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MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Radical Copolymerization of *N,N*-Diallyl-*N,N*-dimethylammonium Chloride and Maleic Acid in Various Solvents

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Abstract—Radical copolymerization of *N,N*-diallyl-*N,N*-dimethylammonium chloride with maleic acid in various solvents was studied. The solvent effect on the relative activity of the monomers and the possibility of preparing copolymers of preset composition were examined.

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Polyfunctional water-soluble copolymers whose macromolecules contain both cationic and anionic groups exhibit amphoteric properties and form one of the most interesting and promising classes of polymers. By varying the ratio of cationic and anionic groups, it is possible to control the total charge of the macromolecule and hence to vary in a wide range the service properties of copolymers such as the solubility, molecular weight, and reactivity toward natural compounds and in polymer-analogous transformations. Therefore, a problem of preparing copolymers of preset composition arises. This problem can be solved only by studying the process in detail and revealing factors affecting the reactivity of the comonomers.

It is known that the radical polymerization of ionizable monomers is strongly affected by the solvent [1–3]. Even relatively weak chemical interaction of functional groups of monomers or radicals with the solvent in the course of copolymerization can significantly affect the copolymer composition and distribution of comonomer units in the macrochain.

In this connection, it is interesting to study copolymerization in various solvents of maleic acid (MA) with *N,N*-diallyl-*N,N*-dimethylammonium chloride (AMAC) whose copolymers exhibit bactericidal, growth-stimulating, and catalytic activity [4–6].

Previously copolymerization of AMAC (M_1) with MA (M_2) was studied in aqueous solution in the presence of potassium persulfate as initiator [7]. Copolymerization occurs with the formation of random copolymers, and AMAC is considerably more active than MA. The copolymers obtained act as high-performance hardeners in leather production [8].

In this study we examined the copolymerization of AMAC with MA in various organic solvents with the aim to find the possibility of controlling the composition and structure of the copolymers.

EXPERIMENTAL

N,N-Diallyl-*N,N*-dimethylammonium chloride was prepared from dimethylamine and allyl chloride as described in [9]. Its purity was checked by elemental analysis, analysis for the content of double bonds, and ^{13}C NMR spectroscopy. Maleic acid of analytically pure grade was recrystallized from acetone and vacuum-dried to constant weight. The initiator, azobis (isobutyronitrile) (AIBN) of analytically pure grade, was recrystallized three times from methanol and vacuum-dried. All the chemicals used in the study (monomers, initiator, solvents) after purification by common procedures had the characteristics consistent with published data.

The copolymerization was performed in organic solvents in a vacuum in the presence of AIBN to low conversions and was monitored gravimetrically. On reaching a definite conversion (5–10%), the poly-

merization was stopped by cooling and subsequent precipitation of the polymer into acetone. The copolymers were purified by fourfold reprecipitation from a methanol solution into acetone. The purified copolymers were vacuum-dried to constant weight at 50°C. The copolymer composition was calculated from the results of elemental analysis and analysis for carboxy groups. The effective copolymerization constants were calculated by the Mayo–Lewis and Kelen–Tudos methods. The intrinsic viscosity [η] of copolymer solutions was determined viscometrically (Ubbelohde viscometer, 0.5–1.0 M aqueous NaCl, 25 ± 0.01°C).

The UV spectrometric measurements were performed on a Shimadzu UV-VIS-NIR 3100 spectrometer. The formation of complexes was monitored by deviation of the optical density of a solution containing a mixture of the monomers from the additive value. The composition of the complexes was determined by the method of isomolar series.

The ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer operating at 75.5 MHz, with broad-band proton decoupling and in the JMOD mode. The solvent was CD_3OD, and the internal reference, tetramethylsilane.

