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Copolymerization of *N*-Vinylsuccinimide with Butyl Methacrylate in Pyridine

N. A. Lavrov, A. G. Pisarev, and E. V. Sivtsov

St. Petersburg State Technological Institute, St. Petersburg, Russia

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Abstract—The kinetics of radical copolymerization of *N*-vinylsuccinimide with *n*-butyl methacrylate in pyridine was studied, and the previously unknown copolymerization constants of the monomers were determined. The calculations were performed using appropriate software and a new procedure for approximation of the experimental data, which allow determination of the kinetic parameters at high conversions with the minimum error. The copolymerization kinetics were compared for the reaction systems constituted by *N*-vinylsuccinimide and *n*-butyl methacrylate and by *N*-vinylsuccinimide and *n*-butyl acrylate.

Copolymers of *N*-vinylsuccinimide (VSI) with *n*-butyl acrylate (BA) were suggested as materials for preparing films for medicobiological purposes [1–3]. The acrylic comonomer acting as internal plasticizer makes it possible to prepare elastic films recommended for protection and treatment of skin wounds. However, copolymers containing more than 80–90% BA are sticky liquids incapable of film formation. This drawback can be eliminated by introducing one more comonomer, i.e., by partially replacing BA with *n*-butyl methacrylate (BMA). Papers on preparation of VSI polymers and copolymers, published in the last 50 years [4], contain no data on binary copolymerization of VSI with BMA. In this study, we examined the copolymerization of VSI with BMA in pyridine.

The monomers and initiator, azobis(isobutyronitrile) (AIBN), were purified as described in [5]. Analytically pure pyridine was double-distilled. The copolymerization of the monomers was performed in glass ampules under Ar at 60°C. The total concentration of the monomers in pyridine was 0.7, and that of AIBN, 0.0165 M. The reaction kinetics was studied gravimetrically, as in [5]. After the copolymerization was complete, the ampule contents were poured into distilled water. The precipitated copolymer was filtered off and dried to constant weight at 20°C (660 Pa). The copolymer compositions (Table 1) were determined by IR spectroscopy from the ratio of the optical density at 1700 cm^{-1}, D_{VSI}, to that at 1725 cm^{-1}, D_{BMA}, using a calibration plot constructed according to [6]. The IR spectra of copolymers were recorded on a Perkin–Elmer spectrophotometer. Samples were prepared as films cast on KBr plates or as free films.

Copolymerization of VSI with both BMA and BA [5] in pyridine is relatively fast, which does not always allow isolation of the copolymers at low conversions. With increasing conversion, the viscosity of the reaction mixture grows, thus complicating a quantitative isolation of the product. Copolymerization occurs under homogeneous conditions and yields copolymers soluble in organic solvents, which allows preparation of films by casting.

Comparison of the kinetics of VSI–BMA copolymerization with that of VSI–BA copolymerization and with the results given in [5] shows that the initial rate of VSI–BMA copolymerization is higher as compared to the VSI–BA system (Table 1). This is due to the higher activity of BMA, compared to BA. However, the rate of copolymerization of VIS with BMA decreases with increasing conversion (Table 1). This may be due to changes in the solution viscosity and in conformations of macromolecules in the course of polymerization, and also to steric factors.

The high viscosity of the reaction system may be responsible for the fact that the gravimetric method used to monitor the copolymerization kinetics gives a certain scatter of experimental points. As a result, the error in calculation of the copolymerization constants increases. Therefore, in studying the kinetics of copolymerization of VSI with BMA, we used the approximation procedure [7] allowing correction of

Table 1. Compositions of copolymers of VSI (M_1) with BMA or BA (M_2), prepared in pyridine at 60°C*

VSI mole fraction in the starting mixture	Co-monomer M_2	τ, min	*K*, %	Mole fraction of VSI units in copolymer
0.25	BMA	60	33	0.15
		180	62	0.17
		240	65	0.18
0.50	BMA	60	37	0.30
		180	70	0.37
		240	73	0.38
0.75	BMA	60	42	0.47
		180	80	0.65
		240	82	0.66
0.25	BA	60	29	0.15
		120	52	0.17
		300	84	0.19
0.50	BA	60	35	0.32
		120	61	0.39
		300	89	0.45
0.75	BA	60	38	0.52
		120	70	0.72
		300	98	0.74

* (τ) Copolymerization time and (*K*) conversion.

