Polymer Bulletin 5, 225–231 (1981)

Polymer Bulletin

Intramolecular Charge Transfer Complexes

18. Solvent Influence in Copolymerization of N-(2-Hydroxyethyl)Carbazolyl Methacrylate with Methacryloyl-β-hydroxyethyl-3,5-dinitrobenzoate

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Dedicated to Professor H. Benoit on his 60th Birthday

SUMMARY

Copolymerization of N-(2-hydroxyethyl)carbazolyl methacrylate and methacryloyl-β-hydroxyethyl-3,5-dinitrobenzoate in bulk and in different solvents gives different apparent reactivity ratios, depending on the solvent dielectric constant and on the homogenous or heterogenous phase. The intramolecular complexation degree depends also on the copolymerization solvent. The copolymers formed present the character of thermally reversible networks.

INTRODUCTION

In the precedent paper (SIMIONESCU et al., submitted) the copolymerization mechanism of N-(2-hydroxyethyl)carbazolyl methacrylate (HECM, M_1) with methacryloyl-β-hydroxyethyl-3,5-dinitrobenzoate (DNBM, M_2) was demonstrated to imply the intermonomeric charge transfer complex (CTC) participation.

Solvent influence on the reactivity ratios is generally not important. Although the polar factor is important for the alternating tendency, the dielectric constant of the copolymerization medium does not affect, except several cases, the copolymer composition (EASTMOND, 1976). For systems non-obeying the terminal model of copolymerization, the solvent dielectric constant and the homogenous or heterogenous phase (precipitating copolymerization) should be important in complexation-decomplexation phenomena and in monomer diffusion toward the growing chain ends.

This paper presents the synthesis of the intramolecular CTC poly(HECM-co-DNBM) in bulk and in different solvents : acetone, methanol and toluene in order to study solvent influence on copolymer composition and on the intramolecular complexation degree.

EXPERIMENTAL

HECM (SIMIONESCU et al. 1980a) and DNBM (SIMIONESCU et al. 1980b) were synthesized according to the described methods. Acetone was distilled on CaH_2 under argon. Toluene was refluxed on Na during two days and then distilled on Na under argon. The anhydrous methanol was dried on Mg and then distilled under argon.

Copolymerizations were performed in sealed ampoules under

0170-0839/81/0005/0225/$01.40

argon at 60°C (in solution) and 100°C (in bulk) with 1% AIBN from monomers and at a total monomer concentration of 0.5 M. The copolymers were separated by precipitation in methanol and purified by reprecipitation in methanol from tetrahydrofuran (THF) solutions. Copolymerization data are presented in table 1.

TABLE 1.
Copolymerization data

In bulk					In acetone				
Sample	x	Time min.	Conversion(%)	y	Sample	x	Time min.	Conversion(%)	y
1b	3.97	45	42.1	4.26	1a	7.00	145	3.0	4.56
2b	2.19	45	44.5	2.45	2a	3.00	150	3.2	2.45
3b	1.68	45	43.9	1.86	3a	1.67	155	2.9	1.56
4b	0.99	45	35.1	1.13	4a	1.00	155	2.4	1.17
5b	0.62	45	45.5	0.72	5a	0.60	160	2.5	0.82
6b	0.26	45	41.1	0.35	6a	0.33	167	2.1	0.56
7b	0.17	45	43.5	0.25	7a	0.14	175	2.2	0.32
In methanol					In toluene				
Sample	x	Time min.	Conversion(%)	y	Sample	x	Time min.	Conversion(%)	y
1m	6.08	44	6.4	4.00	1t	7.00	130	42.4	4.41
2m	3.00	55	3.0	2.23	2t	3.00	130	30.0	2.28
3m	1.66	52	2.3	1.56	3t	1.67	140	23.7	1.47
4m	1.00	108	11.6	1.17	4t	1.00	143	21.1	0.96
5m	0.58	115	17.4	0.85	5t	0.60	148	20.6	0.63
6m	0.34	126	22.1	0.54	6t	0.33	285	35.0	0.41
7m	0.14	133	24.8	0.25	7t	0.14	315	30.1	0.19

$x = [M_1]/[M_2]$; $y = d[M_1]/d[M_2]$

Copolymer composition was determined from the ^{1}H-NMR spectra registered in DMSOd$_6$ solutions at 150°C on a Jeol C-60HL spectrometer.

