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Copolymerization

Methylacrylate with electron-acceptor (β-hydroxyethyl)-3,5-dinitrobenzoyl acrylate and n-butylacrylate with electron-donor N-(2-hydroxyethyl) carbazolyl acrylate

Ulrich Epple[1], Hans Adam Schneider[1]*, and Virgil Percec[2]

[1] Institut für Makromolekulare Chemie, Stefan-Meier-Straße 31, D-7800 Freiburg,
Federal Republic of Germany

[2] Department of Macromolecular Science, Case Western Reserve University,
Cleveland, OH 44106, USA

Summary

The radicalic copolymerization initiated by AIBN in Dioxan at 60°C between n-Butylacrylate and the electron-donor N-(2-Hydroxyethyl)carbazolyl acrylate occured normally in accordance with the terminal model. The copolymerization in the same conditions of Methylacrylate with the electron-acceptor (B-Hydroxyethyl)-3,5-dinitrobenzoyl acrylate, on contrary was possible by "charge transfer" copolymerization only, using N-Ethylcarbazol as inert complexing agent. The reactivity ratios of the binary systems, computed in accordance with the Kelen-Tüdös method were used for constructing the copolymerization diagrams.

Introduction

Intermolecular charge transfer complex (CTC) formation in blends of polymers with electron-donor and electron-acceptor groups improve not only the rheological properties (1), but has also a stabilization effect in incompatible polymer blends (2).

SIMIONESCU, PERCEC and NATANSOHN have analysed in a series of papers the copolymerization behaviour of electron-acceptor with electron-donor monomers, showing that the copolymerization mechanism is strongly influenced by CTC interaction. The observed nonlinearity of the Kelen-Tüdös plots in reactivity ratio determination, characteristic for the nonvalidity of the terminal copolymerization model, was considered generally the evidence for copolymerization mechanism peculiarities, due to the propagation by intermolecular CTC (3). This generally happens when at least one of the comonomers does not homopolymerize (4).

Unfortunately, this correlation between nonlinearity of the Kelen-Tüdös plot and non homopolymerizability of one of the comonomers is not unequivocal and mainly nitro groups containing acceptor monomers may not homopolymerize due to the inhibiting effect of those nitro groups. Nevertheless, "charge transfer" polymerization is possible in the presence of an inert electron-donating compound.

These electron-acceptor monomers copolymerize, however, with electron-donor monomers, showing linear Kelen-Tüdös plots. The electron-acceptor (B-Hydroxyethyl)-3,5-dinitrobenzoyl acrylate, DNBA, for instance is such a nitro group containing acceptor monomer which does not homopolymerize, except in the presence of an inert electrono-donating compound, like N-Ethylcarbazol, but copolymerize normally with electron-donor monomers (5).

Because of the extreme brittleness of blends of electron-donor and electron-acceptor homopolymers, a dilution of the electron-interacting groups and therefore a reduction of the brittleness were attempted by copolymerization of the electron-

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* To whom offprint requests should be sent

TABLE 1. Copolymerization Data and Molecular Weights of the Copolymers

BA-co-HECA							MA-co-DNBA						
Sample	X	Conversion (w/w, %)	Y UV/NMR	Reaction time, h	M_n [b]	M_w [d]	Sample	X	Conversion (w/w, %)	Y UV/NMR	Reaction time, h	M_n	M_w [d]
PBA	-	60.9	-	15	61200	51400	PMA	-	54.6	-	70	46000[b]	44300
BAHE1[a]	15.00	26.6	13.35	15	-	30300	MADN1	11.00	7.3	7.93	171	-	-
BAHE2[a]	6.23	58.6	5.85/6.03	17.5	-	-	MADN2	7.00	4.6	4.33	89	-	5800
BAHE3	2.67	80.7	2.11	15	18800	-	MADN3	3.00	5.6	1.90/4.39	171	6700[c]	-
BAHE4	1.48	77.3	1.40/1.32	8	-	26500	MADN4	1.67	13.6	1.00	168.5	-	-
BAHE5	1.00	60.6	1.08	4.5	24000	-	MADN5	1.00	11.3	0.49	168	6300[c]	-
BAHE6	0.60	67.7	0.70/0.65	4	-	-	MADN6	0.60	6.2	0.24/1.40	170	-	5000
BAHE7	0.33	47.8	0.55	3.5	30000	-	MADN7	0.33	9.0	0.15	167	-	-
BAHE8[a]	0.14	60.6	0.50/012	3	-	23000	MADN8	0.14	7.8	0.07/0.39	169	6400[c]	-
BAHE9[a]	0.07	5.3	0.48	1	-	-							
PHECA	-	92.0	-	12	23000	20600	PDNBA	-	4.8	-	40	-	4100