Table 2. Constants of copolymerization of VSI (M_1) with BMA or BA (M_2) in pyridine (AIBN initiator, 60°C), calculated by the EBR and KT methods

Constant	Comonomer M_2	
	BMA	BA
r_1 (EBR)	0.03 ± 0.04	0.11 ± 0.07
r_1 (KT)	0.03 ± 0.03	0.11 ± 0.07
r_2 (EBR)	1.79 ± 0.04	1.70 ± 0.10
r_2 (KT)	1.79 ± 0.02	1.70 ± 0.09
$1/r_1$	14.2	9.09
$1/r_2$	0.559	0.588
r_2/r_1	25.6	15.5
r_1r_2	0.125	0.187

data on the monomer conversion and copolymer composition by the least-squares method; the error in calculation of the copolymerization constants is thus decreased.

Detailed analysis of the applicability of this procedure to treatment of experimental data obtained at various conversions of the monomers, using computer programs for calculation of the polymerization constants by the Ezrielev–Brokhina–Roskin (EBR) [8] and Kelen–Tüdös (KT) [9] methods, shows that reliable results can be obtained even at conversions exceeding 50%. Using this procedure, we also refined the constants of copolymerization of VSI with BA [5]; the results are listed in Table 2.

In calculation of the VSI–BMA copolymerization constants in pyridine by the EBR and KT methods, the minimum error factor was 0.001. In the system VSI–BA, the copolymerization constants in pyridine could be calculated with an even lower error factor of 0.0001. Calculation of r_1 and r_2 by both methods gives virtually coinciding results (Table 2).

The constants of copolymerization of VSI with BA in pyridine, calculated in [5] ($r_1 = 0.26 \pm 0.05$, $r_2 = 1.86 \pm 0.11$), were determined at a 3–8% conversion of the monomers. However, measurements at low (≤10%) conversions do not always ensure a low error of the copolymerization constants. For example, the error factor was 0.5 in [5].

The use of experimental data for low conversions is quite justified if the methods used for calculating the copolymerization constants are based on solution of differential equations for the copolymer composition. With more up-to-date calculation methods and computer facilities, there is no need to restrict artificially the experimental data. Therefore, we refined in this paper the constants of copolymerization of VSI with BA in pyridine using the approximation treatment of experimental data for <50% conversion (Table 2). The error factor was 0.0001.

The constants of copolymerization of VSI with BMA in pyridine (Table 2) were determined similarly with an error factor of 0.001. Hence, the procedure of approximation of the experimental data on the monomer conversion and copolymer composition allows determination of the copolymerization constants r_1 and r_2 with a minimum error even at conversions exceeding 50% (Table 1). This confirms the conclusion made in [10] that the Kelen–Tüdös method is quite suitable for calculating the copolymerization constants at high conversions. In turn, the copolymerization constants calculated from the approximated experimental data with a very low error factor furnish more reliable information on the reaction kinetics and microstructure of the copolymers.

Using the copolymerization constants for the systems VSI–BMA and VSI–BA (Table 2), we calculated the probability *f* of diad formation and the statistical-mean block lengths *L* in the chains of VSI–BMA and VSI–BA copolymers by the formulas from [11, 12]

Table 3. Probability *f* of diad formation and statistical-mean block length *L* in chains of VSI–BMA and VSI–BA copolymers (copolymerization in pyridine, AIBN initiator, 60°C)

VSI–BMA copolymers						VSI–BA copolymers					
VSI mole fraction	f_{11}	f_{22}	$f_{12} = f_{21}$	L_1	L_2	VSI mole fraction	f_{11}	f_{22}	$f_{12} = f_{21}$	L_1	L_2
0.1	0.0002	0.889	0.055	1.003	17.1	0.1	0.0007	0.884	0.058	1.01	16.3
0.2	0.0008	0.781	0.109	1.008	8.16	0.2	0.003	0.770	0.113	1.03	7.80
0.3	0.002	0.675	0.162	1.013	5.18	0.3	0.008	0.660	0.166	1.05	4.97
0.4	0.004	0.571	0.213	1.02	3.69	0.4	0.016	0.552	0.216	1.07	3.55
0.5	0.008	0.469	0.262	1.03	2.79	0.5	0.029	0.446	0.262	1.11	2.70
0.6	0.014	0.369	0.309	1.05	2.19	0.6	0.050	0.344	0.303	1.17	2.13
0.7	0.025	0.270	0.352	1.07	1.77	0.7	0.086	0.244	0.335	1.26	1.73
0.8	0.047	0.174	0.389	1.12	1.45	0.8	0.154	0.148	0.349	1.44	1.43
0.9	0.109	0.081	0.405	1.27	1.20	0.9	0.311	0.059	0.315	1.99	1.19

Table 4. Variation of the VSI (M_1) content in the monomer mixture in the course of copolymerization with BMA or BA (M_2) in pyridine