RESULTS AND DISCUSSION

Figure 1 gives the copolymerization diagrams and figure 2 the Kelen-Tüdös plots for the four systems studied. The reactivity ratio values are given in table 2.

TABLE 2.
Reactivity ratios and dielectric constants

Solvent	-	dioxan$^+$	acetone	methanol	toluene
r_1	1.08	1.00	0.55	0.54	0.53
r_2	0.75	1.00	0.37	0.38	0.60
r_1r_2	0.81	1.00	0.20	0.21	0.32
Dielectric constant	-	2.2	20.7	32.6	2.4

$^+$ (SIMIONESCU et al. 1980b)

In all cases, the Kelen-Tüdös plots are straight lines, the apparent reactivity ratios, given in table 2, are calculated according to the terminal model. The apparent alternating tendency, illustrated by the reactivity ratios product, increases in the order : dioxan $<$ bulk $<$ toluene $<$ methanol $<$ acetone.

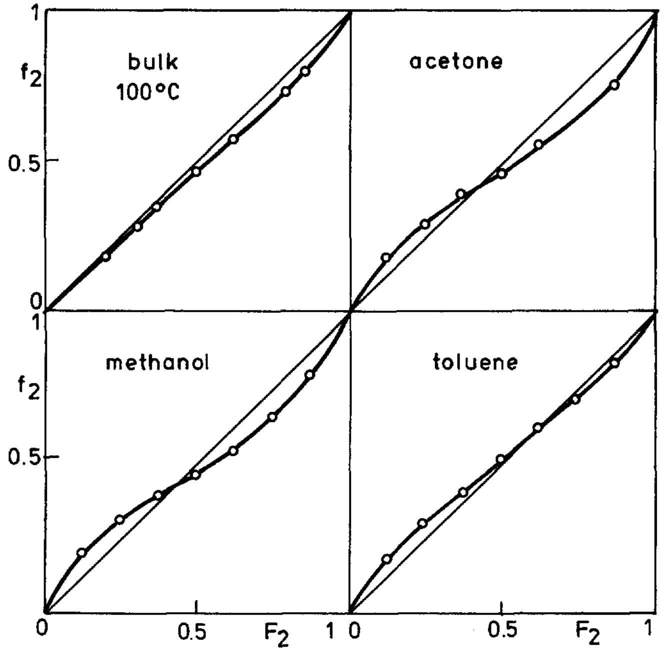

Figure 1. Copolymerization diagrams.

The rather high differences appearing between the reactivity ratio values when changing the copolymerization solvent can be explained by the deviation of this system from the terminal model. Besides the solvent dielectric constant, an important part in this process is played by the copolymer solubility. In methanol and toluene the copolymers are insoluble. In acetone, the conversion was too low to permit the copolymer precipitation. LEDWITH et al. (1979) also observed a significant change of the reactivity ratio values for N-vinyl carbazole (NVC) and methyl methacrylate (MMA) in precipitating copolymerization (in methanol) as compared with copolymerization in benzene. They assigned this change to the solvation differences around the growing chain end.

Taking into account the HECM and DNBM copolymerization mechanism, which implies intermonomeric CTC participation (SIMIONESCU et al., submitted), one can suppose that :
- the reaction medium polarity plays a significant role in the intermonomeric CTC formation and reactivity
- the heterogeneity of the reaction medium favours complexation between the growing chain end and the adding monomer (or complex), increasing the alternating tendency.

The differences in NVC and MMA reactivities suggest a copolymerization mechanism implying intermonomeric CTC participation for this system also.

