straight lines, depending on copolymerization temperature (figure 3).

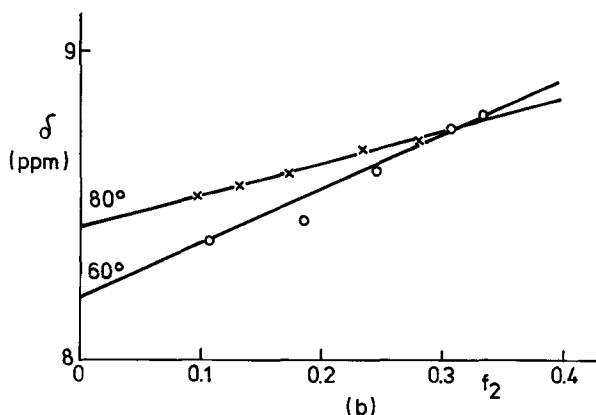
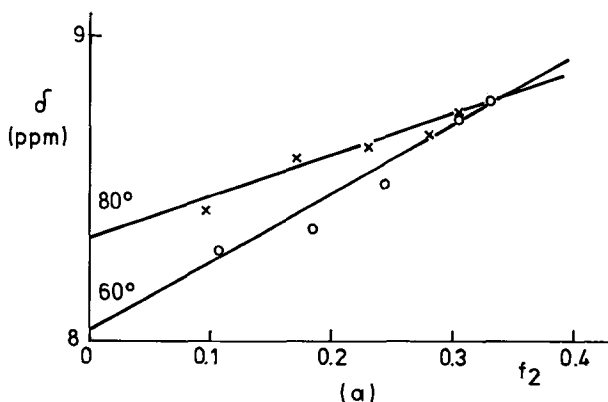


Figure 3. Chemical shift of the aromatic protons from PM structural units against copolymer composition. Spectra registered at a) 23°C and b) 60°C

The differences between the two registration temperatures are a consequence of the different segmental mo-

bility and conformational changes (1,2,4-6).

This shift is an evidence of the intramolecular complexation (1,2,4-6), therefore one can conclude that, performing the copolymerization at 60°C, a stronger intramolecular CTC than at 80°C is obtained. Because the sequence distribution is the same, this phenomenon can be assigned to the chain configuration and/or conformation. The configurational measurements will elucidate this problem.

Conclusions

The HECM-PM copolymerization temperature in the range 60-100°C does not change the intermonomeric CTC concentration, but influences the reactivity ratios through the entropic factor. It also determines the change of the intramolecular complexation in the obtained copolymers.

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