Studies were performed in both proton-donor (methanol, ethanol, isopropanol, acetic acid) and aprotic [dimethyl sulfoxide (DMSO), chloroform] solvents. The results we obtained showed that, when the reaction was performed in organic solvents (except methanol), as in the case of aqueous solutions, the resulting copolymers had random distribution of the comonomer units in the macrochain (Fig. 1, curves *0*–*5*). The effective copolymerization constants (Table 1) indicate that, in aqueous solutions, MA is considerably less active than AMAC, and therefore the resulting copolymers are enriched in AMAC units. In organic solvents, the activities of the comonomers differ less significantly, which favors formation of copolymers highly uniform in the composition. Low products r_1r_2 (<<1) indicate that the copolymers show high tendency toward alternation of the comonomeric units.

In acetic acid, the MA activity considerably increased. This difference between the relative activities of the monomers depending on the solvent is due to different capability of the comonomers for association in organic solvents and water. The capability for association of AMAC with MA in these media and, ultimately, the course of copolymerization are largely determined by the solvating power of the solvents.

Table 1. Effective copolymerization constants of AMAC (M_1) and MA (M_2) in various solvents

Solvent	r_1	r_2	r_1r_2	r_1/r_2
Water[a]	0.44±0.01	0.09±0.02	0.04	4.89
DMSO	0.17±0.01	0.11±0.01	0.02	1.55
Ethanol	0.18±0.02	0.17±0.02	0.03	1.06
Isopropanol[b]	0.15±0.02	0.12±0.02	0.02	1.25
Chloroform[b]	0.15±0.02	0.12±0.02	0.02	1.25
Acetic acid	0.14±0.01	0.26±0.02	0.04	0.54

[a] The constants r_1 and r_2 were obtained in [7].
[b] In the course of copolymerization the copolymer precipitates.

It is well known that water exhibits high solvating activity. As a result, complexation of ionizable monomers such as AMAC and MA is hindered. Interaction of MA with the solvent is manifested in the long-wave shift of the C=O vibration frequency in the IR spectrum by 13–14 cm^{-1} and in a short-wave shift of the C=C vibration frequency by 9 cm^{-1} in aqueous solutions, compared to organic solvents. In aqueous solutions, the probability of formation of stable ion

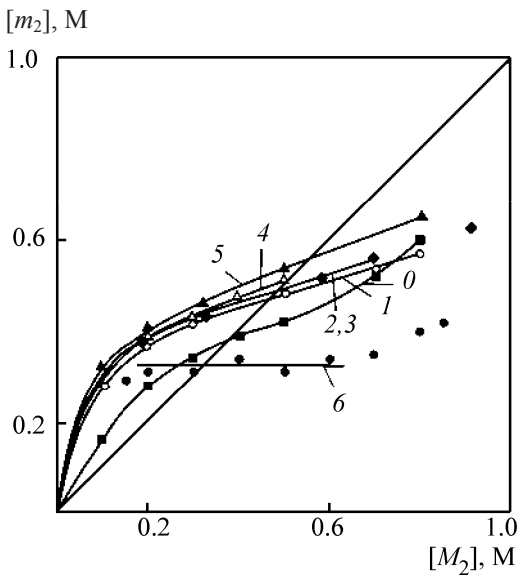


Fig. 1. Composition of AMAC–MA copoolymer as a function of the composition of the initial monomer mixture (90°C). ([M_2], [m_2]) Mole fractions of MA in the initial mixture and copolymer, respectively. (*1*) DMSO, [$M_1 + M_2$] = 2.8 M, [AIBN] = 2.05×10^{-2} M; (*2*) isopropanol, [$M_1 + M_2$] = 3.1 M, [AIBN] = 2.23×10^{-2} M; (*3*) chloroform, [$M_1 + M_2$] = 3.1 M, [AIBN] = 2.44×10^{-2} M; (*4*) ethanol, [$M_1 + M_2$] = 2.3 M, [AIBN] = 1.38×10^{-2} M; (*5*) acetic acid, [$M_1 + M_2$] = 3.0 M, [AIBN] = 2.70×10^{-2} M; (*6*) methanol, [$M_1 + M_2$] = 3.2 M, [AIBN] = 1.20×10^{-2} M; and (0) water [7].

pairs is low, whereas in organic solvents a significant fraction of ionogenic monomers is in the form of ion pairs. Therefore, monomers whose double bonds significantly differ in the electron density can form donor–acceptor complexes in organic media. For this system, donor–acceptor interactions of comonomers in organic media are significant. These interactions are manifested in an upfield shift of NMR signals of both carboxylic (by 4.7 ppm) and olefinic (by 2.7 ppm) carbon atoms of MA in a monomer mixture in organic solutions compared to aqueous solutions.

