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Copolymerization

Copolymerization of Methyl- and Buthylmethacrylate with Electron-Donor N-(2-Hydroxyethyl)Carbazolyl Methacrylate and Electron-Acceptor (β-Hydroxyethyl)-3,5-Dinitrobenzoyl Methacrylate

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Summary

The radical copolymerization of methyl- and butyl methacrylates with an electron-donor monomer: N-(2-hydroxyethyl)-carbazolyl methacrylate and an electron-acceptor monomer: (β-hydroxyethyl)-3,5-dinitrobenzoyl-methacrylate respectively, in dioxane at 60°C was investigated. The reactivity ratios of the binary systems were computed by using the Kelen-Tüdös method. The azeothropic compositions were established according to the respective copolymerization diagrams.

Introduction

In a series of papers SIMIONESCU, PERCEC and NATANSOHN (1980, 1981a and 1981b) have discussed the copolymerization behaviour of the electron-acceptor monomer (β-hydroxyethyl)-3,5-dinitrobenzoyl methacrylate (DNBM) with the donor monomer N-(2-hydroxyethyl) carbazolyl methacrylate (HECM), showing that the copolymerization is influenced by intermolecular charge-transfer complexation of the electron-donor and the electron-acceptor monomer pair. Although copolymerization ratios were dependent on both temperature and solvent, in the particular case of dioxane at 60°C, copolymerization occured ideal azeothropic (r_1=r_2=1).

Beacause of the improvement of the rheological properties of the above systems (SCHNEIDER et al., 1982) it seemed of interest to extend the study of the influence of CT-complexation on viscoelastic properties of polymer systems with variable content of donor and acceptor groups respectively, obtained by copolymerization of the donor and acceptor monomers respectively, with methylmethacrylate (MMA) and butylmethacrylate (BMA).

Experimental

Copolymerizations were carried out in Argon and/or vacuum in Dioxane at 60°C using 1w/w% of AIBN and a global monomer content of 0.5 mole/l.

HECM (SIMOINESCU et al., 1980a) and DNBM (SIMIONESCU et al., 1980) were synthesized as previously reported, whilst MMA and BMA were purified by conventinal methods. Copolymers were precipitated with methanol and than vacuum dried. The contents of HECM and DNBM respectively, in copolymers were measured by UV-spectroscopy, using for calibration low-molecular model compounds, i.e. the corresponding acetates, (β-hydroxyethyl)-3,5-dinitrobenzoyl-acetate (DNBAc) and N-(2-hydroxyethyl) carbazolyl acetate (HECAc).

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Both the acetates were synthesized by the reaction between acetyl chloride and the respective alcohol, followed by a rigorous purification. The UV spectra of the low-molecular model compounds are presented in Fig.1.

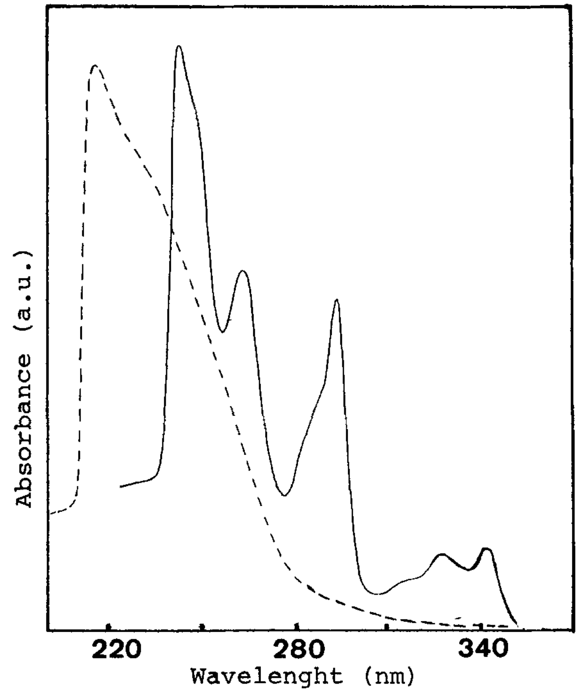

Fig.1 UV spectra of HECAc - full line - and of DNBAc - dotted line - in $CHCl_3$ at 25°C

