ISSN 1070-4272, Russian Journal of Applied Chemistry, 2009, Vol. 82, No. 4, pp. 618−621. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © N.A. Nesterova, I.I. Gavrilova, E.F. Panarin, 2009, published in Zhurnal Prikladnoi Khimii, 2009, Vol. 82, No. 4, pp. 624−627.

MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Radical Copolymerization of *N*-Vinylformamide with Unsaturated Carboxylic Acids

N. A. Nesterova, I. I. Gavrilova, and E. F. Panarin

Institute of Macromolecular Compounds, Russian Academy of Sciences, St. Petersburg, Russia

Received January 21, 2008

Abstract—Radical precipitative copolymerization of *N*-vinylformamide with acrylic and methacrylic acids in isopropanol at 60°C, with azobisisobutyric acid dinitrile as initiator, was studied. The conditional values of the relative reactivities were found: $r_1 = 0.068 \pm 0.008$ and $r_2 = 1.638 \pm 0.025$ for the *N*-vinylformamide–methacrylic acid copolymer and $r_1 = 0.15 \pm 0.03$ and $r_2 = 0.19 \pm 0.09$ for the *N*-vinylformamide–acrylic acid copolymer.

DOI: 10.1134/S1070427209040168

Poly-*N*-vinylamides are of considerable interest because of their wide use in medicine and biotechnology [1]. The best studied of these are polyvinylpyrrolidone and copolymers of *N*-vinylpyrrolidone with comonomers, containing various functional groups. The latter are used as carriers of biologically active substances. Less studied are *N*-vinylamides with an open chain and polymers based on these compounds. Of particular interest among *N*-vinylamides is *N*-vinylformamide (*N*-VFA), which contains a formyl group easily removable by acid hydrolysis, and water-soluble copolymers on its basis. However, data on the reactivity of N-VFA in homo- and copolymerization, reported in the scientific literature, are scarce. In this context, of indubitable scientific and practical interest is a study of the copolymerization of N-VFA with functional monomers.

The aim of this study was to examine the copolymerization of *N*-vinylformamide with unsaturated carboxylic acids, methacrylic (MAC) and acrylic (AC), in isopropanol.

The copolymerization of N-VFA with MAC and AC in isopropanol occurs by the heterophase mechanism. This is due to the presence in the copolymers of vinylformamide units forming firm hydrogen bonds N–H...O=C both with the neighboring carboxyl-containing units in the polymer chain and between macromolecule chains [1, 2]. Just this circumstance hinders dissolution of the resulting copolymers in alcohols. The precipitative copolymerization cannot be described in terms of the classic theory of radical copolymerization, in which the relative activities of monomers are determined solely by the chemical structure of monomers and radicals. Therefore, we consider the calculated copolymerization constants and structural parameters of the polymers to be conditional.

EXPERIMENTAL

N-Vinylformamide, AC, and MAC purchased from Aldrich were purified by vacuum distillation: bp 65.0°C (4 mm Hg), bp 48.0°C (15 mm Hg), and bp 163.6°C (12 mm Hg), respectively. Azobisisobutyric acid dinitrile (AAD) was twice recrystallized from ethanol, mp 103°C.

The copolymerization was performed in isopropanol at 60.0°C in sealed ampules in an inert medium (argon), with AAD as initiator. The copolymers were white powders, which were separated on a Schott filter, washed with acetone, and dried in a vacuum at room temperature to constant weight. The characteristic viscosity of the copolymers was determined in 0.2 M NaCl at 25°C with an Ubbelohde viscometer. All the copolymers VFA–AC and VFA–MAC are soluble in water, with the exception of VFA–MAC samples containing more than 20 mol % MAC units, which are easily dissolved in water in the salt form.

