Copolymerization of Acrylonitrile with Haloalkyl Acrylates and Methacrylates

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ABSTRACT

Acrylonitrile (M_1) was copolymerized with haloalkyl acrylates/
methacrylates (M_2) in a water-acetone [2:1 (v/v)] medium at
40°C. The composition of the copolymers was determined from
the nitrogen content, and the reactivity ratios were calculated by
the Kelen-Tüdos method. The low r_1 values (acrylonitrile) in
acrylonitrile (AN)-2-bromoethyl acrylate (BEA)/2-bromoethyl
methacrylate (BEMA) as compared to acrylonitrile-2-chloroethyl
acrylate (AN-CEA) and acrylonitrile-2-chloroethyl methacrylate
(AN-CEMA) may be attributed to the higher reactivity of bromo-
alkyl monomers (BEA and BEMA) toward the polyacrylonitrile
radical. Further, r_1 tends to decrease when M_2 is changed from
acrylate to methacrylate, viz., r_1 (AN-BEA) > r_1 (AN-BEMA),
while the trend is reversed in chloroalkyl acrylate monomers,
i.e., r_1(AN-CEA) < r_1 (AN-CEMA).

INTRODUCTION

Acrylonitrile has been copolymerized with a number of hydroxy-
alkyl acrylates and other hydrophilic or polar monomers to yield fiber-
forming polymers with higher moisture regain [1-4]. The effects of

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medium on the reactivity ratios of acrylonitrile/acrylate copolymeri-
zations in some free radical polymerizations (for example, in acrylo-
nitrile-methyl methacrylate [5], acrylonitrile-2-hydroxyalkyl meth-
acrylate [6], and acrylonitrile-3-chloro,2-hydroxypropyl acrylate and
methacrylate [7]) have also been reported.

In the present investigation a number of haloalkyl acrylates/meth-
acrylates have been synthesized and the effect of the alkyl group on
the reactivity of alkyl acrylate/methacrylate monomers in their radi-
cal copolymerizations with acrylonitrile is reported.

EXPERIMENTAL

The purification of acrylonitrile and the preparation of 3-chloro-
2-hydroxypropyl acrylate have been reported previously [7].

SYNTHESIS OF HALOALKYL ACRYLATES/ METHACRYLATES

2-Bromoethyl acrylate (BEA) and 2-bromoethyl methacrylate
(BEMA) were prepared by the esterification of acrylic/methacrylic
acid and bromoethanol using p-toluene sulfonic acid catalyst according
to the method reported by Lee [8].

2-Chloroethyl acrylate (CEA) and 2-chloroethyl methacrylate
(CEMA) were synthesized according to the method reported by Askarov
and Pinkhasov [9].

The reactions proceed as follows:

$$CH_2=CH-COOH + HOCH_2CH_2Br \longrightarrow CH_2=CH-\overset{\overset{\text{O}}{\|}}{C}-O-CH_2CH_2Br + H_2O$$

(BEA)

$$CH_2=\overset{\overset{\text{CH}_3}{|}}{C}-COOH + HOCH_2CH_2Br \longrightarrow CH_2=\overset{\overset{\text{CH}_3}{|}}{C}-\overset{\overset{\text{O}}{\|}}{C}-O-CH_2CH_2Br + H_2O$$

(BEMA)

$$CH_2=CH-COOH + HOCH_2CH_2Cl \longrightarrow CH_2=CH-\overset{\overset{\text{O}}{\|}}{C}-O-CH_2CH_2Cl + H_2O$$

(CEA)

$$CH_2 =C-COOH + HOCH_2 CH_2 Cl \longrightarrow CH_2 =C-\overset{CH_3}{\underset{}{|}}-\overset{O}{\overset{\|}{C}}-O-CH_2 CH_2 Cl + H_2 O$$