Hydrogen bonding of MA with the solvents also significantly contributes to the formation of the macrochain in the system. In particular, appreciably increased MA activity in acetic acid is probably due to the fact that the MA–acetic acid hydrogen bonding decreases the electron-withdrawing effect of carboxy groups on the double bond of MA, which becomes more active, and the macrochains become enriched in MA units.

A study of the copolymerization of AMAC with MA in methanol showed that, in a wide range of monomer ratios in the initial mixtures (AMAC : MA from 0.85 : 0.15 to 0.25 : 0.75), the resulting copolymers have a constant composition with the ratio of AMAC and MA units equal to 2 : 1 (Fig. 1, curve *6*). These data suggest that the copolymerization in this case occurs via complexation. The formation of a complex between the monomers in methanol solution was confirmed by UV spectroscopy. The electronic absorption spectra of AMAC, MA, and their mixture in methanol show a strong deviation from additivity: The sum of the optical densities of individual AMAC and MA solutions considerably differs from the measured optical density of the mixture at the same monomer concentrations (Fig. 2a). In water, the optical density of a mixture of AMAC with MA shows an additive behavior (Fig. 2b). Deviations of the optical density from additivity in a methanol solution depend on the AMAC : MA ratio in the monomer mixture, but the position of the maximum deviation remains constant and corresponds to an AMAC to MA ratio of 2 : 1.

The data we obtained suggest that, in methanol, AMAC and MA form a donor–acceptor complex of the composition 2AMAC–1MA. The associates consisting of one MA molecule and two AMAC molecules act as intermediates in formation of macrochains and favor formation of alternating copolymers with high composition uniformity. Indeed, in the ^{13}C NMR spectra of the copolymers prepared in methanol, the carbon signals are narrow, well-resolved peaks (Fig. 3), suggesting high structural and stereochemical uniformity of the copolymers, whereas in the spectra of the copolymers formed in aqueous solutions the carbon signals are broad, suggesting structural and configurational diversity of combinations of AMAC and MA units. The copolymers prepared in DMSO have a more regular structure (with respect to distribution of AMAC and MA units) than the copolymers formed in water, but are less regular than the copolymers prepared in methanol. This follows from the width of the ^{13}C signal from two AMAC methylene groups adjacent to MA units. The data we

