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

Ulrich Epple and Hans Adam Schneider

Institut für Makromolekulare Chemie der Universität Freiburg, Stefan-Meier-Straße 31,
D-7800 Freiburg, Federal Republic of Germany

Summary

The radicalic copolymerization at 60° C, initiated by AIBN, in the mixture of the none chain transfer solvent benzene and the chain transfer solvent dioxane of methylacrylate with the electron-donor N-(2-hydroxyethyl)carbazolyl acrylate obeys the terminal model. The copolymerization in the same conditions of n-butylacrylate with the electron-acceptor (β-hydroxyethyl)-3,5-dinitrobenzoyl acrylate failed and the desired copolymers were synthesized by radical copolymerization of n-butylacrylate with acryloylchlorid at 85° C in benzene, followed by the polymer analogue reaction with β-hydroxyethyl-3,5-dinitrobenzoate in benzene/THF and with pyridine as base. The reactivity ratios of the binary system, computed in accordance with the Kelen-Tüdös method were used for constructing the copolymerization diagramm, to calculate the sequence distribution and to proof the glass transition - sequence distribution correlations.

Introduction

Recently a great attention has been given to polymer blends containing carbazole and dinitrobenzoyl polymers due to their electrical and photoelectrical properties (1). The increasing interest in this class of polymers is obviously related with the increased photoinduced "memory effect" of polymers containing intramolecular electron donor-acceptor (EDA) complexes of N-(2-hydroxyethyl)carbazolyl acrylate and (β-hydroxyethyl)-3,5-dinitrobenzoyl methacrylate (2). The most important drawbacks of the methacrylate copolymers with poly(N-vinylcarbazole) or poly(N-(2-hydroxyethyl)carbazolyl methacrylate) are the high glass transition temperatures (227° C/146° C) and their brittleness (3,4,5). The decrease of both the glass transition temperature and the brittleness of carbazole containing polymers can be realized either by the increase of the distance of the pendant carbazolyl group or by the increase of the flexibility of the polymer backbone as in case of the acrylate copolymers with (N-2-hydroxyethyl)carbazolyl acrylate (6).

Not only photoelectrical properties of inter- and intramolecular EDA complexes are of great interest. The controlable miscibility through the strength and number of donor acceptor

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*Herrn Professor Rüchardt zum 60. Geburtstag herzlich gewidmet

(DA) interactions can be used to obtain thermodynamical miscible blends. Intermolecular charge transfer complex (CTC) formation in blends of methacrylate polymers with electron-donor and electron-acceptor groups incorporated improve not only the rheological properties (7), but has also a stabilization effect in incompatible polymer blends (8).

The present paper deals about the copolymerization of the electron-donor monomer N-(2-hydroxyethyl-)carbazolyl acrylate (HECA) with methylacrylate (MA) and the indirect synthetic way for copolymers of the electron-acceptor (β-hydroxyethyl)-3,5-dinitrobenzoyl acrylate (DNBA) with n-butylacrylate (BA).

Experimental

Methylacrylate (MA), n-butylacrylate (BA) and acryloylchlorid (ACl) were of p. a. degree (Fluka) and freshly redistilled before use under nitrogen atmosphere in the presence of CaH_2 and Cu(I)Cl.

The electron-donor N-(2-hydroxyethyl)carbazolyl acrylate -HECA- (9) and the electron-acceptor (β-hydroxyethyl)-3,5-dinitrobenzoate (10), respectively, were synthesized and purified in accordance with the literature cited.

Radical copolymerization of the comonomers HECA and MA initiated by AIBN was carried out under argon in mixtures of dioxane:benzene (1:1 and 5:95, respectively) at 60° C, in the conditions used for the acrylate system HECA with BA (11), i.e. 1 % w/w AIBN and a global monomer content of 0.5 mole/l.

Due to the increased inhibiting effect of the nitro-groups the (β-hydroxyethyl)-3,5-dinitrobenzoyl acrylate (DNBA) was not copolymerizable with BA, even by using the charge transfer polymerization technique (11).
This copolymer was obtained by radical copolymerization of the comonomers ACl and BA with AIBN under argon in benzene at 85° C, followed by polymer analogue transformation. The intermediate ACl-BA copolymer was just refluxed with a 1.25 mole excess of β-hydroxyethyl-3,5-dinitrobenzoate (compared to ACl) using pyridine as base and benzene:THF (4:3) as solvent.