Starting with the method described by CHERNOBAI et al. (1965) the relations were deduced:

$$X_{HECM} = A_{copol} \cdot M_1 \,/\, (A_{HECAc} \cdot M_2 - A_{copol} \cdot (M_2 - M_1))$$

$$X_{DNBM} = A_{copol} \cdot M_1 \,/\, (A_{DNBAc} \cdot M_1 - A_{copol} \cdot (M_3 - M_1))$$

X_{HECM} and X_{DNBM} are the mole fractions of the respective monomers in the copolymers. A_{copol}, A_{HECAc} and A_{DNBAc} are the absorbances of the copolymer and the model compounds, respectively measured at the same wavelength in $CHCl_3$ at 25°C. A_{HECAc} (294 nm) = 6.5×10^{-2} and A_{DNBAc} (250 nm) = $4.1 \times 10^{-2} l.mg^{-1}.cm^{-1}$ in the Lambert-Beer range.

The molecular weights are of the monomer units: M_1 for the Methyl- and the Butyl Methacrylate, respectively, M_2 for the HECM and M_3 for the DNBM monomer unit.

The copolymerization data for 60°C and 0.5 M total monomer concentration are prezented in TABLE I.

Except the system MMA-DNBM copolymerization was conducted up to high conversion.

TABLE I. Copolymerization Data of MMA and BMA with DNBM and HECM, respectively

MMA-co-DNBM					MMA-co-HECM				
Sample	X	Conver-sion,%	Y	Reaction time	Sample	X	Conver-sion,%	Y	Recation time
MADN1	7.00	5.9	7.06	3h26min	MAHE1	7.00	33.8	7.62	4h53min
MADN2	3.00	1.7	3.18	3h12min	MAHE2	3.00	43.1	3.18	4h53min
MADN3	1.67	11.3	2.22	4h58min	MAHE3	1.67	45.8	1.92	3h56min
MADN5	1.00	3.0	1.28	3h53min	MAHE5	1.00	53.6	2.29[a]	3h38min
MADN6	0.60	6.4	0.82	3h49min	MAHE6	0.60	57.4	0.90	3h19min
MADN7	0.33	4.2	0.45	4h17min	MAHE7	0.33	43.3	0.64	1h25min
MADN8	0.14	2.1	0.21	3h48min	MAHE8	0.14	70.2	1.25[a]	1h25min
BMA-co-DNBM					BMA-co-HECM				
BMDN1	7.00	41.7	5.80	11h30min	BMHE1	7.00	43.9	7.85	4h30min
BMDN2	3.00	28.6	2.76	11h30min	BMHE2	3.00	56.9	3.37	5h10min
BMDN3	1.67	23.0	1.69	11h30min	BMHE3	1.67	57.3	2.14	4h38min
BMDN5	1.00	30.5	1.03	11h30min	BMHE5	1.00	63.0	1.30	4h17min
BMDN6	0.60	27.8	0.70	11h30min	BMHE6	0.60	58.1	1.02	3h06min
BMDN7	0.33	34.5	0.47	12h48min	BMHE7	0.33	62.8	0.80	2h47min
BMDN8	0.14	34.0	0.20	12h48min	BMHE8	0.14	63.7	0.55	2h32min

$X = M_1/M_2$ (monomer feed) ; $Y = dM_1/dM_2$ (copolymer composition by UV measurement)

[a] were not used for calculation of copolymerization ratios

Consequently the method of TÜDÖS et al. (1975) was used for computing reactivity ratios.

Results and Discussion

Using the data of Table I, in Figure 2 are presented the respective KELEN-TÜDÖS plots for both the low and high conversion level.