$$\underset{CH_3}{|} \qquad\qquad\qquad (CEMA)$$
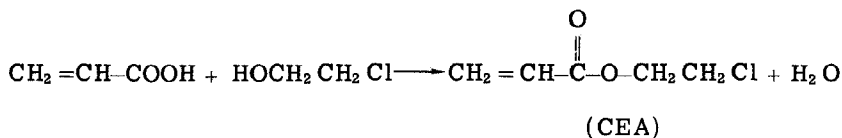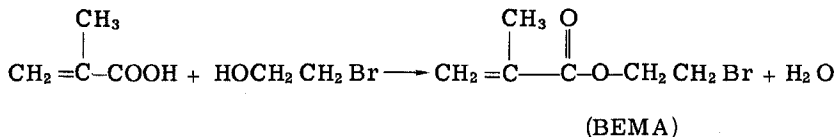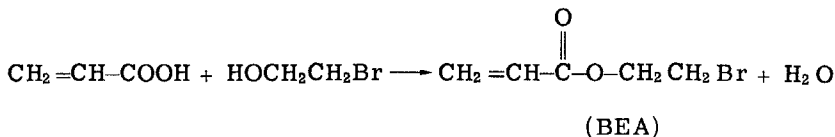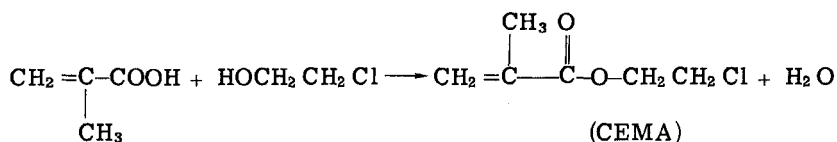
The reactants were refluxed in benzene medium in the cases of CEA, CEMA and BEMA, with water as a by-product which was removed from the reaction mixture periodically as an azeotropic mixture. BEA was synthesized using toluene as the high refluxing medium.

The boiling points (bp) under reduced pressure and the halogen contents estimated by Stepnow's method [10] are given in Table 1.

COPOLYMERIZATION

Copolymerizations were carried out in a two-necked flask fitted with a reflux condenser and a glass inlet tube at 40°C in a deionized water-acetone (2:1 v/v) medium with a monomer dilution of 1 mol/L

TABLE 1

| Monomer code	Structure	Boiling point (°C/min)	Halogen content, %: Found (calculated)
BEA	$CH_2 =CH-\overset{O}{\overset{\|}{C}}-OCH_2 CH_2 Br$	51/3.5	44.3 (44.7)
BEMA	$CH_2 =C-\overset{CH_3}{\underset{}{|}}-\overset{O}{\overset{\|}{C}}-OCH_2 CH_2 Br$	45/3.0	41.2 (41.5)
CEA	$CH_2 =CH-\overset{O}{\overset{\|}{C}}-OCH_2 CH_2 Cl$	71/3.0	26.1 (26.4)
CEMA	$CH_2 =C-\overset{CH_3}{\underset{}{|}}-\overset{O}{\overset{\|}{C}}-OCH_2 CH_2 Cl$	62/10	23.7 (23.9)

in a nitrogen atmosphere. The mole fraction of BEA, BEMA, CEA, and CEMA comonomers was varied between 0.05 and 0.25 and CHPA between 0.05 and 0.35. $K_2 S_2 O_8$ and $Na_2 S_2 O_5$ (0.01 and 0.004 mol% with respect to total monomer feed) were used for the initiation of polymerization. The copolymerizations were carried out for the time necessary to obtain conversions between 10 and 25%. After the polymerization, the reaction mixture was poured into water and the copolymer was filtered with repeated washings. The purified copolymers were dried at 50°C under reduced pressure.

The composition of copolymers was found from the nitrogen content as estimated by the modified Kjeldahl method [11].

RESULTS AND DISCUSSION

The comonomer concentration in the feed and the copolymer compositions (in mole fraction m_2) are shown in Tables 2 and 3. From these data, reactivity ratios were calculated by the Kelen-Tüdos [12] method applied for high conversions [13]. The dependence of the composition of the copolymers on the composition of monomer feed is illustrated in Fig. 1. In all cases the copolymers show a much higher content of haloalkyl acrylate/methacrylate than the comonomer feed. This indicates that all the acrylates/methacrylates (M_2) used in the present study are more reactive toward the acrylonitrile radical.