All copolymers were precipitated in methanol and then purified by several reprecipitations from chloroform solution into methanol.

The contents of HECA and DNBA, respectively, were measured either by UV spectroscopy (Perkin Elmer 330 spectrophotometer), using for calibration the corresponding acetates as low molecular model compounds or by ^{1}H-NMR spectroscopy (Bruker WP 80 CW spectrophotometer).
IR measurements were performed with polymer films on NaCl plates (Perkin Elmer 1330 infrared spectrophotometer).
Molecular weights were determined by GPC in THF, using PS standards for calibration.
Glass transition temperatures (Tg) were measured using a Perkin

Table 1. Copolymerization data and characteristics of the copolymers

MA-co-HECA							
Sample	X	Conversion (w/w, %)	Y NMR	Reaction time (h)	$\bar{M}_w$-RI[g] (g/mole)	U $\frac{M_w}{M_n} - 1$	T_g[h] (K)
PMA[b]	-	71	-	43	59200	2.10	282.4
MAHE1[b]	18.00	31	23.82	95.5	-	-	-
MAHE2[c]	15.00	76	19.00	48	90800	2.41	300.3
MAHE3[c]	12.00	76	14.87	44	-	-	-
MAHE4[b]	7.00	74	8.80	70	33700	1.91	313.1
MAHE5[c]	3.00	89	4.08	45	-	-	331.7
MAHE6[c,e]	1.67	58	2.73	24	71400	1.71	344.6
MAHE7[c]	1.00	44	1.66	21.5	-	-	352.2
MAHE8[c]	0.60	73	0.71	24	71800	3.35	361.8
MAHE9[c]	0.42	80	0.57	23	-	-	363.9
MAHE10[c]	0.22	93	0.31	20	72700[f]	2.91	367.7
MAHE11[c]	0.07	83	0.10	24	-	-	368.2
PHECA[a]	-	92	-	12	20600[f]	1.34	371.3

BA-co-DNBA							
Sample	X	Conversion (w/w, %)	Cont. DNBA UV (Mol%)	Reaction time (h)	$\bar{M}_w$-RI[g] (g/mole)	U $\frac{M_w}{M_n} - 1$	T_g[h] (K)
PBA[a]	-	61	-	15	51400[f]	0.73	218.4
BACDN1[d]	19.00	14	7.7	12	65600	1.55	237.8
BACDN2[d]	9.00	42	14.8	24	129700	1.58	258.6
BACDN3[d]	1.00	75	63.0	24	35800	1.50	293.8
PDNBA[a]	-	5	-	40	4100	0.28	325.8

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

Solvent: [a] dioxane, [b] dioxane/benzene 1:1, [c] dioxane/benzene 5:95, [d] benzene
global monomer content 0.5 mole/l, 1 % w/w AIBN

[e] were not used for calculation of the reactivity ratio

[f] M_n membran osmose in THF at 30° C : MAHE10 37000, PHECA 23000, PBA 61200 (g/mole)

[g] GPC in THF (polystyrene standards)

[h] DSC 7 extrapolated zero heating rate

Elmer DSC-7 differential scanning calorimeter. After a first controled heating-cooling cycle, scans were run with heating rates of 10°, 20°, 30° and often 40°/min. Tg data were extrapolated for zero heating rate.

The glass transition - sequence distribution correlations (using the obtained r-parameters) were proved according to the diad approximation method of Barton (12) and/or the triad approximation of Ham (13).

Results and Discussion

The copolymerization data and characteristics of the studied MA-co-HECA and BA-co-DNBA systems, respectively, are shown in table 1.
Taking into account the achieved high conversion levels, copolymerization ratios were computed in accordance with the respective Kelen-Tüdös method (14). Best correlation with the experimental data is characterized by the r-parameters ranging between:

$$r1 = 1.563 \text{ to } 1.506$$
$$\text{and} \quad r2 = 0.547 \text{ to } 0.489.$$

The calculated reactivity ratios were then used for construction of the copolymerization diagramm shown in Fig. 1a.