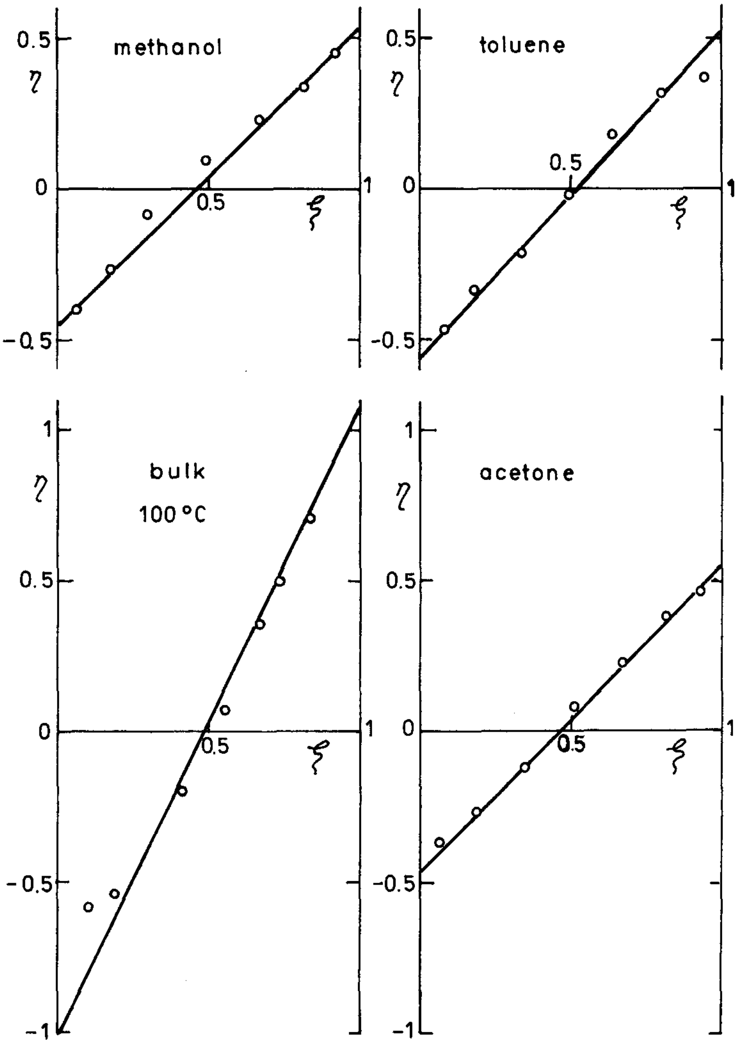

Figure 2. Kelen-Tüdös plots.

The intramolecular complexation degree, estimated from the chemical shift of the aromatic protons of DNBM structural units, depends also on the copolymerization solvent. Figure 3 gives this chemical shift against copolymer composition.

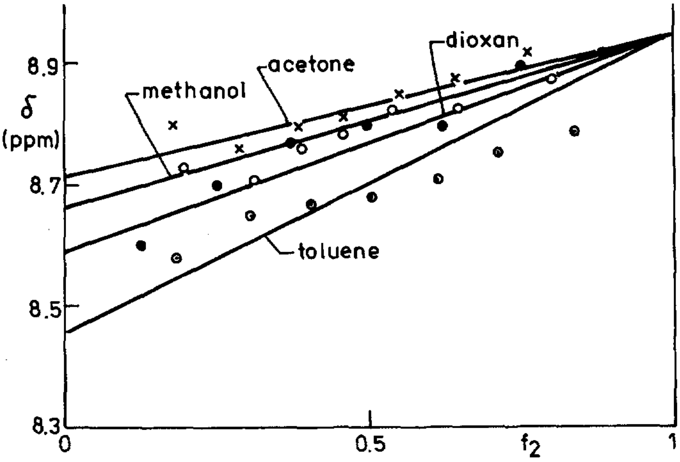

Figure 3a. Chemical shift of DNBM structural units aromatic protons for copolymerizations in different solvents at 60°C.

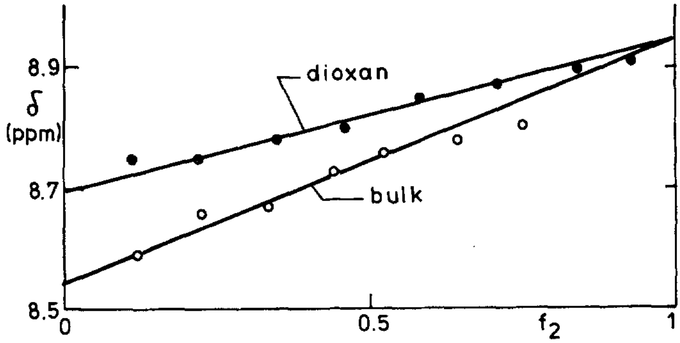

Figure 3b. Chemical shift of DNBM structural units aromatic protons for copolymerizations at 100°C.