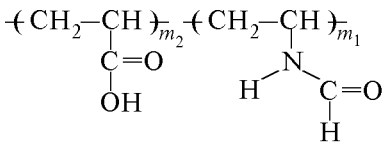
The fractionation was performed from a 0.6% aqueous solution of sodium chloride by the fractional precipitation method, with a 90 : 10 mixture of acetone and isopropanol as the precipitating agent. The fractions were purified by dialysis and subjected to freeze drying.

Table 1. Results of copolymerization of VFA–MAC and VFA–AC mixtures

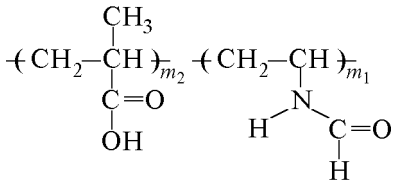
Composition of a starting mixture, mol. fraction		Time, min	Yield, %	Analytical data on the copolymer composition, mol. fraction	
M_1	M_2			m_1	m_2
VFA–MAC					
0.9	0.1	4.5	4.5	0.58	0.42
0.7	0.3	8.0	6	0.40	0.60
0.5	0.5	5.5	5.9	0.28	0.72
0.3	0.7	5.5	5.9	0.17	0.82
0.1	0.9	5.5	5.9	0.06	0.94
VFA–AC					
0.9	0.1	4.5	5	0.70	0.30
0.7	0.3	3.5	8	0.54	0.46
0.5	0.5	3.5	5	0.50	0.50
0.3	0.7	5.0	5	0.47	0.52
0.1	0.9	5.5	5	0.26	0.74

The composition of VFA–AC and VFA–MAC was determined by potentiometric titration with a 0.1 N NaOH solution.

The structure of the copolymers was confirmed by IR spectroscopy (Bruker Vertex-70 instrument):



AC–VFA



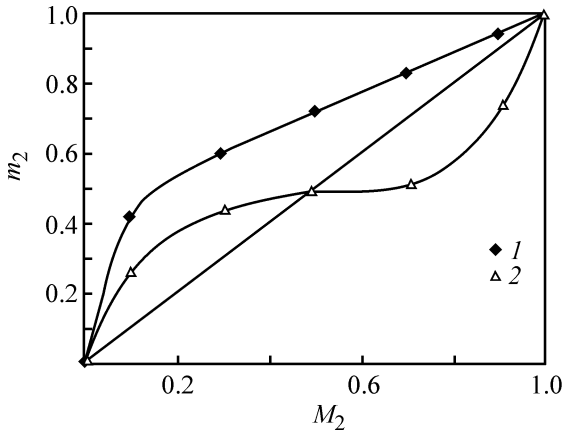
MAC–VFA

Table 2. Copolymerization constants of VFA (r_1)–MAC (r_2) and VFA (r_1)–AC (r_2)

Method for calculation of r_1 and r_2	r_1	r_2	$1/r_1$	$1/r_1$	$r_1 r_2$
VFA–MAC					
Fineman–Ross	0.07 ± 0.005	1.7 ± 0.01	14.29	0.59	0.119
Kelen–Tüdös	0.07 ± 0.018	1.7 ± 0.02	14.49	0.59	0.117
Mayo–Lewis integral	0.06	1.68	16.67	0.60	0.101
Ezrielev–Brokhina–Roskin	0.07 ± 0.008	1.64±0.025	14.7	0.61	0.111
VFA–AC					
Fineman–Ross	0.11 ± 0.1	0.13 ± 0.10	9.1	7.7	0.014
Kelen–Tüdös	0.12 ± 0.032	0.09 ± 0.08	8.3	11.1	0.011
Mayo–Lewis integral	0.11	0.15	9.1	6.7	0.017
Ezrielev–Brokhina–Roskin	0.15 ± 0.03	0.19 ± 0.09	6.7	5.3	0.029