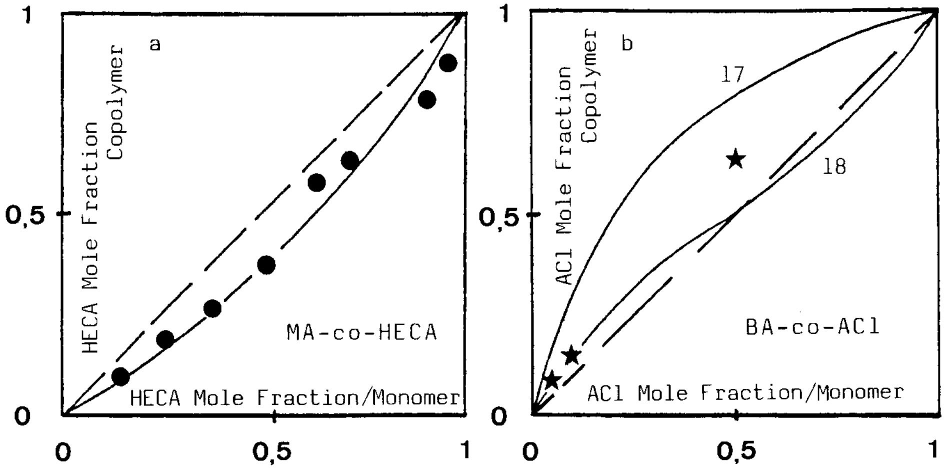


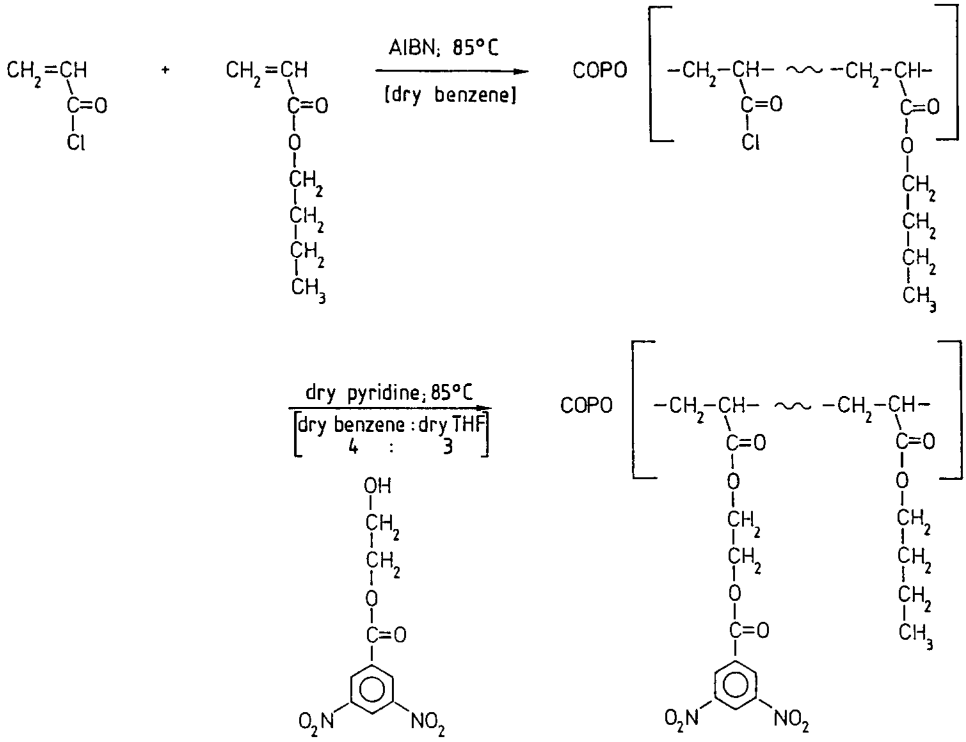
Fig.1 Copolymerization diagramms of the studied copolymer systems
a. MA-co-HECA (r1 = 1.506, r2 = 0.489)
b. BA-co-ACl (r1 = 0.269, r2 = 3.708 lit. 17)
(r1 = 0.518, r2 = 0.614 lit. 18)
Full lines: Calculated curves for the indicated reactivity ratios
● ★ experimental data

