Intramolecular Charge Transfer Complexes

17. Evidence for Complex Participation in Copolymerization of N-(2-Hydroxyethyl)Carbazolyl Methacrylate with Methacryloyl-β-hydroxyethyl-3,5-dinitrobenzoate

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Dedicated to Professor W. J. Bailey on his 60th Birthday

SUMMARY

Copolymerization of N-(2-hydroxyethyl)carbazolyl methacrylate and methacryloyl-β-hydroxyethyl-3,5-dinitrobenzoate in dioxan at different temperatures and total monomer concentrations demonstrates the deviation of this system from the terminal model, although the Kelen-Tüdős plots are always straight lines. The intramolecular charge transfer complexes obtained present different intramolecular complexation degrees, depending on synthesis conditions, indicating important microstructural differences.

INTRODUCTION

The possible mechanisms of copolymerization for electronodonor and electrono-acceptor monomer pairs were discriminated up to now by the Kelen-Tüdős plot. If it was a straight line, then the mechanism was considered terminal and the reactivity ratio values could be determined. If it was a curve, like in cases when one monomer could not homopolymerize or for strong electrono-donor monomers, the terminal mechanism was proved to be incorrect, due to the intermonomeric charge transfer complex (CTC) participation in propagation.

Recently, a case was evidenced when the Kelen-Tüdős plot was a straight line, but the terminal mechanism could not be valid, because the acceptor monomer : acryloyl-β-hydroxyethyl-3,5-dinitrobenzoate does not homopolymerize, but can give succesive additions in complexed state (PERCEC et al. 1981). Also, there are indirect proofs for intermonomeric CTC participation for other cases when the Kelen-Tüdős plots are straight lines; e.g. the copolymerization rate is higher than the homopolymerization rates. Therefore, one can suppose that the Kelen-Tüdős plot has not sufficient power of discrimination for the copolymerization model, at least in the cases implying intermonomeric CTCs. In order to demonstrate this, the effect of the copolymerization temperature and of the total monomer concentration on the copolymerization of N-(2-hydroxyethyl)carbazolyl methacrylate (HECM, M_1) and methacryloyl-β-hydroxyethyl-3,5-dinitrobenzoate (DNBM, M_2) was studied.

Part 16 - J.Polym.Sci., Polym.Chem.Ed., in press

This system was previously (SIMIONESCU et al. 1980a) proven to be apparently azeotropic in dioxan at 60°C and 0.5 M total monomer concentration.

EXPERIMENTAL

HECM (SIMIONESCU et al. 1980b) and DNBM (SIMIONESCU et al. 1980a) were synthesized as described. The copolymerizations were performed in sealed ampoules in dioxan solutions, with 1% AIBN from monomers, under argon. Copolymers were separated by precipitation in methanol and purified by reprecipitation in methanol from tetrahydrofuran solutions. Table 1 gives the copolymerization data.

TABLE 1.
Copolymerization data

x	0.5 M, 80°C				0.5 M, 100°C				0.25 M, 100°C			
	Sam-ple	Time min.	Con-ver-sion	y	Sam-ple	Time min.	Con-ver-sion	y	Sam-ple	Time min.	Con-ver-sion	y
7.00	81	79	54.0	7.33	101	45	66.8	8.09	1d	45	35.2	7.33
3.00	82	63	29.9	3.16	102	45	43.3	3.55	2d	45	31.6	3.44
1.67	83	65	25.8	1.78	103	45	42.2	1.86	3d	50	24.7	1.99
1.00	84	68	25.0	1.08	104	45	30.6	1.18	4d	55	19.9	1.27
0.60	85	70	27.3	0.69	105	45	26.5	0.72	5d	55	20.4	0.90
0.33	86	72	19.1	0.39	106	45	24.0	0.41	6d	53	16.9	0.55
0.14	87	73	18.0	0.18	107	45	20.8	0.19	7d	56	14.0	0.33

$x = [M_1]/[M_2]$; $y = d[M_1]/d[M_2]$; conversion (%).

Copolymer composition was determined from the ^{1}H-NMR spectra registered in DMSOd$_6$ at 150°C on a Jeol C-60HL spectrometer. The copolymerization data for 60°C and 0.5 M total monomer concentration were taken from the previous paper (SIMIONESCU et al. 1980a).