$X = [M_1] / [M_2]$(monomer feed); $Y = d[M_1] / d[M_2]$ (Copolymer composition); **M_1 = MA , BA**

[a] were not used for calculation of the reactivity ratio, [b] membrane osmose in THF at 30°C

[c] vapour phase osmose in $CHCl_3$ at 30/36°C, [d] GPC in THF (Polystyrene Standards)

donor N-(2-Hydroxyethyl)carbazolyl methacrylate -HECM- and of the electron-acceptor (β-Hydroxyethyl)-3,5-dinitrobenzoyl methacrylate -DNBM- with Methyl- and n-Butylmethacrylate, respectively (6).

The aim of the present paper is to extend the copolymerization of electron-interacting monomers to the respective acrylate compounds, taking into account the lower Tg of the acrylates as compared to those of the methacrylates in expectation of further improvement of the rheological properties by enlargement of the rubber plateau into the lower temperature range.

Experimental

Methylacrylate -MA- and n-Butylacrylate -BA- were both of p.a. degree (FLUKA) and redistilled before use in the presence of CaH_2 and Cu(I)Cl in Nitrogen atmosphere.

The electron-donor N-(2-Hydroxyethyl)carbazolyl acrylate -HECA- (3) and the electron-acceptor DNBA monomers (5), respectively, were synthesized and purified in accordance with the literature cited.

Radical copolymerization of the comonomers with AIBN was carried out under Argon in Dioxan at 60°C. The copolymerization of HECA with BA was conduced in the same conditions used for the methacrylate systems (6), i.e. 1% w/w AIBN and global monomer content of 0.5 mole/l. The homopolymers poly(n-BA), poly(MA) and poly(HECA) were obtained in the same conditions.

In opposition to the observed copolymerization behaviour of the methacrylic electron-acceptor monomer DNBM (6), the acrylic compound DNBA showed an increased inhibiting effect of the nitro groups. This monomer was both homopolymerizable and copolymerizable with acrylates in sytems with high DNBA content by charge transfer poymerization only, in the presence of the inert electronodonating agent, N-Ethylcarbazol in 1:1 mole/mole proportion. Also the initiator content was increased to 2% w/w AIBN.

All copolymers were precipitated with methanol and then purified by several precipitations from chloroform solution.

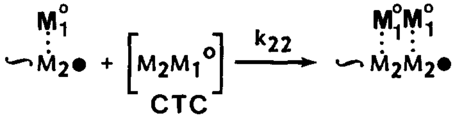
The contents of HECA and DNBA, respectively, were measured by both UV spectroscopy, using for calibration the corresponding acetats as low molecular model compounds, and ^{1}H-NMR spectroscopy. Molecular weights were determined by osmometry in THF at 30°C or vapour phase osmometry in $CHCl_3$ at 30°/36°C and by GPC in THF, using PS standards for calibration, which may explain the discrepancies between osmometric $\bar{M}_n$ and GPC $\bar{M}_w$ values.

The copolymerization data and characteristics of the studied BA-co-HECA and MA-co-DNBA systems, respectively, are shown in TABLE 1.