This also implies that $k_{12} > k_{11}$, where k_{11} and k_{12} are the rate constants for the addition of acrylonitrile and haloalkyl acrylates, respectively, to the acrylonitrile radical. The high reactivity of acrylates/methacrylates can be attributed to the electronic interactions due to the conjugation between the vinyl and carbonyl double bond:

$$CH_2 = CH-\overset{\overset{\displaystyle O}{\|}}{C}-OR \longrightarrow CH_2 -CH-\overset{\overset{\displaystyle O^{\delta^-}}{\|}}{\underset{\delta^+}{C}}-OR$$
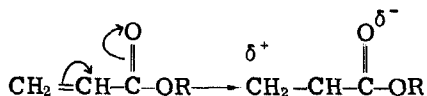
Conjugation in methyl acrylate is reported to enhance the reactivity of the monomer toward growing radicals [14].

Kelen-Tüdos plots are given in Figs. 2 and 3, and the values of r_1 and r_2 were calculated from these data by the linear least-squares method. From the perusal of data (Table 4), it is evident that r_1 (AN) < 1 and r_2 (BEA, BEMA, CHPA, and CEA) > 1, except in the AN-CEMA system where haloalkyl acrylates are more reactive than acrylonitrile toward both the propagating species. The copolymers therefore contain a larger proportion of the more reactive monomer at a given feed ratio as shown in Fig. 1.

The relative reactivity of acrylonitrile ($1/r_1$) decreases with a change in haloalkyl substituted comonomer from 8.475 (BEMA) to 2.369 (CEMA). This supports the higher reactivity of the AN radical toward BEMA as compared to CEMA.

TABLE 2. Copolymerization of AN-BEA/BEMA[a] in Water-Acetone (2:1 v/v) Medium[b] at 40°C

Mole fraction of BEA/BEMA in feed (M_2)	Conversion (%)	Nitrogen content (%)	Mole fraction (m_2)
		Copolymer composition	
	(A) AN-BEA		
0.05	16.9	12.0	0.227
0.10	17.5	9.3	0.317
0.15	18.0	7.5	0.393
0.20	18.6	5.4	0.503
0.25	19.2	4.2	0.581
	(B) AN-BEMA		
0.05	17.8	12.8	0.204
0.10	15.1	9.9	0.294
0.15	17.7	6.7	0.432
0.20	15.7	5.8	0.480
0.25	16.3	5.0	0.528

[a]BEA = 2-bromoethyl acrylate; BEMA = 2-bromoethyl methacrylate.
[b]Dilution = 1 mol/L.

TABLE 3. Copolymerization of AN-CHPA/CEA/CEMA[a] in Water-Acetone (2:1 v/v) Medium[b] at 40°C

Mole fraction of CHPA/CEA/CEMA in feed (M_2)	Conversion (%)	Copolymer composition	
		Nitrogen content (%)	Mole fraction (m_2)
(C) AN-CHPA			
0.05	18.9	13.3	0.219
0.10	14.5	10.6	0.303
0.15	9.6	7.6	0.423
0.25	10.0	6.0	0.504
0.35	12.7	3.6	0.657
(D) AN-CEA			
0.05	21.3	17.7	0.121
0.10	18.1	14.2	0.211
0.15	17.3	12.4	0.267
0.20	12.0	9.0	0.393
0.25	11.0	6.3	0.524
(E) AN-CEMA			
0.05	16.9	18.4	0.096
0.10	11.3	14.9	0.177
0.15	14.8	11.6	0.274
0.20	13.5	11.0	0.295
0.25	9.6	9.5	0.351

