NOTES

Radical Copolymerization of Potassium Methacrylate and Acrylonitrile in the Presence of 18-Crown-6 Ether in Ethyl Alcohol as Solvent

INTRODUCTION

The effect of dissociation of acrylic and methacrylic acids on their behavior in radical homo- and copolymerization reactions in an aqueous medium was the subject of a number of papers starting from the early 1950s. Alfrey, Overberger, and Pinner[1] found that the transformation of un-ionized methacrylic acid (MA) into its dissociated alkali-metal salt resulted in a decrease of the e value from 0.7 for the acid to ca. -1 for the methacrylate anion. As a consequence of the decrease of the methacrylate anion e parameter toward that of methacrylic acid, a greater tendency of alkali-metal methacrylate to the cross-propagation reaction in the copolymerization with electron acceptor monomers were observed. The ionized methacrylate salts were found to be less reactive than methacrylic acid in the homo- and copolymerization reactions.[2] Although the polymerization of acrylic and methacrylic ionogenic monomers has recently been exhaustively reviewed,[3] there is not much information on the polymerizability of these monomers in nonaqueous media.

Hamoudi and McNeill[4] described the copolymerization of alkali-metal methacrylates with methyl methacrylate initiated by 2,2'-azobisisobutyronitrile (AIBN) in a methanolic solution. The Q and e parameters of potassium methacrylate (MAK) calculated for the above system appeared to be the same as those obtained from the copolymerization in an aqueous medium.

This note describes the polymerization of MAK complexed by 18-crown-6 ether (MAKCE) in ethanol as a solvent in which uncomplexed MAK is practically insoluble.[4] The copolymerization of MAKCE and acrylonitrile (AN) in an ethanolic solution was studied in order to compare with that of MAK and AN carried out in an aqueous medium.

EXPERIMENTAL

Before use the reactants and solvents were deoxidized and dried, and all operations were carried out under deoxidized and dried nitrogen.

Materials

MAK, obtained by hydrolysis of methyl methacrylate in a 20% ethanolic solution of potassium hydroxide, was purified by crystallization from 96% ethyl alcohol and dried at room temperature under reduced pressure (0.1 mm Hg, 12 h).

ANAL. Calcd for MAK: C, 38.69%; H, 4.06%. Found: C, 38.60%; H, 3.95%.

CE (1,4,7,10,13,16-hexaoxacyclooctadecane) was obtained and purified according to the common method.[5] Pure analytical-grade ethyl alcohol (Reactivul, Bucuresti, Rumania) was refluxed with metallic magnesium and rectified. Other pure analytical-grade materials were further purified by known methods.

Polymerization and Isolation Procedures

AN, MAKCE (a 5 mol % excess of CE with respect to MAK was used) and AIBN were mixed in ethanol and the solution obtained was heated under stirring. The homogeneous reaction mixture was then cooled and the unreacted AN and ethyl alcohol were distilled off as an azeotrope with cyclohexane, which was added at the end of the distillation. The precipitated solid consisting of the polymeric product and unreacted MAKCE was filtered off, washed with cyclohexane, and then dried

TABLE I
Copolymerization of Potassium Methacrylate Complexed by 18-Crown-6 Ether (MAKCE) and Acrylonitrile (AN) in Ethyl Alcohol Initiated by AIBN[a]

Monomer feed (mmol)		MA[b]-AN copolymer composition (mol %)		Monomer conversion (mol %)		
MAKCE	AN	MA	AN	MAKCE	AN	MAKCE&AN
30	0	100	...	5.5	...	5.5
25	5	65.3	34.7	8.6	22.8	10.9
24	6	62.2	37.8	9.0	22.0	11.6
22.5	7.5	61.0	39.0	6.7	12.8	8.2
20	10	57.0	43.0	13.1	19.8	15.3
15	15	52.9	47.1	7.5	8.5	8.0
10	20	49.3	50.7	18.3	9.4	12.4
7.5	22.5	45.3	54.7	18.7	7.5	10.3
6	24	44.8	55.2	16.7	5.2	7.5
5	25	42.1	57.9	17.6	4.8	7.0
0	30[c]	...	100	...	73.0	73.0

[a] Copolymerization conditions: AIBN, 3 mmol; volume of reaction solution, 30 cm^3; temperature 65°C, time 23 h.

[b] Methacrylic acid unit.