Taking into account the achieved conversion levels, copolymerization ratios were computed in accordance with the corresponding Kelen-Tüdös methods.

Results and Discussion

The copolymerization data in Table 1 were used for constructing the Kelen-Tüdös plots shown in Fig.1. The straight line behaviour in both the systems confirms the validity of the terminal copolymerization model. Taking into account that DNBA homopolymerizes in the presence of an inert electrono-donating coupling agent only, the respective propagation step by CTC for the homopolymerization of DNBA may be written:



$$\sim\overset{\overset{M_1^{o}}{\vdots}}{M_2}\bullet + \underset{CTC}{\left[M_2M_1^{o}\right]} \xrightarrow{k_{22}} \sim\overset{\overset{M_1^{o}M_1^{o}}{\vdots\ \ \vdots}}{M_2M_2}\bullet$$

with M_1^{o}, the inert electrono-donating agent, N-Ethylcarbazol.

As N-Ethylcarbazol is soluble in methanol, it is washed out during the precipitation of the copolymers with methanol. The complete removal of the inert electron-donating agent during precipitation with methanol is confirmed by the absence of the UV characteristic bands of N-Ethylcarbazol in homopoly(DNBA).

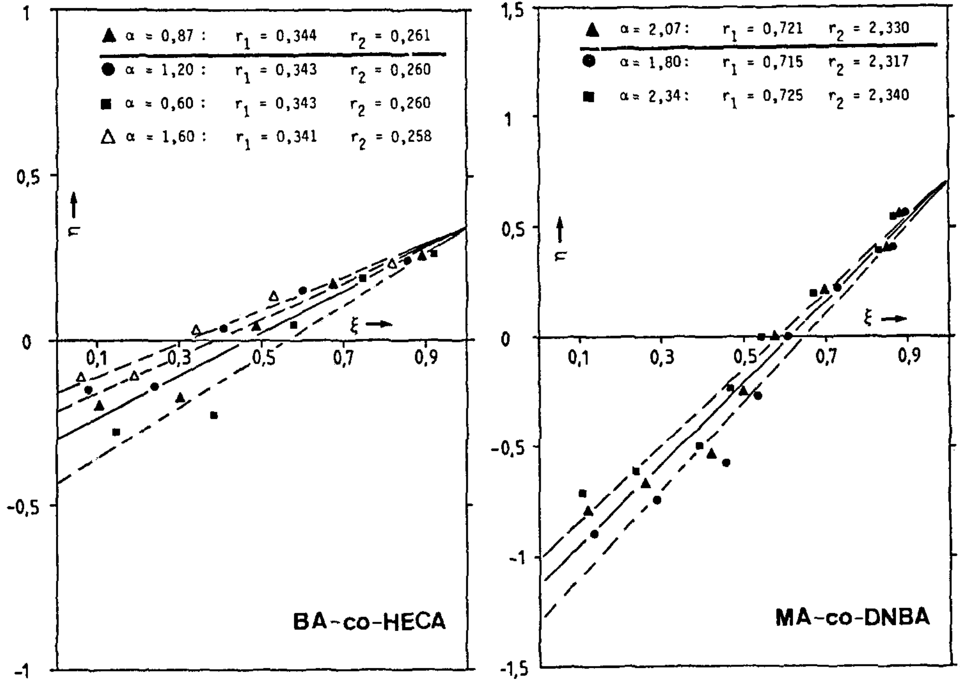


Fig.1 Kelen-Tüdös Plots of the Studied Copolymer Systems
a. BA-co-HECA (high conversion) ; computed α -value: 0.87
b. MA-co-DNBA (low conversion) ; computed α -value: 2.07
Underlined: Reactivity ratio data for computed α -value, $(F_{min} \cdot F_{Max})^{1/2}$

The reactivity ratios were estimated from the two intercepts ($\xi = 0{,}1$) of the best straight lines computed by the last square method, in accordance with the expressions for low conversion (7)

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

and high conversion (8), respectively, when

$$\eta = Z(Y-1)/(\alpha Z^2 + Y)$$

and

$$\xi = Y/(\alpha Z^2 + Y)$$

with $Z = Y/\bar{X}$. η and ξ are conversion related functions, $\eta = G/(\alpha + F)$ and $\xi = F/(\alpha + F)$, with $G = X(Y-1)/Y$ and $F = X^2/Y$. (For X and Y see Table 1).