RESULTS AND DISCUSSION

Temperature influence

Copolymerization diagrams at three copolymerization temperatures : 60, 80 and 100°C are given in figure 1. The increase of the reaction temperature leads to a decrease of the acceptor structural units content in copolymer. Data processing through TUDOS et al. (1976) method gives the plots in figure 2 and the relative reactivities summarized in table 2.

TABLE 2.
Reactivity ratios

Temp. (°C) / r	60	80	100
r_1	1.00	1.02	1.16
r_2	1.00	0.71	0.66

r_1 increases with the reaction temperature, whereas r_2 decreases. These data are analysed by Arrhenius equation :

$$\ln r_i = \Delta S/R - \Delta E/RT$$

in order to determine the activation energies and enthalpies of the relative reactivities. Figure 3 gives the Arrhenius plots and in table 3 there are the thermodynamic parameters.
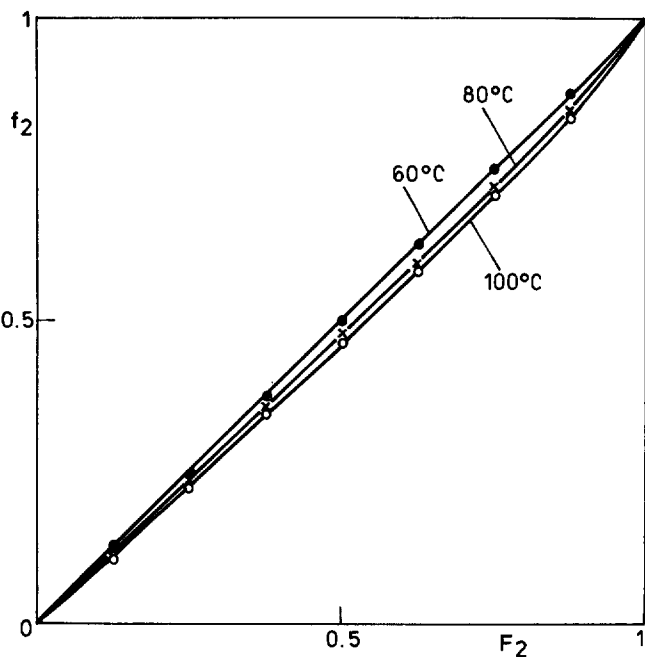
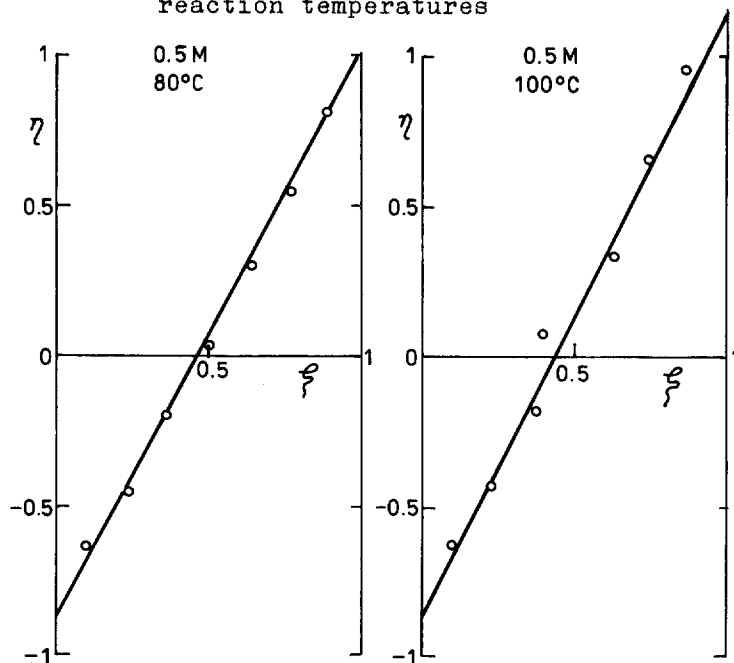Figure 1. Copolymerization diagrams : 0.5 M and three reaction temperatures
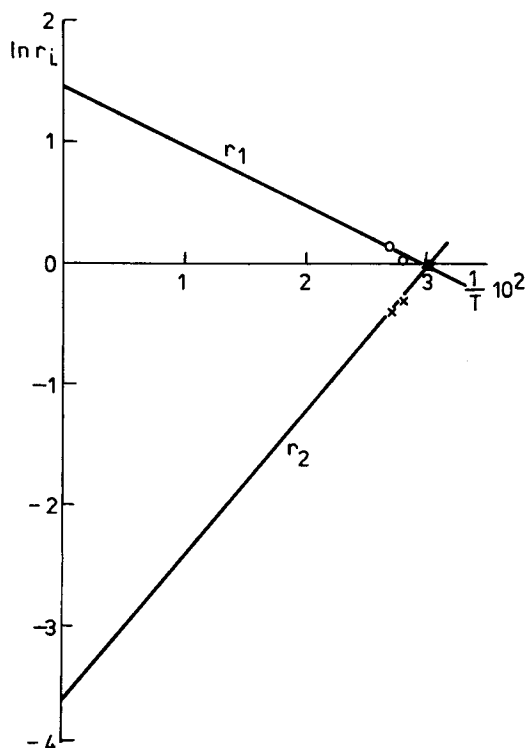