The different slopes are due to microstructural differences : sequence distribution and configuration. Both for copolymers obtained in homogenous (acetone, dioxan) and heterogenous (methanol, toluene) phase, the increase of the solvent dielectric constant leads to a weaker intramolecular CTC. For similar values of the dielectric constant, the precipitating copolymerization generates stronger complexes than that obtained in homogenous phase. Sequence distribution analysis by ^{13}C-NMR correlated with the kinetic parameters of each reaction in the CTC copolymerization mechanism will elucidate this yet unclear behaviour.

One of the copolymers properties which must be correlated with the intramolecular complexation is the solubility at room temperature in different solvents. We already pointed out that in copolymers having as acceptor structural units methacryloyl- and acryloyl-β-hydroxyethyl-3,5-dinitrobenzoate (SIMIONESCU et al. 1980b, PERCEC et al. 1981 a and b) or 2'-ethylacryl- and 2'-ethylmethacryl-4,5,7-trinitro-9-fluorenon-2-carboxylate (SIMIONESCU et al. 1980c, 1981) the solubility at room temperature in THF, DMSO, dioxan and DMF decreases when the copolymer composition is nearly 1:1. The 1b-7b samples were dissolved in THF (2.5%), the soluble part was filtered and the insoluble fraction was represented against copolymer composition (figure 4).

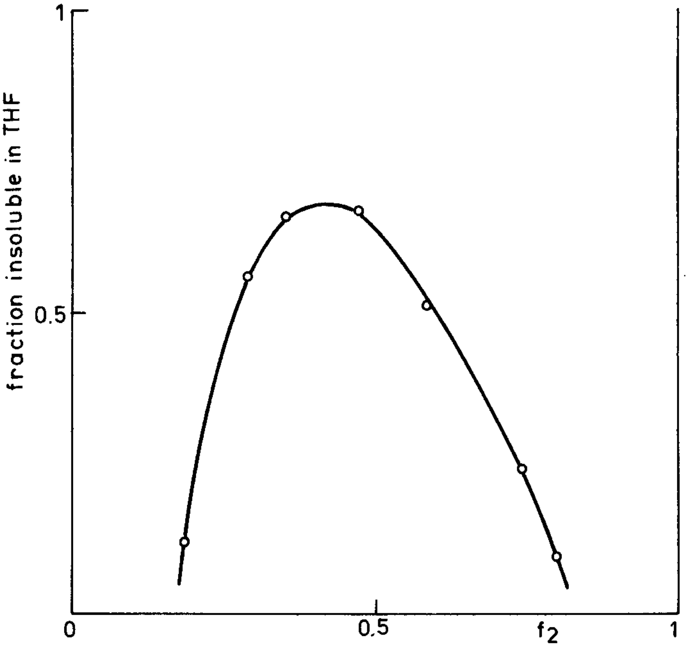

Figure 4. Solubility in THF at room temperature of samples obtained in bulk.

Indeed, this plot has a maximum at ca. 40% DNBM structural units. This is probably the maximum of alternating diad sequences being in the configuration the most favourable for complexation. The samples were then completely dissolved in THF by heating, the solvent was slowly evaporated at room temperature and then an attempt was made to redissolve the samples in THF at room temperature. The insoluble part was constantly between 95 and 100%. The slow solvent evaporation permits an optimum intramolecular and intermolecular complexation, giving a thermally reversible "crosslinking". The reversibility is realized through the thermal reaction of complexation-decomplexation.

CONCLUSIONS

One can design the poly(HECM-co-DNBM) microstructure choosing a suitable copolymerization solvent. Both in homogenous and heterogenous phase, the decrease of the solvent dielectric constant leads to an increase of the intramolecular complexation degree for the same copolymer composition. Precipitating copolymerization gives stronger intramolecular CTCs.

The slow evaporation of the THF solutions favours a maximum intra- and intermolecular complexation degree, giving completely insoluble copolymers at room temperature. The redissolution can be realized by thermal decomplexation, which gives to the copolymers the behaviour of thermally reversible networks.

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Received July 16, 1981
Accepted July 18, 1981