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MACROMOLECULAR COMPOUNDS AND POLYMERIC MATERIALS

Solvent Effect on Radical Copolymerization of *N,N*-Diallyl-*N,N*-dimethylammonium Chloride and Vinyl Acetate

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Abstract—Radical copolymerization of *N,N*-diallyl-*N,N*-dimethylammonium chloride with vinyl acetate in various solvents was studied. The solvent effect on the relative activity of the comonomers was analyzed. The kinetic features of the reactions were studied, the structure of the copolymers was determined, and their properties were examined.

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Polyelectrolytes containing quaternary ammonium groups, including polymers derived from *N,N*-diallyl-*N,N*-dimethylammonium chloride (AMAC), exhibit a number of valuable properties and are widely used in various fields [1–5], mainly as aqueous solutions. Poly-*N,N*-diallyl-*N,N*-dimethylammonium chloride forms films from solutions. These films, however, are brittle and have poor strength. The mechanical (in particular, elastic) properties of polymers can be improved by copolymerization. It is known that poly(vinyl acetate) has excellent adhesive and binding properties. Film materials and fibers of poly(vinyl acetate) exhibit high strength and elasticity. In copolymerization with other monomers, vinyl acetate (VA) imparts to the resulting copolymers unique properties characteristic of poly(vinyl acetate), enhancing their elasticity, film-forming ability, adhesion, and light resistance. Furthermore, vinyl acetate copolymers can readily enter into various polymer-analogous transformations [6, 7], which allows their chemical modification and synthesis of new polymers.

Therefore, it seemed interesting to examine the copolymerization of AMAC with VA under the conditions of radical initiation and the possibility of preparing film-forming copolymers of AMAC with VA. This would allow the applications of polymers derived from AMAC to be expanded. In particular, such polymers can find use in biotechnology, production of paper and leather (as aftertanning and filling reagents), textile industry, and agriculture (for protecting seeds and planting material from diseases).

Here we report on radical copolymerization of AMAC with VA in various solvents and on certain properties of the resulting copolymers.

EXPERIMENTAL

N,N-Diallyl-*N,N*-dimethylammonium chloride (M_1) was prepared from dimethylamine and allyl chloride [8]. Its purity was checked by elemental analysis, from the content of double bonds, and by NMR spectroscopy. Chemically pure grade vinyl acetate was washed with four portions of 7% aqueous NaOH to remove the stabilizer and then with distilled water to neutral reaction, after which it was dried over calcined $CaCl_2$ and double-distilled. For the copolymerization we took the fraction with bp 73°C, n_D^{20} = 1.3958. The initiator [azobis(isobutyronitrile), AIBN] and solvents used in the study were purified by standard procedures. Their characteristics corresponded to the published data.

Copolymerization of AMAC with VA was performed in a vacuum in the presence of AIBN. The process kinetics was monitored gravimetrically at low conversions (≤8%).