Table 3. Calculation of structural parameters of VFA–MAC and VFA–AC copolymers

Copolymer composition, mol. fraction		m_1/m_2	$f_{M_1-M_1}$	$f_{M_1-M_2}$	$f_{M_2-M_2}$	L_{M1}	L_{M_2}
m_1	m_2						
VFA–MAC							
0.58	0.42	1.38	0.029	0.3	0.37	1.097	2.2
0.40	0.60	0.67	0.010	0.218	0.553	1.046	3.537
0.28	0.72	0.39	0.004	0.157	0.683	1.025	5.350
0.17	0.82	0.21	0.0014	0.099	0.801	1.015	9.098
0.06	0.94	0.06	0.0001	0.033	0.934	1.003	29.303
VFA–AC							
0.70	0.30	2.33	0.14	0.53	0.03	1.27	1.06
0.54	0.46	1.17	0.06	0.43	0.07	1.14	1.16
0.50	0.50	1.0	0.06	0.43	0.08	1.14	1.19
0.475	0.525	0.9	0.06	0.43	0.09	1.14	1.21
0.26	0.74	0.35	0.05	0.39	0.21	1.13	1.54



Phase diagram of the copolymers. (m_2) Molar fraction of MAC (AC) units in a copolymer and (M_2) molar fraction of an MAC (AC) monomer in the mixture of monomers. Experimental curve for a copolymer composition: (*1*) VFA–MAC and (*2*) VFA–AC.

The absorption bands at 3270 and 3050 cm^{-1} are associated with stretching vibrations of the bound NH group in the *trans*-form of the amide group of VFA. The bands at 1530 cm^{-1} (Amide II band) and 1660 cm^{-1} (Amide I band), both related to the C=O group, confirm the presence of VFA units in the polymer. Our results are in good agreement with published data [3]. The presence of carboxy groups is confirmed by the fact that the spectra contain bands at 1720, 1236, and 1255 cm^{-1} [4], characteristic of the C=O groups of carboxylic acids.

To evaluate the relative activities of the monomers, we performed a set of experiments on copolymerization of monomer mixtures VFA–MAC and VFA–AC of various compositions. The experimental conditions were chosen so that the conversion did not exceed 10%. The results of these experiments are listed in Table 1.

Using the data in Table 1, we calculated the copolymerization constants for VFA–MAC and VFA–AC by the Fineman–Ross and Kelen–Тьдцs methods and the Mayo–Lewis integral method [5]. The data obtained were verified by analytical calculation of the copolymerization constants with the use of symmetric equations that enable calculation of root-mean-square errors in determination of the copolymerization constants [6]. Table 2 lists the calculated values of the copolymerization constants.

The figure shows how the copolymer compositions depend on the compositions of the starting monomer mixtures at small conversions. For the VFA–MAC copolymer, the curve corresponds to the case of $r_2 < 1$ and $r_2 > 1$, i.e., under the given copolymerization conditions, MAC is a more active monomer than VFA. For the VFA–AC copolymer, the curve corresponds to $r_1 < 1$ and $r_2 < 1$ and intersects the line of the azeotrope at a point corresponding to the 1 : 1 mixture composition. For this pair of monomers, a strong tendency toward unit alternation is observed. The composition of the copolymers obtained at deep conversions (99% yield) corresponds to the composition of monomers in the starting mixture.

Table 4. Results of fractionation of VFA–MAC and VFA–AC copolymers

Fraction composition, mol %	Fraction composition, mol %		[η], dl g^{-1}
	m_1	m_2	
VFA–MAC 73:27 mol%, [η]=1.6 dl g^{-1}			
1	64.7	35.3	2.47
2	74.5	25.5	2.23
3	76.5	23.5	1.98
4	78.0	22.0	0.82
VFA–MAC 80:20 mol%, [η]=0.39 dl g^{-1}			
1	80.0	20.0	0.45
2	72.0	28.0	0.25

Further, we calculated the structural parameters of the VFA–MAC and VFA–AC copolymers, listed in Table 3.

It can be seen in Table 3 that the statistical-average length L of VFA units is about unity, irrespective of the copolymer composition in both cases. This means that there are almost no adjacent VFA units, and the copolymer with AC contains almost no adjacent AC units [7].