Beside the recommended value of the correcting parameter $\alpha = (F_{min} \cdot F_{Max})^{1/2}$ the use of other values produced no substantial changes in the computed reactivity ratios, confirming the high accuracy of the obtained data.

The calculated reactivity ratios were then used for the copolymerization diagram plots shown in Fig.2

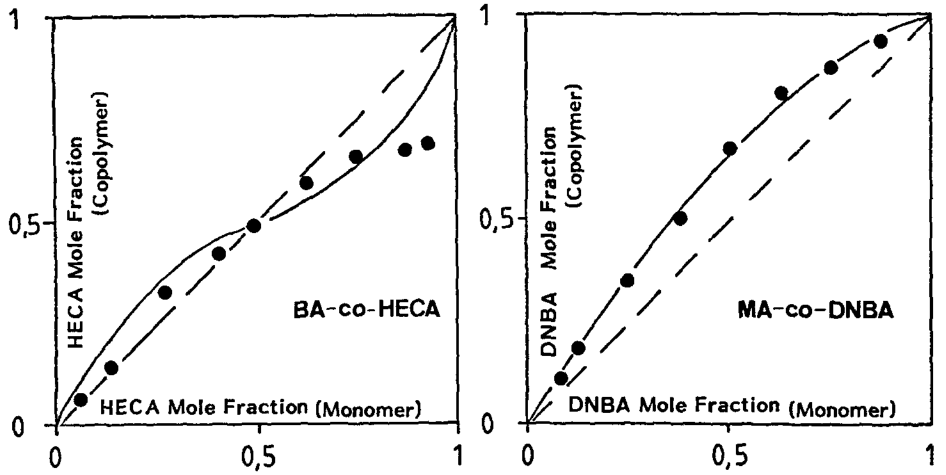


Fig.2 Copolymerization Diagrams of the Studied Copolymer Systems
a. BA-co-HECA (r_1=0.344, r_2=0.261), b. MA-co-DNBA (r_1=0.721, r_2=2.33)
Full lines: Calculated curves for the indicated reactivity ratios,
● experimental data

The composition diagram of the BA-co-HECA system, showing an azeothrope at about 50 mole% HECA, is similar to those observed for the methacrylate systems with both the electron-donor HECM and the electron-acceptor DNBM monomers (6). The molecular weights and the reaction times are also of the same order of magnitude.

Quite different is, on the contrary, the copolymerization behaviour of the MA-co-DNBA system, which obeys the "charge transfer" copolymerization mechanism. Not only the molecular weights of the copolymers are much lower, but also the copolymerization diagram differs by the simple convex shape, showing no azeothrope. This is related with the value of the reactivity ratio r_2>1, i.e. with the fact that the probability of homopolymerization of DNBA is much increased by CTC formation with an inert electrono-donating coupling agent. Due to this CT interaction the probability of approaching of the comonomer is reduced sterically and correspondingly the copolymerization tendency too.

The inhibiting effect of the nitro groups in the acrylic electron-donor monomer DNBA is increased if in copolymerization MA is substitutd by BA and up to now all copolymerization attemptes failed in the BA-co-DNBA system, even when using the inert electrono-donating coupling agent, N-Ethylcarbazol.

In conclusion, the differences observed in the copolymerization behaviour of the methacrylate and acrylate systems using electron-acceptor monomers is due to the increased inhibiting effect of the nitro groups in the acrylates when compared with the methacrylates. The copolymerization with electron-donor monomers occures similar in both the methacrylate and acrylate sytems.

Acknowledgements

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