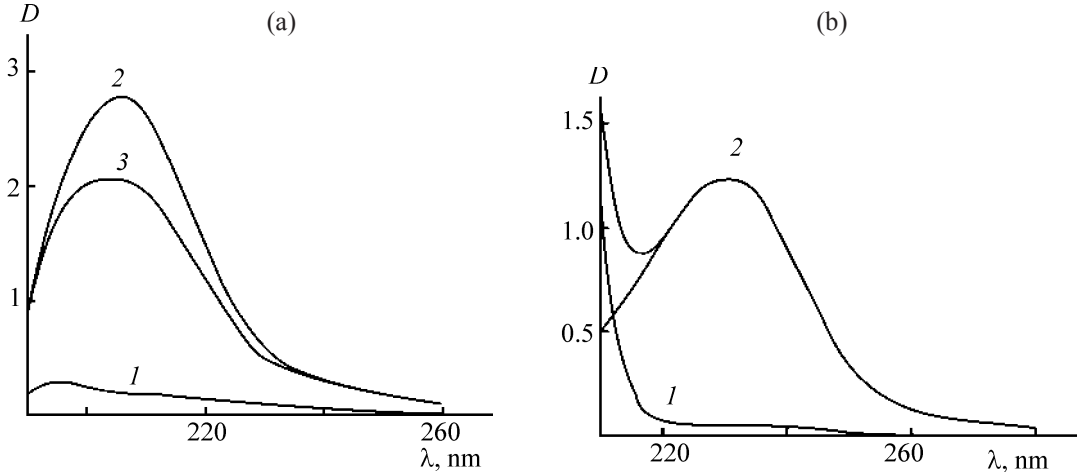


Fig. 2. Electronic absorption spectra of solutions of AMAC, MA, and their mixture in (a) methanol and (b) water. (*D*) Optical density and (λ) wavelength. (*1*) [AMAC] = 2×10^{-4} M; (*2*) [MA] = 1×10^{-4} M; and (*3*) [AMAC] = 2×10^{-4} M and [MA] = 1×10^{-4} M.

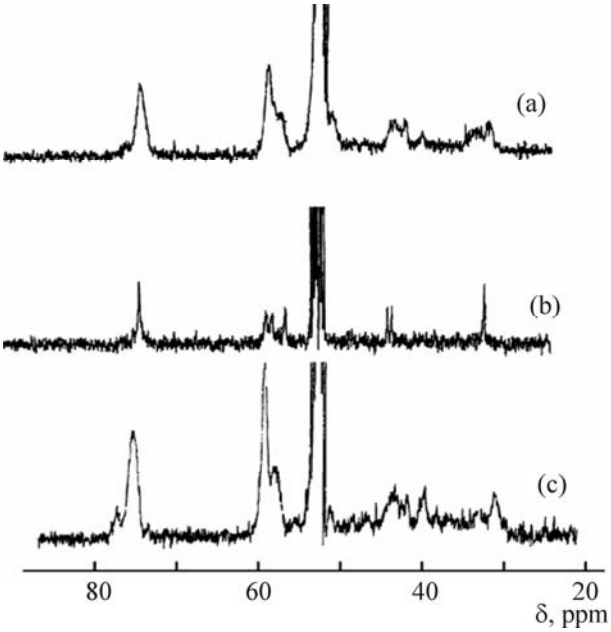


Fig. 3. ^{13}C NMR spectra of AMAC–MA copolymers prepared in (a) water, (b) methanol, and (c) DMSO.

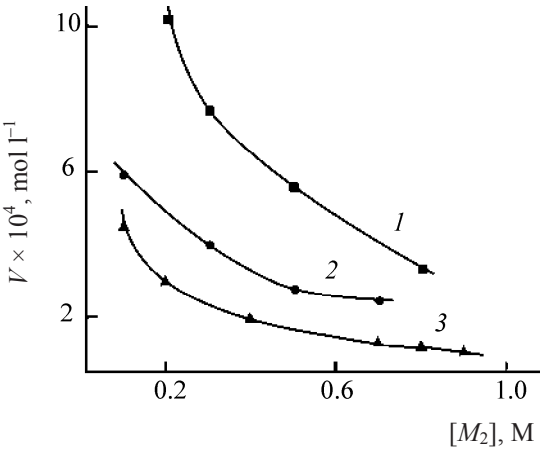
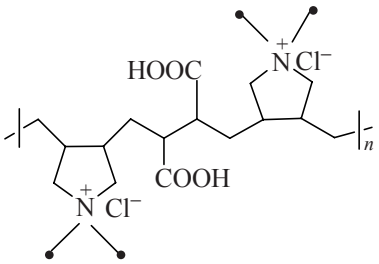


Fig. 4. Initial rate V of copolymerization of AMAC with MA (M_2) as a function of the composition of the initial comonomer mixture. Solvent: (*1*) water, (*2*) methanol, and (*3*) DMSO. $[M_1 + M_2] = 3.2$ M, $T = 90°C$. (*1*) Water, [PP] = 1.20×10^{-2} M; (*2*) methanol, [AIBN] = 1.20×10^{-2} M; and (*3*) DMSO, [AIBN] = 2.05×10^{-2} M.

obtained suggest the following chain structure for the AMAC–MA copolymer obtained in a methanol solution:



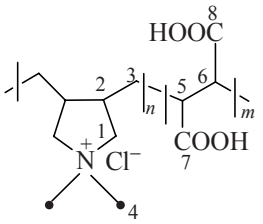
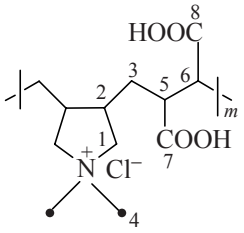
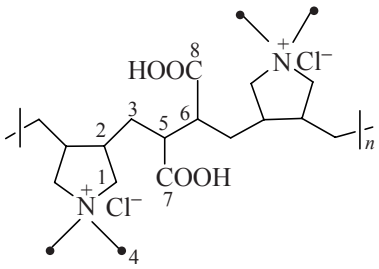
Irrespective of the reaction conditions (initiator, solvent, temperature), AMAC enters into copolymerization with MA (as in the case of its homopolymerization and copolymerization with other monomers [10, 11]) to form five-membered pyrrolidinium structures (Table 2) in the cyclolinear macrochain.

A kinetic study of the copolymerization of AMAC with MA showed that, irrespective of the solvent, the reaction order with respect to the initiator was 0.5, which is common for radical polymerization. We found that the reaction order with respect to the sum of the monomers (at their equimolar ratio) was unusually high (Table 3). The same, high reaction order with respect to the monomer (4.7) was found in polymerization of *N,N*-diethylaminoethyl methacrylate hydrochloride [12] and of other ionic monomers [13].

Unusual kinetic features of copolymerization of AMAC with MA in strongly polar media are apparently associated with a number of factors: pronounced complexation between the comonomers differing in the polarity, hydrogen bonding of the monomers with the solvent, electrostatic interactions of the reacting species, and high viscosity of the multicomponent polar system. The overall activation energies of copolymerization in the AMAC–MA system, calculated from the Arrhenius dependences, are given in Table 3. The lower activation energy of the reaction in DMSO is apparently due to more favorable steric arrangement of the reacting species, propagating radicals and monomers, under these conditions. The relatively higher activation energies for the reaction in methanol may be due to a steric factor, formation of a bulky associate of the comonomers.

Examination of the dependence of the AMAC–MA copolymerization rate on the comonomer ratio showed that, with an increase in the MA content in the initial mixture, the reaction rate decreases both in aqueous solutions and in organic solvents. It can be seen (Fig. 4) that, in the entire range of monomer ratios, the reaction rate in water is higher than in organic solvents, which is consistent with the well-known data [2] that polymerization of water-soluble monomers accelerates in aqueous solutions.

Table 2. ^{13}C NMR spectra of AMAC–MA copolymers prepared in different solvents

Structure	Solvent	Chemical shifts δ, ppm, and multiplicities of signals					
		C_1	C_2	C_3	C_4	C_5, C_6	C_7, C_8
	Water [7]	72.52 72.88 t	39.99 40.77 d	28.68 30.93 t	56.93 57.07 q	38.42 39.36 d	176.77 s
	DMSO	71.63 73.40 t	40.13 44.61 d	28.03 32.24 t	53.77 55.46 q	36.06 38.07 d	176.33 177.64 s
	Methanol	71.74 72.31 t	38.91 40.08 d	28.09 32.43 t	53.65 55.54 q	48.36 49.25 d	177.20 s

AMAC–MA copolymers are white powders soluble in water, methanol, and, at low conversions, in DMSO, ethanol, chloroform, and acetic acid but insoluble in tetrahydrofuran, acetone, benzene, and ethyl acetate. Aqueous solutions of copolymers exhibit a polyelectrolytic effect. The intrinsic viscosities of solutions (0.5–1.0 M NaCl) of AMAC–MA copoly-mers prepared in methanol are 0.60–0.63 dl g^{-1}, whereas the [η] values of random copolymers prepared, e.g., in DMSO depend on the monomer ratio and are within 0.10–0.20 dl g^{-1}.