The reactivity ratios were computed from the two intercepts ($\xi = 0,1$) of the best straight lines according to the recommended expression

$$\eta = (r_1 + r_2/\alpha)\,\xi - (r_2/\alpha)$$

being an adjustable parameter for uniform distribution of experimental data.

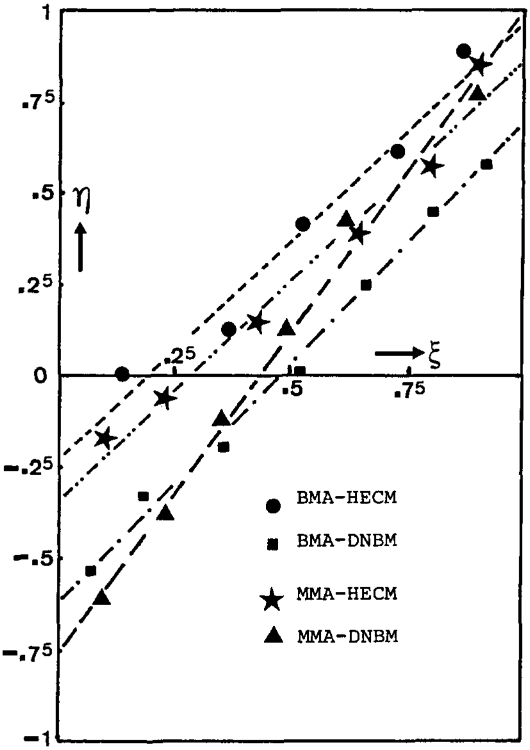

Fig.2. Kelen-Tüdös plots of the studied copolymer systems

The obtained values of reactivity ratios, together with the respective quadratic correlation factors, β^2, and the used adjustable parameter, α , are summarized in TABLE II.

The copolymerization reactivity ratios presented in Table II were then used to draw in Figure 3 the copolymerization diagrams of the studied systems.

It is evident that the concordance between experimetal data (points) and calculated conversion curves (full lines) is quite satisfactory in both the copolymeric systems with the acceptor monomer, DNBM, irrespective of the different conversion degrees reached.

TABLE II. Copolymerization Ratios

Polymer system	r_1	r_2	α	β^2	Azeothrope
MMA-DNBM	1.01	0.60	0.819	0.984	-
BMA-DNBM	0.71	0.54	0.891	0.989	39.5% DNBM
MMA-HECM	0.87	0.33	0.707	0.961	14.4% HECM
BMA-HECM	0.98	0.21	0.891	0.968	2.4% HECM