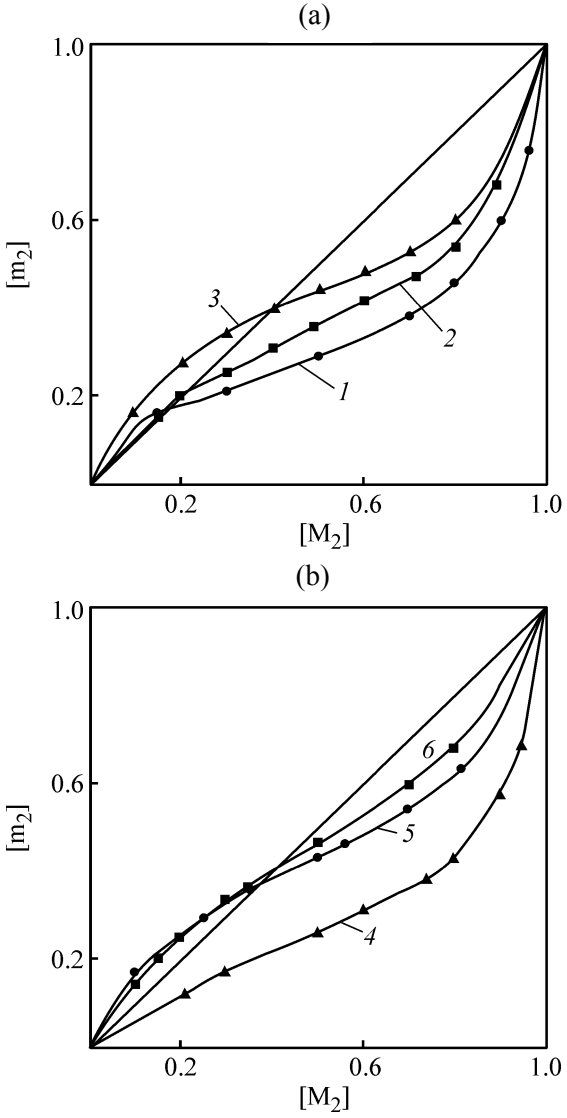


Fig. 1. Composition of AMAC–VA copolymers as a function of the composition of the initial monomer mixture. $T = 70°C$. ($[M_2]$, $[m_2]$) VA mole fractions in the initial mixture and in the copolymer, respectively. (a) (*1*) Methanol, $[M_1 + M_2] = 3.5$ M, [AIBN] = 1.70×10^{-2} M; (*2*) DMSO, $[M_1 + M_2] = 3.0$ M, [AIBN] = 2.25×10^{-2} M; (*3*) benzyl alcohol, $[M_1 + M_2] = 3.0$ M, [AIBN] = 3.05×10^{-2} M; (b) (4) chloroform, $[M_1 + M_2] = 3.0$ M, [AIBN] = 2.70×10^{-2} M; (*5*) acetic acid, $[M_1 + M_2] = 3.0$ M, [AIBN] = 2.70×10^{-2} M; and (*6*) methanol–water mixture (70 : 30), $[M_1 + M_2] = 3.2$ M, [AIBN] = 2.73×10^{-2} M.

On reaching the required conversion, the reaction was stopped by cooling, and the polymer was precipitated into acetone. The copolymers were purified by triple reprecipitation from a methanol solution into acetone (methanol : acetone ~1 : 2) at an AMAC concentration in the initial mixture of 30 mol % and more, or into diethyl ether at an AMAC concentration less than 30 mol %. The purified copolymers were vacuum-dried at 50°C to constant weight. The copolymer purity was checked by NMR spectroscopy. The copolymer compositions were determined by elemental analysis. The effective copolymerization constants in the initial steps of the reaction were calculated by the Mayo–Lewis and Kelen–Tьdцs methods. The intrinsic viscosity [η] was measured viscometrically (Ubbelohde viscometer, 0.5 N aqueous NaCl, 25 ± 0.01°C).

UV spectrometric studies were performed with a Shimadzu UV-VIS-NIR 3100 spectrometer. The samples were taken as solutions in methanol (main substance content 99.93%). The spectra were recorded in the range 190–700 nm using a 0.2-cm-thick cell. The complexation was judged from deviation of the optical density of the solution of the monomer mixture from the additive value.

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

Thermomechanical tests were performed with powdered samples pelletized under a pressure of 185 MPa for 5 min. Measurements were performed at a constant load with uniform heating at a rate of 2.5 deg min^{-1}. The thermal behavior of the samples was studied with a Q-1000 derivatograph (MOM, Hungary) in air at a heating rate of 5 deg min^{-1}.

The results of studying copolymerization of AMAC with VA in various solvents (DMSO, chloroform, methanol, benzyl alcohol, glacial acetic acid, methanol–water mixture) are presented in Fig. 1 and Table 1. The dependences of the copolymer composition on the composition of the initial monomer mixture and the effective copolymerization constants indicate that, irrespective of the solvent, the copolymers have random distribution of monomeric units in the macromolecule and that AMAC is a more active comonomer. These results are unusual, because vinyl monomers are considerably more active in radical polymerization reactions than allyl monomers. In the majority of previously studied copolymerizing systems of vinyl monomers with AMAC [9–11], the relative activity of AMAC was considerably lower. One of the causes of the observed specific course of AMAC–VA copolymerization is the formation of heteroassociates, which was confirmed by UV spectra of methanol solutions of AMAC, VA, and their mixtures. The UV spectrum of an AMAC–VA mixture exhibits