Table 3. Reaction orders with respect to the monomer and overall activation energies of copolymerization of AMAC with MA in various solvents

Solvent	Order with respect to monomer	E_a±2.0, kJ mol^{-1}
Water[a]		62.7
Methanol	4.7	82.9
DMSO	3.7	52.9
Acetic acid	3.0	56.2

[a] The reaction order with respect to monomer is 1.0 at the total monomer concentration not exceeding 3.4 M and 2.7 at [M_1 + M_2] from 3.5 to 5.0 M [7].

Evaluation of the acute toxicity of AMAC–MA copolymers revealed no signs of intoxication at doses of up to 5000 mg kg^{-1}. This means that the compound is apparently nontoxic, and therefore higher doses were not examined. Thus, the copolymers obtained are nontoxic and belong to hazard class IV (LD_{50} >> 3000 mg kg^{-1}). Furthermore, they exhibit pronounced bactericidal activity toward gram-positive and gram-negative bacteria (minimal suppressing concentration 1.25 mg kg^{-1}). Thus, AMAC–MA copolymers show promise for medicine and biotechnology.

Furthermore, as shown previously [8], AMAC–MA copolymers are high-performance hardeners in leather

production. With respect to the retanning efficiency (elasticity, strength, organoleptic properties), they well compete with analogs produced beyond Russia (Relugan RE).

CONCLUSIONS

(1) Copolymerization of *N,N*-diallyl-*N,N*-dimethylammonium chloride with maleic acid in solution yields copolymers with random distribution of comonomer units in the macrochain. The copolymerization in water yields products enriched in *N,N*-diallyl-*N,N*-dimethylammonium chloride units. The copolymerization in organic solvents, except methanol, yields copolymers with high composition uniformity. The macrochains formed in acetic acid are enriched in maleic acid units.

(2) Copolymerization of the monomers in methanol occurs via formation of donor–acceptor complexes and yields random copolymers with 2 : 1 ratio of the chloride and acid units.

(3) Both double bonds of *N,N*-diallyl-*N,N*-dimethylammonium chloride are involved in the copolymerization, with the formation of pyrrolidinium structures.

(4) The copolymers obtained are nontoxic, belong to hazard class IV, and exhibit pronounced antimicrobial activity toward gram-positive and gram-negative bacteria.

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REFERENCES

1. Kabanov, V.A. and Topchiev, D.A., *Polimerizatsiya ioniziruyushchikhsya monomerov* (Polymerization of Ionizable Monomers), Moscow: Nauka, 1975.
2. Kabanov, V.S., Zubov, V.P., and Semchikov, Yu.D., *Kompleksno-radikal'naya polimerizatsiya* (Coordination Radical Polymerization), Moscow: Khimiya, 1987.
3. Sivtsov, E.V., Lavrov, N.A., and Nikolaev, A.F., *Plast. Massy*, 2001, no. 10, p. 32.
4. RF Patent 2095056.
5. USSR Inventor's Certificate no. 1744797.
6. USSR Inventor's Certificate no. 1530631.
7. Vorob'eva, A.I., Gaisina, Kh.A., Vasil'eva, E.V., and Prochukhan, Yu.A., *Vysokomol. Soedin., Ser. B*, 1999, vol. 41, no. 4, p. 726.
8. RF Patent 2145978.
9. Harada, S. and Arai, K., *Macromol. Chem*., 1967, vol. 107, p. 64.
10. Kabanov, V.A. and Topchiev, D.A., *Vysokomol. Soedin., Ser. A*, 1988, vol. 30, no. 4, p. 675.
11. Vorob'eva, A.I., Vasil'eva, E.V., Gaisina, Kh.A., et al., *Vysokomol. Soedin., Ser. A*, 1996, vol. 38, no. 10, p. 1663.
12. Loginova, N.N., Gavurina, R.K., and Aleksandrova, M.L., *Vysokomol. Soedin., Ser. B,* 1969, vol. 11, no. 9, p. 643.
13. Wandrey, Ch., Jaeger, W., and Reinisch, G., *Acta Polym*., 1981, vol. 32, no. 4, p. 197.