[a]CHPA = 3-chloro-2-hydroxy propylacrylate; CEA = 2-chloroethyl acrylate; CEMA = 2-chloroethyl methacrylate.
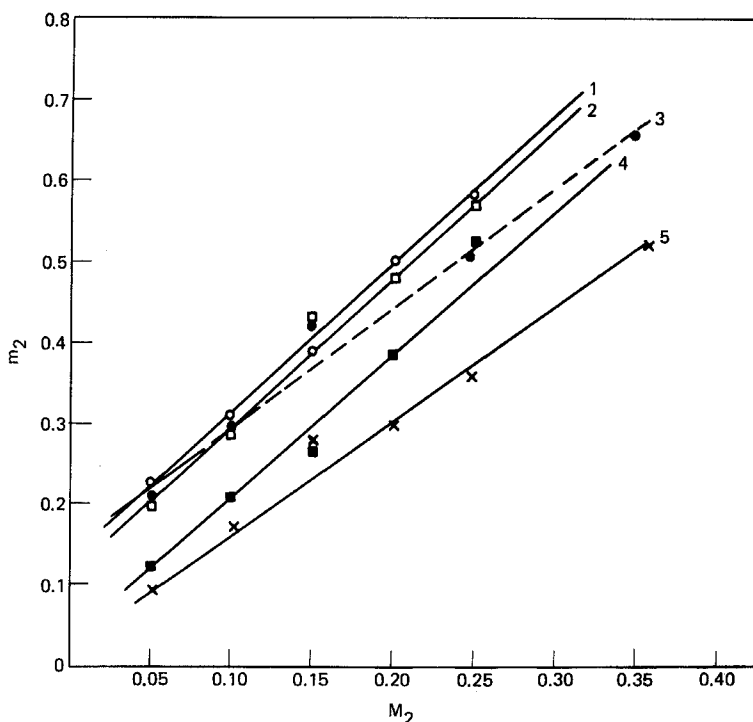[b]Dilution = 1 mol/L.

FIG. 1. Plot of mole fraction of acrylate/methacrylate (m_2) in copolymer versus mole fraction acrylate/methacrylate in feed (M_2). (1) AN-BEA, (2) AN-BEMA, (3) AN-CHPA, (4) AN-CEA, and (5) AN-CEMA.

Among the chloroalkyl acrylates/methacrylates, if chlorine is substituted in the γ-position ($-CH_2 CHOHCH_2 Cl$) of the alkyl group, the reactivity is more as compared to the one substituted in the β-position ($-CH_2 CH_2 Cl$) of the alkyl group. For example, 3-chloro-2-hydroxypropyl acrylate is more reactive than 2-chloroethyl acrylate toward the growing polyacrylonitrile radical.

Further, higher r_2 values of bromine-substituted alkyl acrylates/methacrylates than those of chlorine-substituted alkyl esters suggest the participation of polar or electronic effects in the copolymerization kinetics. Since chlorine is more electronegative than bromine (Cl = 3, Br = 2.8), the inductive effect due to chlorine is more significant on the vinyl group than to bromine:

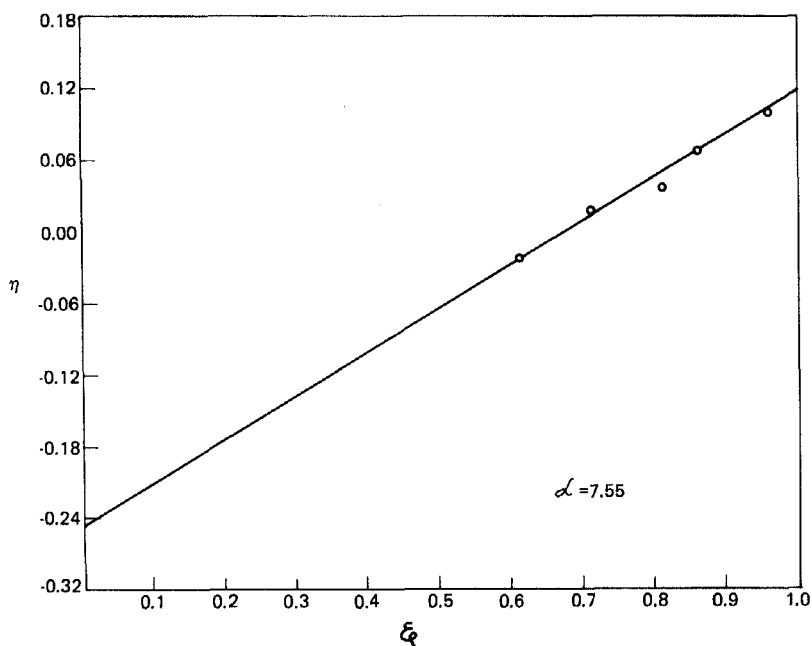$$CH_2 = CR - C - O \longrightarrow CH_2 \longrightarrow CH_2 X$$
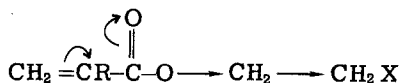
FIG. 2. Kelen-Tüdös plot for the copolymerization of AN-BEMA in water-acetone (1:2, v/v) medium at 40°C.