Table 1. Relative activities of monomers in copolymerization of AMAC (M_1) with VA (M_2), T = 70°C

Solvent	r_1	r_2	r_1r_2	r_1/r_2
Chloroform	1.68 ± 0.02	0	–	–
Methanol	1.27 ± 0.02	0.06 ± 0.01	0.076	21.17
DMSO	0.95 ± 0.02	0.10 ± 0.01	0.095	9.31
Benzyl alcohol	0.46 ± 0.02	0.14 ± 0.02	0.064	3.29
Glacial acetic acid	0.57 ± 0.02	0.18 ± 0.02	0.103	3.17
Methanol–water (70 : 30)	0.57 ± 0.02	0.37 ± 0.02	0.211	1.54

a new band at about 235 nm, untypical of any of the comonomers (λ_{max} for AMAC and VA in methanol 201 and 200 nm, respectively). In addition, because of the absence of conjugated double bonds, VA is always less active in copolymerization than other vinyl monomers.

It is seen from Table 1 that, in an aprotic solvent, dimethyl sulfoxide (DMSO), the VA activity is considerably higher (r_1/r_2 = 9.31) than in methanol (r_1/r_2 = 21.17). The VA activity in methanol decreases owing to hydrogen bonding of VA with the solvent.

The decreased activity of AMAC in benzyl alcohol is apparently due to lower mobility of the hydrogen atom compared to methanol and to different solubility of the comonomers in benzyl alcohol. Limited solubility of AMAC in benzyl alcohol leads to increased local concentration of VA in the vicinity of active centers. As a result, the macrochain is enriched in VA units.

Low activity of VA in chloroform may be due to high activity of VA radicals in chain transfer to the solvent which is characterized by a high chain-transfer constant. The chloroform radicals generated in the process have low activity and are incapable of adding weakly active VA molecules. As a result, the macrochain is enriched in AMAC units.

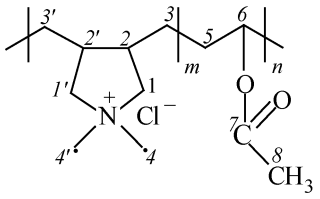
In acetic acid (AA), a decrease in the VA activity could be expected as a result of VA–AA hydrogen bonding. However, the relative activity of VA increased relative to copolymerization in an aprotic solvent. In the ^{13}C NMR spectrum of a VA–AA mixture, the C^1 and C^3 signals of VA are shifted downfield by 1.0 ppm relative to VA without AA. This fact indicates that, under the action of a strong proton donor, acetic acid, the electron density in VA molecule is shifted toward the protonated oxygen atom, i.e., the electronic structure of VA molecule undergoes rearrangement leading to enhancement of the

Table 2. Average statistical length of AMAC (L_{AMAC}) and VA (L_{VA}) blocks in copolymers of various compositions[a]

AMAC content, mol %		L_{AMAC}	L_{VA}
in initial monomer mixture	in copolymer		
Chloroform			
35	62	1.79	1.12
50	68	2.50	1.18
80	88	7.67	1.05
Methanol			
30	57	1.53	1.15
40	63	1.85	1.07
50	68	2.28	1.05
60	73	2.89	1.05
DMSO			
20	46	1.21	1.42
30	53	1.39	1.25
40	59	1.63	1.16
50	64	1.95	1.10
Benzyl alcohol			
30	47	1.63	1.22
50	62	1.83	1.17
70	66	2.06	1.13
Glacial acetic acid			
20	37	1.06	1.80
40	54	1.42	1.23
50	57	1.57	1.18
Methanol–water (70 : 30)			
30	41	1.26	1.85
50	54	1.57	1.37
70	67	2.33	1.16

[a] L_{AMAC} and L_{VA} were calculated by the method described in [13].