Figure 2. Kelen-Tüdös plots ; 0.5 M

Figure 3. Arrhenius plots.

TABLE 3.
Thermodynamic parameters

	ΔS (cal/mol.dgr)	ΔE (kcal/mol)
r_1	2.88	0.10
r_2	-7.15	-0.20

Like in the systems previously analysed from the thermo-dynamic point of wiew (SIMIONESCU et al. 1980c, in press), here also the frequency factor is the main one in these processes. The thermodynamic values are, also, higher in absolute value for r_2 than for r_1, which means that DNBM reactivity is more affected by temperature.

Total monomer concentration influence

Copolymerization diagrams at 100°C and 0.25 M and 0.5 M total monomer concentrations are given in figure 4. The differences in copolymer composition indicate the non-validity of the terminal model. Data processing according to TUDOS et al. (1976) (figure 5) gives the reactivity ratio values (100°C, 0.25 M) :
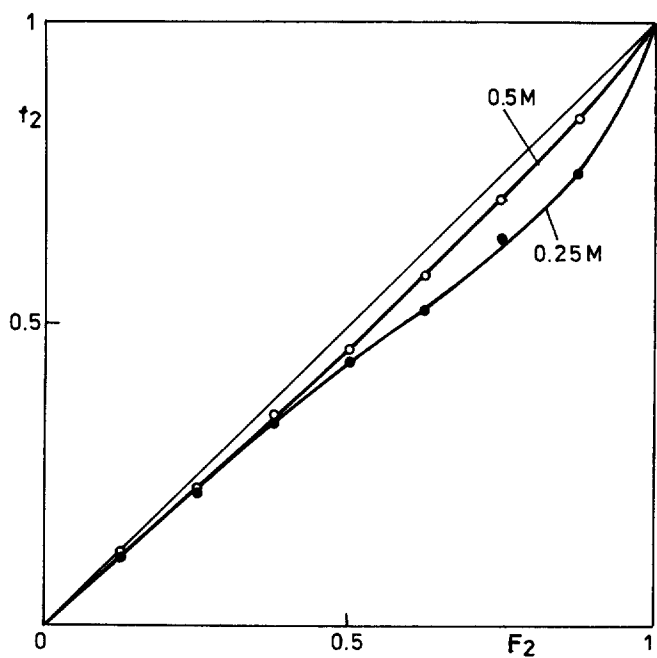
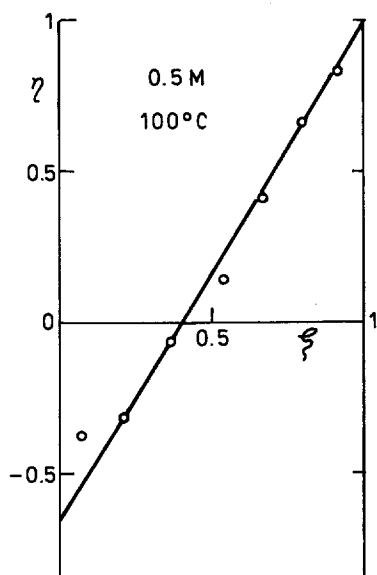$$r_1 = 1.00 \qquad r_2 = 0.44$$

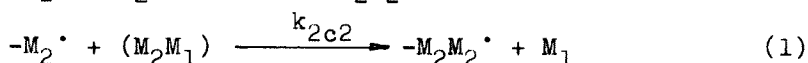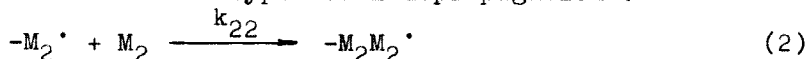Figure 4. Copolymerization diagrams ; 100°C.