TABLE 4. Reactivity Ratios of AN-BEA, AN-BEMA, AN-CHPA, AN-CEA, and AN-CEMA Systems Calculated by the Kelen-Tüdös Method

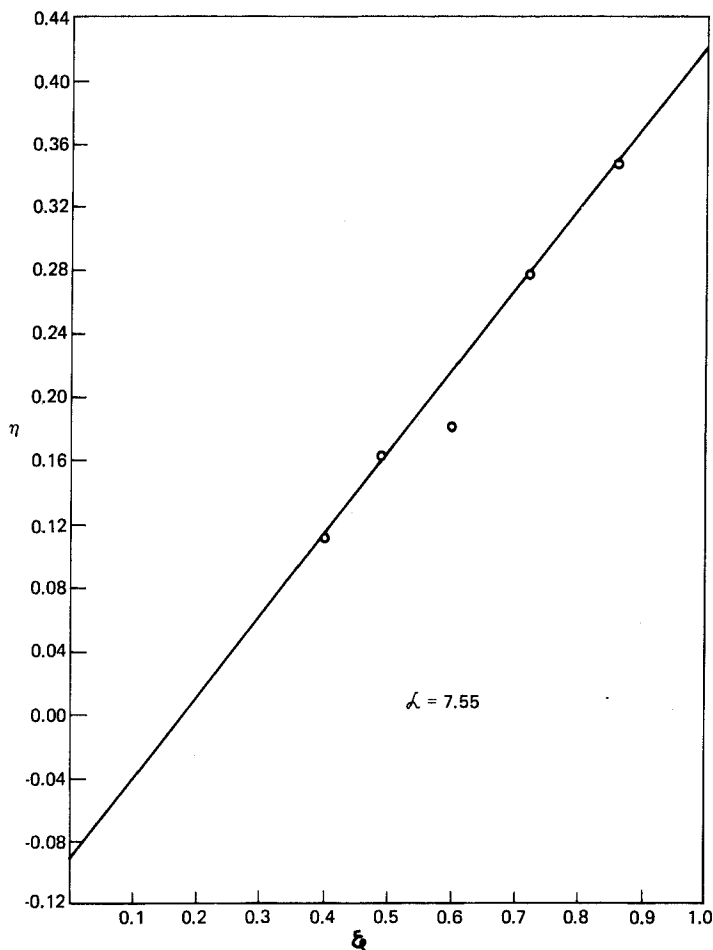| Monomer pair	r_1 (AN)	$1/r_1$	r_2 (acrylate/ methacrylate)	$1/r_2$	$r_1 r_2$
AN-BEA	0.142	7.040	2.850	0.351	0.405
AN-BEMA	0.118	8.475	1.888	0.530	0.223
AN-CHPA	0.124	8.065	1.890	0.529	0.234
AN-CEA	0.290	3.448	1.359	0.736	0.394
AN-CEMA	0.422	2.369	0.680	1.471	0.284

FIG. 3. Kelen-Tüdös plot for the copolymerization of AN-CEMA in water-acetone (2:1, v/v) medium at 40°C.

Similar results were noted by Maksanova et al. [15] in copolymerization studies of acrylates. According to them, the greater the electronegativity of the β-substituent in the alkyl ester, the slower is the polymerization rate. A high inductive effect would tend to reduce the electron density around the polymerizable olefinic double bond. Otsu et al. [16] have also reported that the radical reactivities of alkyl methacrylates depend on the polar character of the alkyl groups but not on their steric factors.

Comparison of the relative reactivities of haloalkyl acrylates and methacrylates ($1/r_2$) shows that the methacrylates are less reactive than the corresponding haloalkyl acrylates. These results suggest that both the steric and electronic effects influence haloalkyl methacrylate-acrylonitrile copolymerization kinetics.

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