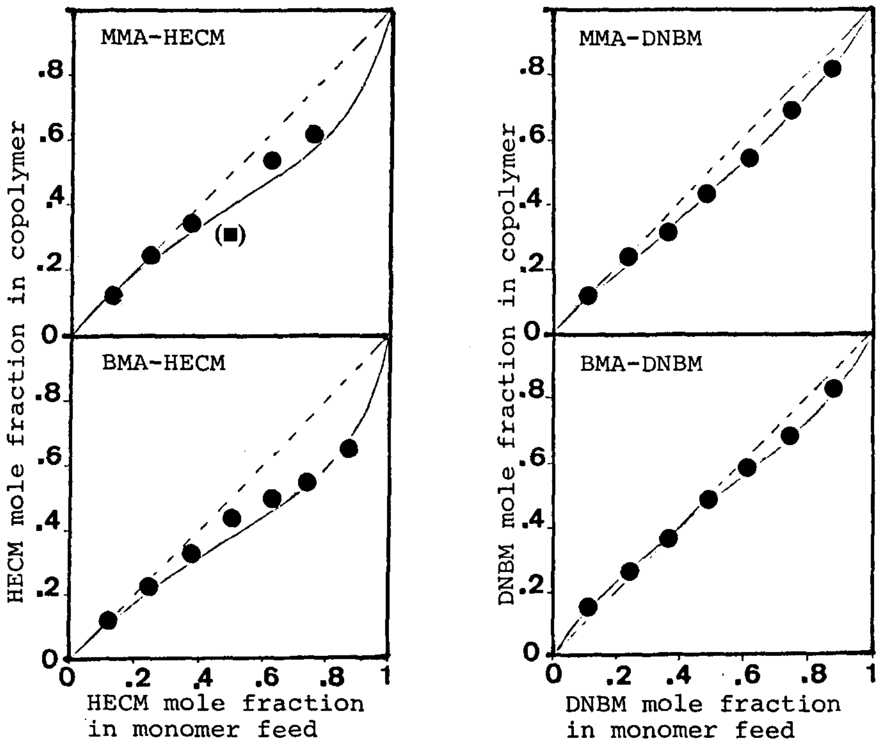

Fig.3. Copolymerization Diagrams. Full lines calculated conversion curves.

Taking into account the values of the r_2 reactivity ratios (in both the systems higher than 0.5) it may be assumed that the chemical heterogeneity is not substantial affected by the higher conversion degree in the second polymeric system. This will be valid mainly for copolymers with lower DNBM content.

On the contrary in the systems with the donor comonomer, HECM, the deviation between experimental data and the calculated conversion curves increases with increasing HECM content in the monomer feed. The reactivity ratios r_2 of both the systems are distinctly below 0.5. The chemical heterogeneity of those copolymers will therefore increase substantially mainly at higher HECM content and for higher conversion. Again chemical heterogeneity will be perhaps neglijible in copolymers with low HECM content, which are of main interest for studying the influence of CT-complexation on the rheological properties in polymer systems.

The differences observed in the copolymerization behaviour of the donor and the acceptor comonomers respectively, are reflected also in some properties of the obtained copolymers.

The molecular weights of the donor copolymers, for instance, are increasing with increasing HECM content, whilst the increasing DNBM content is accompanied sooner by a decrease of the molecular weights of the respective copolymers, although the initiator/overall monomer ratio was allways maintained the same in the copolymerization feed. This is exemplified by the data shown in TABLE III for both the copolymer systems of butylmethacrylate.

TABLE III. Characteristics of the Copolymers of the Buthylmethacrylate Systems

Copolymer	$\bar{M}_n$[a]	T_g[b],K	Copolymer	$\bar{M}_n$[a]	T_g[b],K
PBMA[c]	55,000	285.8			
BMDN1	59,800	298.7	BMHE1	57,400	310.3
BMDN2	39,500	306.2	BMHE2	135,200	330.7
BMDN3	45,900	309.0	BMHE3	100,000	342.9
BMDN5	47,200	311.6	BMHE5	127,200	369.3
BMDN6	49,700	312.3	BMHE6	125,300	380.3
BMDN7	36,000	315.6	BMHE7	160,600	390.2
BMDN8	37,800	317.8	BMHE8	197,700	394.0
PDNBM[c]	12,000	353.1	PHECM[c]	57,000	408.6

[a]measured by osmometry in 1,2-dichlorethane at 30°C,
[b]measured by DSC and extrapolated to zero heating rate,
[c]polymerized in the same conditions as the copolymers

In the same table are also included T_g values of the copolymers. It may be of interest to notice that T_g data of copolymers with HECM exhibit positive deviations from additivity rules and may be explained in the diad approximation of the sequence distribution-glass transition correlation, whilst the data of the copolymers of DNBM show negative deviations and obey to the triad approximation of that correlation (SCHNEIDER and NORTHFLEET NETO, 1983). Differences are also observed in the rheological behaviour of the copolymers (SCHNEIDER, 1984).

Conclusion

In conclusion it may be stated that copolymerization of methacrylic monomers proceeds much more regular with the acceptor DNBM-comonomer than with the donor HECM-comonomer. At low comonomer content of the electron-active component, however, the copolymerization will occure allmost azeothropic as evidenced by the copolymerization diagrams, indiferent of the nature of the active comonomer.

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