Comonomer M_2	VSI mole fraction at indicated conversion, %					
	0	10	20	40	50	70
BMA	0.25	0.28	0.30	0.33	0.35	0.40
	0.50	0.54	0.59	0.63	0.66	0.69
	0.75	0.78	0.81	0.83	0.86	0.89
BA	0.25	0.27	0.29	0.32	0.34	0.38
	0.50	0.52	0.55	0.59	0.62	0.65
	0.75	0.77	0.79	0.83	0.85	0.87

Table 5. Probability *f* of diad formation and statistical-mean block length *L* in the chains of copolymers of VSI (M_1) with BMA or BA (M_2), calculated taking into account the monomer conversion (copolymerization in pyridine)

Comonomer M_2	Mole fraction of M_1	*K*, %	f_{11}	f_{22}	$f_{12} = f_{21}$	L_1	L_2
BMA	0.25	0	0.001	0.728	0.136	1.010	6.37
		10	0.002	0.696	0.151	1.012	5.60
		20	0.002	0.675	0.162	1.013	5.18
		40	0.003	0.643	0.177	1.015	4.63
		50	0.003	0.622	0.187	1.016	4.32
		70	0.004	0.571	0.213	1.020	3.69
BA	0.50	0	0.029	0.446	0.262	1.11	2.70
		10	0.032	0.425	0.271	1.12	2.57
		20	0.038	0.395	0.284	1.13	2.39
		40	0.047	0.354	0.299	1.16	2.18
		50	0.056	0.323	0.310	1.18	2.04
		70	0.065	0.293	0.321	1.20	1.92
BA	0.75	0	0.114	0.196	0.345	1.33	1.57
		10	0.128	0.177	0.348	1.37	1.51
		20	0.144	0.158	0.349	1.41	1.45
		40	0.186	0.121	0.347	1.54	1.35
		50	0.213	0.103	0.342	1.62	1.30
		70	0.246	0.085	0.334	1.74	1.25