The copolymerization behaviour of the MA-co-HECA system exhibits a simple concave shape without azeotrope, which is quite different of the BA-co-HECA system (11) and the homologue methacrylate MMA-co-HECM system (15). Nevertheless all three systems show r1-parameters higher than the r2-parameters.
The higher molecular weight of the copolymers obtained changing

the solvent from pure dioxane to a mixture dioxane/benzene 1:1 and 5:95, respectively, is probably related with the higher chain transfer constant of the solvent dioxane. This affirmation is based on the results obtained in the polymerization of vinyl acetate showing in dioxane at 70° C a 9-fold higher transfer constant than in benzene (16).

The scheme I illustrates the one step reaction for the copolymers BA-co-DNBA.

Scheme I



Quantitative transformation is supported by the absence of low molecular (β-hydroxyethyl)-3,5-dinitrobenzoate (UV detection in GPC) and the presence of the NO_2-bands (1340 and 1545 cm^{-1}) in IR without the 2600 cm^{-1} band of polyacrylic acid. This is also confirmed by the ^1H-NMR (Fig. 2) showing no free polyacid above δ = 9.5 ppm.

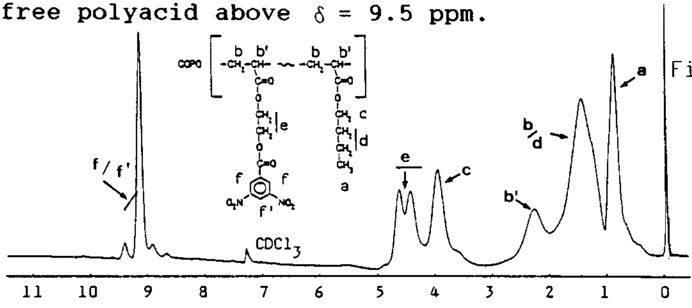


Fig.2

90 MHz ^1H-NMR
($CDCl_3$, TMS / RT)

BACDN3 63.0% DNBA

(Bruker Pulse
NMR CXP 90)

The r-parameters of the system BA-co-ACl were calculated using the Q-e-values (17,18). The corresponding copolymerization diagramm plot is shown in Fig. 1b. In spite of the inherent disadvantages of the Q-e model, the fit of the experimental data is quite satisfactory.

The molecular weights of the copolymers are high in the non chain transfer solvent benzene. In both systems, MA-co-HECA and BA-co-DNBA, polydispersities suggest that branched copolymers are obtained because of the reactive H in α-position to the carboxyl group.

Taking into account the importance of Tg, several attempts are known to correlate Tg data with the sequence distribution and structural factors, mainly those related with chain mobility (rotatable bonds). For the system MA-co-HECA the respective experimental and calculated data are shown in Fig. 3a,b.