Table 3. ^{13}C NMR spectrum of AMAC–VA copolymer



Stereoisomer	Chemical shift δ (ppm) and multiplicity of signals of indicated atoms							
	C_1, $C_{1'}$	C_2, $C_{2'}$	C_3, $C_{3'}$	C_4, $C_{4'}$	C_5	C_6	C_7	C_8
cis-	71.58	40.13	28.05	55.49	32.26	74.64	172.63	21.33
trans-	72.30	44.94	33.99	56.12				
	t	d	t	q	t	d	s	q

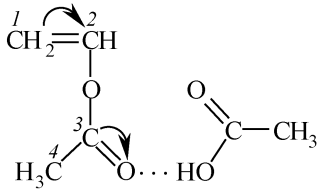
Table 4. Intrinsic viscosities of AMAC–VA copolymers (0.5 N aqueous NaCl, 25 ± 0.01°C)

Solvent	Mole fraction of VA units in copolymer	[η], dl g^{-1}
DMSO	0.25	0.41
	0.36	0.36
	0.40	0.33
Methanol	0.20	0.57
	0.27	0.50
	0.36	0.43
Methanol–water (70 : 30) (70:30)	0.20	0.34
	0.46	0.20
	0.68	0.18

Table 5. Thermomechanical characteristics of AMAC–VA copolymers

Mole fraction of VA units in copolymer	Transition temperature, °C	
	T_g	T_{flow}
0.15	51	128
0.20	44	106
0.36	37	86
0.60	36	86

activity of the double bond in the VA molecule:



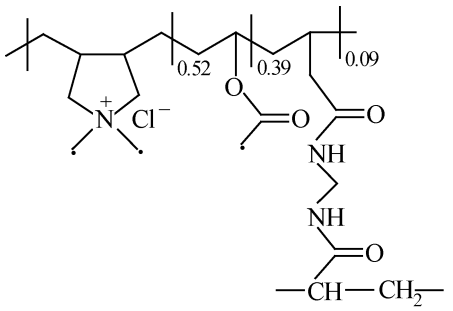
A considerable change in the monomer reactivity due to monomer–AA hydrogen bonding was found previously for *N*-vinylpyrrolidone [12].

Table 1 shows that the AMAC activity in the methanol–water mixture is considerably lower than in DMSO and methanol. This is due to ionization of ionogenic groups in aqueous medium and to electrostatic repulsion between the ionized AMAC molecule and a propagating macroradical with an AMAC terminal unit, which leads to a decrease in the rate constant of chain propagation k_{11}.

At an AMAC concentration in the initial monomer mixture exceeding 50 mol %, certain increase in the length of AMAC blocks, L_{AMAC}, in the copolymers is observed irrespective of the solvent (Table 2). However, the tendency to unit alternation in the macrochain remains strong, as indicated by low values of the product r_1r_2 (Table 1).

Copolymerization of AMAC with VA in the presence of cross-linking agents (compounds containing two double bonds) yields cross-linked insoluble and partially cross-linked swelling copolymers. In particular,

copolymerization of equimolar amounts of AMAC and VA in the presence of 6 mol % *N,N'*-methylenebisacrylamide (bis-AA) in DMSO gave a terpolymer (yield 66%) insoluble in organic solvents and swelling in water to form transparent gels:



Introduction into the polymer chain of more than 10 mol % bis-AA leads to the formation of insoluble cross-linked copolymers. By varying the comonomer ratio and amount of the cross-linking agent, it is possible to vary the composition and properties of the copolymers in a wide range.

A kinetic study of the copolymerization of AMAC with VA at low conversions showed that the copolymerization rate depended on the starting mixture composition in a complex fashion (Fig. 2). On adding a small amount of AMAC to VA, the reaction rate sharply decreased, and with a further increase in its content in the starting mixture (10–20 mol %) it increased again. Such a dependence of the reaction rate on the monomer ratio in the starting mixture is due to the fact that the activity of VA as monomer is low, whereas the activity of VA radicals is high. As a result, highly active VA radicals rapidly reacting with the more active monomer, AMAC, transform into weakly active terminal AMAC radicals, which react with weakly active VA molecules at a low rate. The reaction of the propagating radicals containing the AMAC terminal unit with AMAC molecules is also slow because of low concentration of AMAC in the reaction mixture. As a result, AMAC at its low content inhibits the VA polymerization.