As shown by the results of fractionation (Table 4), the VFA–MAC copolymers are more compositionally inhomogeneous than VFA–AC, which is characteristic of systems polymerized by the heterophase mechanism [8]. For a 73 : 27 (mol %) VFA–MAC copolymer sample, four fractions were isolated, and the 80 : 20 (mol %) VFA–AC copolymer was separated into two fractions differing in both the molecular mass and the composition.

For the VFA–MAC and VFA–AC copolymers, the key factors determining the molecular mass (MM) are the concentration and composition of the starting monomer mixture (Table 5). For the VFA–MAC copolymers, the MM increases with the MAC content of the starting monomer mixture, whereas for the VFA–AC system, the

Table 5. Effect of the conditions of VFA (*M*1) copolymerization with MAC (*M*2) and AC (*M*2) on the properties of the resulting copolymers AAD concentration 1 wt %, copolymerization time 4 h

Monomers		VFA–MAC			VFA–AC		
reaction mixture composition $M_1 : M_2$, mol %	comonomer concentration, wt %	copolymer composition $m_1 : m_2$, mol %	[η], dl g^{-1}	yield, wt %	copolymer composition $m_1 : m_2$, mol %	[η], dl g^{-1}	yield, wt %
90:10	5	87:13	0.28	80	78:22	0.14	45
80:20	5	75:25	0.9	75	65:35	0.09	49
50:50	5	45:55	1.2	77	50:50	0.06	72
90:10	15	90:10	0.4	97	90:10	0.31	82
80:20	15	77:23	1.1	90	76:24	0.23	84
50:50	15	46:54	1.4	91	50:50	0.14	96
90:10	30	90:10	0.55	99	90:10	0.53	94
80:20	30	80:20	1.45	99	80:20	0.39	99
50:50	30	50:50	2.4	97	50:50	0.16	97

MM decreases as the AC content becomes larger, which is probably due to the different reactivities of MAC and AC.

CONCLUSIONS

(1) The radical precipitative copolymerization of *N*-vinylformamide with acrylic and methacrylic acid in isopropanol at 60°C was studied.

(2) The relative reactivity constants of the comonomers were determined.

REFERENCES

1. Kirsh, Yu.E., *Poli-N-vinilpirrolidon i drugie poli-N-vinilamidy* (Poly-*N*-vinylpyrrolidone and Other Poly-N-vinylamides), Moscow: Nauka, 1998.
2. Kalninsh, K.K. and Panarin, E.F., *Vozbuzhdennye sostoyaniya v khimii polimerov* (Excited States in Polymer Chemistry), St. Petersburg: IPTs SPb. Gos. Univ.Tekhnol. Dizaina, 2007.
3. Kirsh, Yu.E., Semina, N.V., Kalninsh, K.K., and Shatalov, G.V., *Vysokomol. Soedin., Ser. B*, 1996, vol. 38, no. 11, pp. 1905–1908.
4. Tarutina, L.I. and Pozdnyakova, F.O., *Spektral'nyi analiz polimerov* (Spectral Analysis of Polymers), Leningrad: Khimiya, 1986.
5. Mayo, P.T. and Lewis, T.M., *J. Am. Chem. Soc*., 1944, vol. 66, pp. 1694–1699.
6. Sutyagin, V.M. and Lyapkov, A.A., *Opredelenie otnositel'nykh konstant sovmestnoi polimerizatsii vinil'nykh monomerov* (Determination of Relative Copolymerization Constants of Vinyl Monomers), Tomsk: Tomsk. Politekhn. Univ., 1995.
7. Gindin, L.M., Abkin, A.D., and Medvedev, S.S., *Dokl. Akad. Nauk SSSR,* 1974, vol. 56, no. 1, pp. 177–179.
8. Smirnova, L.A., Semchikov, Yu.D., Slavnitskaya, N.N., et al., *Dokl. Akad. Nauk SSSR,* 1982, vol. 263, no. 5, pp. 1170–1173.