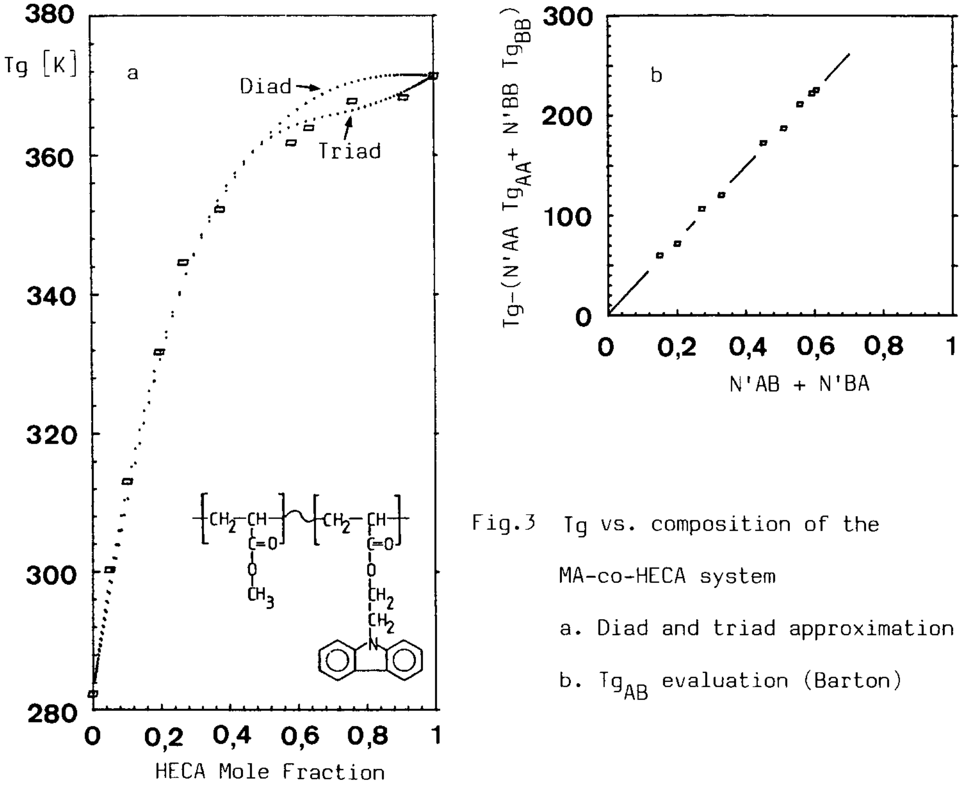


Fig.3 Tg vs. composition of the MA-co-HECA system

a. Diad and triad approximation

b. Tg_{AB} evaluation (Barton)

Starting with the Gibbs-DiMarzio additivity rule for the Tg of copolymers, Barton's diad approximation (12) accounts for specific interactions reflected in different Tg contributions of the hetero AB diad as compared to those of the homo AA and BB diads

$$Tg = N'AA\ Tg_{AA} + N'BB\ Tg_{BB} + (N'AB + N'BA)\ Tg_{AB} \quad (1).$$

N'ij are the weighted mole fractions of the rotatable bonds in the respective diad sequence. The Tg_{AB} of the hetero diad is

computed starting with the experimental data of the sequence distribution, taking into account the mobility of the monomeric units (rotatable bonds).
Linearity of the data, presented in Fig. 3b in accordance with Barton's equ. (1) is only obtained for a reduced number of 3 rotatable bonds in the MA monomeric unit. A possible explanation could be the intramolecular H-bonding accompanied by the formation of stiff 5 atom rings within the polymer backbone (Fig. 4). It is remarkable that the computed Tg_{AB} of 374.1 K is higher than the Tg values of both homopolymers.

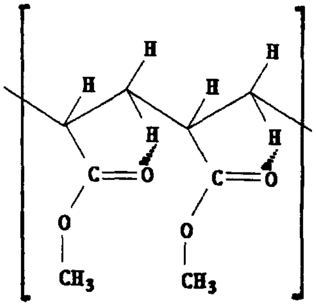


Fig.4 MA monomeric units intramolecular H-bonding

The fit of the experimental Tg-composition data can be improved by using the triad approximation of Ham (13). The superiority of this triad approximation is evident mainly in the higher HECA-range and the used Tg-parameters of the triads and the pertaining rotatable bonds are shown in table 2, together with the respective values for the diad approximation.

Table 2. T_g Increments and rotatable bonds (RB) of diads and triads

Diad-sequence approximation		T_g Increments, K	
RB (MA/MA)	6	282.4	
RB (MA/HE)	12	374.1	intercept 0.5
RB (HE/HE)	14	371.3	
Triad-sequence approximation		T_g Increments, K	
RB (MA/MA/MA)	9	282.4	
RB (MA/MA/HE)	13	385.0	
RB (MA/HE/MA)	16	375.0	
RB (HE/MA/HE)	16	362.5	
RB (HE/HE/MA)	18	345.0	
RB (HE/HE/HE)	20	371.3	

Both the values of the triad Tg-parameters and of the rotatable bonds suggest a strong decrease in the fractional free volumne and/or a diminution of the mobility by incorperating HECA in the MA polymer chain. Strong interactions may be supposed and the acrylate groups seem to act also as acceptor for the electron-donor HECA. This behaviour is observed in all the studied acrylic (methacrylic) / donor copolymer systems (6).

Additional studies are in progress to verify these assumptions concerning the Tg vs. composition dependence of copolymers on the nature and size of the interacting monomeric units.

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