In copolymerization of AMAC with VA, the reaction order with respect to the initiator is independent of the solvent and is equal to 0.5, which is indicative of the bimolecular mechanism of termination of the propagating chains. Determination of the reaction order with respect to the monomer (to the sum of the monomers at their equimolar ratio) in the concentration range $[M_1 + M_2]$= 1.5–3.5 M revealed a deviation of the dependence of the

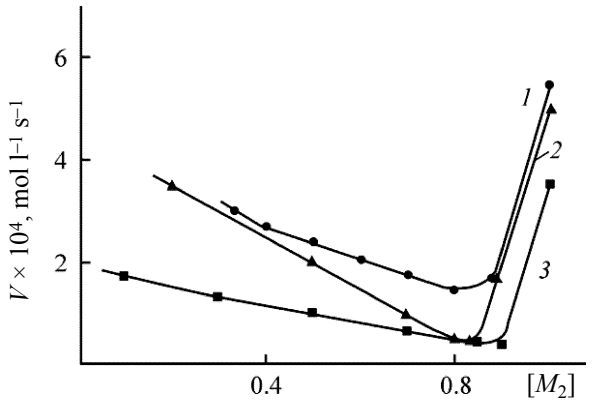


Fig. 2. Initial rate V of copolymerization of AMAC with VA (M_2) as a function of the composition of the initial monomer mixture, T = 70°C. (*1*) DMSO, $[M_1 + M_2]$ = 3.0 M, [AIBN] = 2.0×10^{-2} M; (*2*) methanol, $[M_1 + M_2]$ = 3.5 M, [AIBN] = 2.0×10^{-2} M; and (*3*) methanol–water mixture (70 : 30), $[M_1 + M_2]$= 3.0 M, [AIBN] = 3.0×10^{-2} M.

reaction rate on the monomer concentration from the linearity: The reaction order was 1.5 in methanol, 2.6 in acetic acid, and 2.0 in the methanol–water mixture. This specific dependence of the reaction rate on the monomer concentration may be due to high viscosity of the reaction medium [14] and to electrostatic interactions in the polar system [15].

The overall activation energies of the copolymerization of AMAC with VA in DMSO, methanol, and methanol–water mixture, found from the Arrhenius dependences, are close: 79.6, 83.8, and 85.4 ± 2.0 kJ mol^{-1}, respectively. These values are typical of radical polymerization.

A ^{13}C NMR study (Table 3) showed that both double bonds in AMAC were involved in the copolymerization with VA. The reaction occurred as intramolecular cyclization with the formation of pyrrolidinium rings in the macrochain, which is consistent with published data on homo- [14, 16] and copolymerization of AMAC [17]. The spectroscopic data (number of signals, their intensity, number of signals of linking units) show that the copolymers are characterized by the ordered structure of the polymer chain.

AMAC–VA copolymers are white powders soluble in water and methanol. The copolymers prepared at low conversions are also soluble in DMSO, chloroform, benzyl alcohol, and acetic acid. The copolymers are insoluble in tetrahydrofuran, dioxane, acetone, and ethyl acetate. From 20% methanol solutions, at a VA content in the copolymer of 20 mol % and higher, elastic films are formed on drying. The intrinsic viscosity of the copolymers depends on their composition (Table 4). With

an increase in the VA content, [η] decreases, which may be due to high constant of chain transfer to the monomer, characteristic of VA [18]. The copolymers are nontoxic (hazard class 4).

Thermomechanical tests of AMAC–VA copolymers revealed the area of rubbery elasticity (Table 5). With an increase in the content of VA units in the polymer chain, the glass transition point T_g and flow point T_{flow} decrease. Thermal gravimetric analysis showed that the polymers started to decompose at approximately 185°C.

CONCLUSIONS

(1) *N,N*-Diallyl-*N,N*-dimethylammonium chloride shows high activity in radical copolymerization with vinyl acetate. The copolymers formed have random distribution of comonomeric units in the macrochain.

(2) The effective copolymerization constants depend on the medium. By varying the solvent, it is possible to control the copolymerization and prepare copolymers of preset composition and high compositional uniformity.

(3) Copolymerization of *N,N*-diallyl-*N,N*-dimethylammonium chloride with vinyl acetate involves both double bonds of the former and occurs via intramolecular cyclization with the formation of pyrrolidinium rings in the macrochain.

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