Figure 5. Kelen-Tüdös plot (100°C, 0.25 M).

Both values are lower when lowering the total monomer concentration, and r_2 is more decreased than r_1. Consequently, one can deduce that, at higher monomer concentrations, when the intermonomeric concentration is higher, the homopropagation rates of both monomers increase. This phenomenon is analogous to that observed for DNBA (PERCEC et al. 1981), which does not homopolymerize without complexation. The homopropagation takes place according to equation (1) :

$$-M_2{}^{\bullet} + (M_2M_1) \xrightarrow{\quad k_{2c2} \quad} -M_2M_2{}^{\bullet} + M_1 \qquad (1)$$
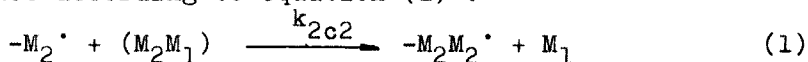
For DNBM there are two types of homopropagation :

$$-M_2{}^{\bullet} + M_2 \xrightarrow{\quad k_{22} \quad} -M_2M_2{}^{\bullet} \qquad (2)$$

$$-M_2{}^{\bullet} + (M_2M_1) \xrightarrow{\quad k_{2c2} \quad} -M_2M_2{}^{\bullet} + M_1 \qquad (1)$$

The increase of complex concentration leads to the increase of eq.(1) rate, giving an apparent increase of the r_2 value (calculated with the terminal model, implying only eq.(2)).

HECM behaves analogously, but in a smaller extent. The fact that r_1 increases with the total monomer concentration indicates a mechanism implying intermonomeric CTC participation for HECM also.

According to these results, it is clear why DNBM reactivity strongly decreases when increasing the copolymerization temperature. This increase causes decomplexation and the rate of eq.(1) decreases, giving a lower k_{22} apparent value. The increase of HECM reactivity can be explained by the real k_{11} increase with the temperature (SIMIONESCU and PERCEC, unpublished).

Therefore, the copolymerization system implying intermonomeric complexes are mainly thermodynamic determined of the frequency factor (SIMIONESCU et al. 1980c, in press), probably because of complexation-decomplexation equilibria.

The chemical shift of the aromatic protons in DNBM structural units is a measure of the intramolecular complexation degree (SIMIONESCU et al. 1980a). Figure 6 represents this chemical shift against copolymer composition.
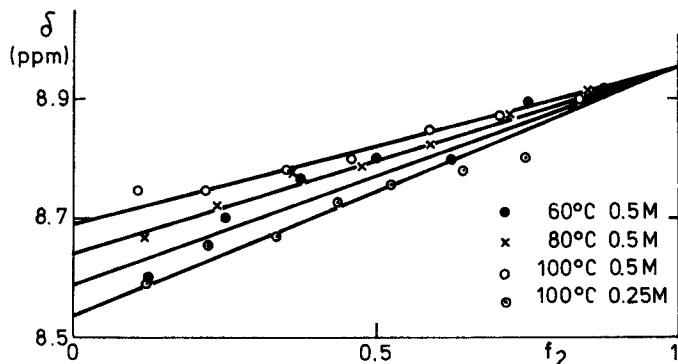

Figure 6. Chemical shift of the aromatic protons in DNBM structural units.

The plot against calculated diad fraction has no physical significance, because the reactivity ratio values are apparent. As it can be seen, the copolymerizations at 0.5 M total concentration give weaker complexes when increasing the copolymerization temperature. An analogous phenomenon was observed for HECM-picryl methacrylate copolymers (SIMIONESCU et al. 1980c) where the mechanism through intermonomeric CTC was evidenced. Surprisingly, the copolymerization at 100°C and 0.25 M generates the strongest complexes. Up to now we cannot find any explanation for this phenomenon.

CONCLUSIONS

For a system having a straight line in the Kelen-Tüdös plot, the intermonomeric CTC participation in copolymerization was evidenced varying the copolymerization temperature and the total monomer concentration. Consequently, in systems presenting complexation-decomplexation equilibria and the possibility of intermonomeric CTC participation in propagation, the Kelen-Tüdös plot is not sufficient for model discrimination. The relative reactivity values determined up to now according to the terminal model are, therefore, apparent for all systems analysed.

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