[c] Polymerization time 2.5 h.

under reduced pressure. It was then dissolved in water and the MA-AN copolymer was precipitated by adding 10% hydrochloric acid to the solution. The copolymer was then filtered off, washed with water, and dried under reduced pressure. The copolymer was purified by twofold dissolution in ethyl alcohol and precipitation in water slightly acidified with 10% hydrochloric acid. The dried MA-AN copolymers were weighed and studied by means of IR spectroscopy (KBr pellets) on a Zeiss IR-71 spectrometer; IR (KBr): 3600–3100 s (ν_{OH}), 2980 s (ν_{CH}, —CH$_2$—), 2930 s (ν_{CH}, C—CH$_3$), 2240 m ($\nu_{C\equiv N}$), 1710 s ($\nu_{C=O}$), 1470 m (δ_{CH}), 1200 cm^{-1} s (ν_{C-O}). The composition of MA-AN copolymers was determined by means of elemental analysis with a Perkin–Elmer MC-1 apparatus and potentiometric titration of carboxylic groups with an ethanolic KOH solution in a DMSO solution against a glass electrode, which gave convergent results.

The cyclohexane filtrate obtained after filtering off the copolymer was concentrated and the remaining small amount of MAKCE isolated from it by crystallization. MAKCE was washed with cyclohexane and then dried.

ANAL. Calcd for equimolar MAKCE complex: C, 49.43%; H, 7.53%. Found: C, 49.35%; H, 7.49%.

TABLE II
Copolymerization of Potassium Methacrylate (MAK) and Acrylonitrile (AN) in Water Initiated by K$_2$S$_2$O$_8$[a]

Monomer feed (mmol)		MA[b]-AN copolymer composition (mol %)		Monomer conversion (mol %)		
MAK	AN	MA	AN	MAK	AN	MAK&AN
27	3	79.1	20.1	19.3	44.1	21.8
24	6	66.0	34.0	16.5	34.0	20.0
22.5	7.5	61.9	38.1	13.7	25.4	16.7
20	10	52.0	48.0	11.7	21.6	15.0
15	15	50.0	50.0	10.2	10.2	10.2
10	20	47.9	52.1	16.3	8.9	11.4
7.5	22.5	39.1	60.9	21.7	11.1	13.8
6	24	35.0	65.0	24.8	11.5	14.2
3	27	19.0	81.0	21.4	14.8	15.4

[a] Copolymerization conditions: K$_2$S$_2$O$_8$, 0.3 mmol; volume of reaction solution, 30 cm^3; temperature 60°C, time 3 h.

[b] Methacrylic acid unit.

The MAKCE and AN homopolymerizations were carried out by the procedure applied for the copolymerizations of these monomers. The MAKCE homopolymer was isolated (as poly-MA) and purified in the same way as the MA-AN copolymer; the poly-AN was isolated by pouring the heterogeneous reaction mixture into water.

The copolymerization of MAK and AN in aqueous medium was carried out in the presence of $K_2S_2O_8$ as initiator at elevated temperature under stirring. The homogeneous reaction mixture was then cooled and poured into water slightly acidified with hydrochloric acid. The MA-AN copolymer was next filtered off, washed with water, and dried under reduced pressure. It was purified and analyzed as described above. The IR spectrum of the MA-AN copolymer obtained in water was identical to those of the copolymers obtained in ethanol.

The reaction conditions, monomer conversions, and compositions of MA-AN copolymers and the corresponding homopolymers obtained in ethanol and water are presented in Tables I and II, respectively.

RESULTS AND DISCUSSION

From the data presented in Tables I and II it appears that MAKCE requires much higher initiator concentration and longer time to be converted in homo- and copolymerization reactions run in ethanol than MAK does in corresponding reactions run in water. It is also evident from Table I that the MAKCE conversion in the homopolymerization reaction is much lower than that of AN.

The reactivity ratios of monomers in the systems studied were calculated tentatively according to the Fineman–Ross[6] and Kellen–Tüdös[7] methods (Table I) and the Fineman–Ross method (Table II). For the MAKCE-AN copolymerization in ethanolic solution they are $r_{MAKCE} = 0.19 \pm 0.02$, $r_{AN} = 0.08 \pm 0.02$, and for the MAK-AN copolymerizations in water $r_{MAK} = 0.22 \pm 0.02$, $r_{AN} = 0.22 \pm 0.02$. On the basis of the above reactivity ratios the e and Q parameters of MAKCE and MAK were calculated assuming for AN the following values: $e_{AN} = 1.2$ and $Q_{AN} = 0.6$.[8] For the copolymerization in an ethanolic solution those parameters are $e_{MAKCE} = -0.85$ and $Q_{MAKCE} = 0.64$, and for that in water $e_{MAK} = -0.54$ and $Q_{MAK} = 0.34$.

The preliminary results obtained show that MAKCE, as a stronger electron donor monomer in comparison with MAK, has a greater tendency to alternation in copolymerization with AN. The MAKCE terminal macroradical also appeared to be less reactive than the MAK one, in agreement with the respective Q values.

References

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