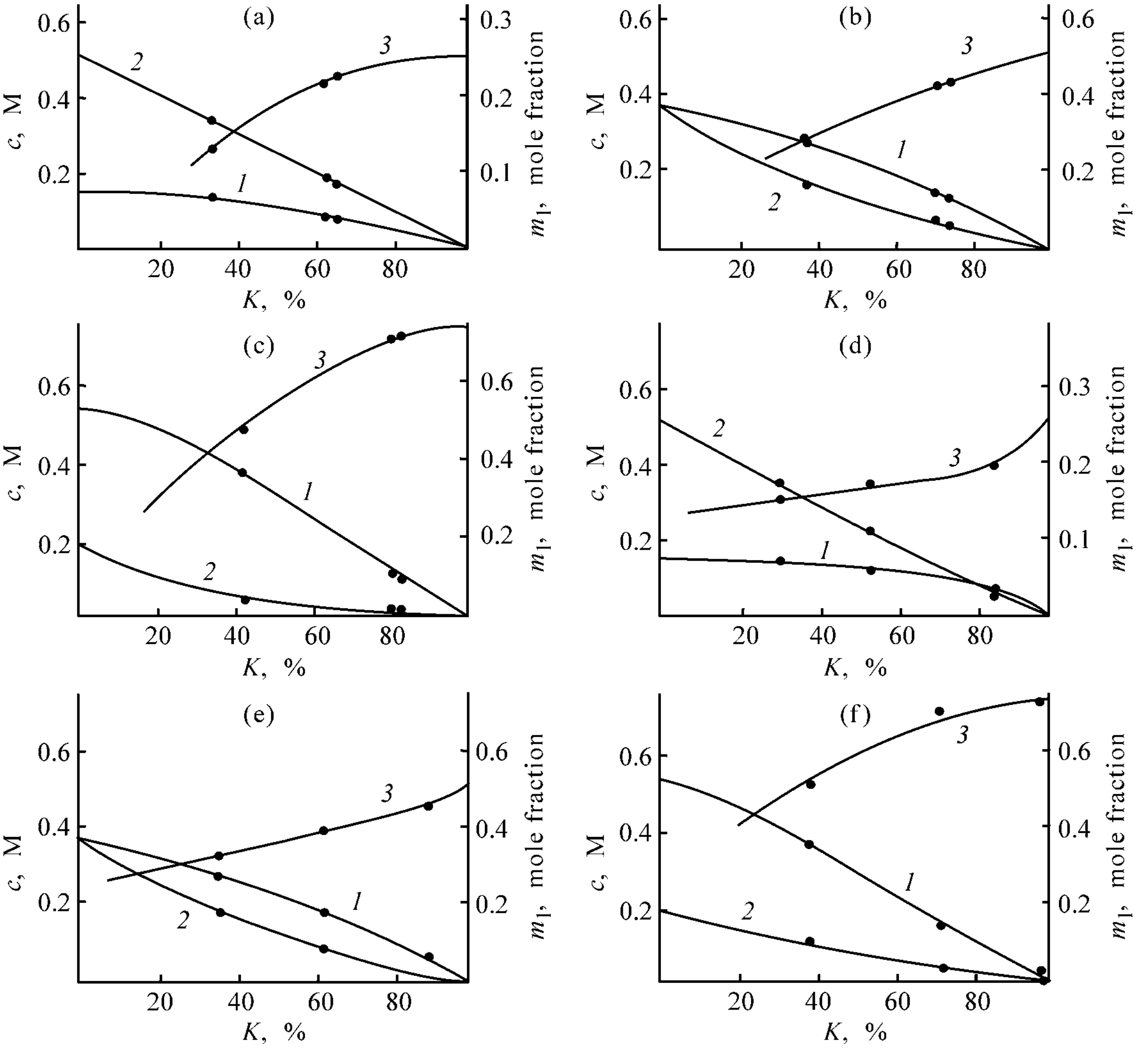

Fig. 1. Concentrations *c* of (*1*) VSI and (*2*) BMA or BA in the reaction mixture and (*3*) the mole fraction of VSI units in the copolymer m_1 vs. the conversion *K*. Solvent pyridine; total monomer concentration 0.7 M; AIBN concentration 0.0165 M; 60°C. VSI mole fraction in the monomer mixture: (a, d) 0.25, (b, e) 0.50, and (c, f) 0.75. Copolymerization: (a–c) VSI + BMA and (d–f) VSI + BA.

using the appropriate software [13]. The results obtained (Table 3) show that the tendency toward formation of alternating copolymers in copolymerization of VSI with BMA in pyridine appears at the VSI mole fraction in the monomer mixture equal to 0.80–0.90, and in the system with BA in the same solvent it appears at the VSI mole fraction of 0.70–0.80.

Taking into account changes that occur in the VSI content in the monomer mixture as the conversion grows from 0 to 70% (Table 4), we determined, according to [14], the probability of diad formation and the statistical-mean block length in the chains of VSI–BMA and VSI–BA copolymers prepared in pyridine at various conversions (Table 5), using the diagrams shown in Fig. 1.

Table 4 shows that the high reactivity of BMA and BA, which determines higher rate of their consumption in the reaction mixture, results in an enrichment of the monomer mixture with the less active monomer, VSI. Therefore, with increasing conversion, the probability of formation of M_1M_2 and M_2M_2 diads ($f_{12} = f_{21}$) grows, and that of formation of diads consisting of BMA or BA units (f_{22}) decreases. Also, with increasing conversion, the statistical-mean block lengths L_1 and L_2 approach each other (Table 5).

Tables 3–5 show that the highest probability of unit alternation, f_{12} = 0.349, in VSI–BA copolymers prepared in pyridine is observed at the VSI mole fraction in the monomer mixture equal to 0.7–0.8. The maximum probability of cross addition of units, f_{12} =

0.349, is attained at the VSI mole fraction of 0.79 and a 20–40% conversion.

The microstructure of VSI–BMA copolymers prepared in pyridine was analyzed similarly. The highest probability of unit alternation, f_{12} = 0.406, is observed at the VSI mole fraction in the monomer mixture equal to 0.7–0.9. The maximum probability of cross addition of units, f_{12} = 0.406, is attained at the VSI mole fraction of 0.87 and a 50–70% conversion.

The BSI–BMA copolymers prepared in pyridine are characterized by better alternation of units than the VSI–BA copolymers prepared in the same solvent. The maximum probability of unit alternation, $f_{12} = f_{21}$, is 0.406 for VSI–BMA copolymers and 0.349 for VSI–BA copolymers. The minimum difference between the mean block lengths L_1 and L_2 (ΔL) for the VSI–BMA copolymers is 0 at VSI mole fraction of 0.88–0.89 and $K \approx 70\%$ (Table 5). For the VSI–BA copolymers, the minimum ΔL is 0.01 at the VSI mole fraction of 0.79–0.80 and $K \approx 20\%$ (Table 5). This fact confirms the conclusion made in [5] that pyridine as a solvent ensures a better compositional uniformity of copolymers, compared to other solvents, e.g., dimethyl sulfoxide.

Our experimental results can be used in planning and simulation of ternary copolymerization of VSI with BA and BMA with the aim to obtain elastic films for medical and biological purposes.

CONCLUSIONS

(1) The kinetics of copolymerization of *N*-vinylsuccinimide with *n*-butyl methacrylate was studied for the first time, and the constants of copolymerization in pyridine were determined: $r_1 = 0.03 \pm 0.04$ and $r_2 = 1.79 \pm 0.04$.

(2) Application of the approximation procedure to data on monomer conversion and copolymer composition made it possible to determine the constants of copolymerization of *N*-vinylsuccinimide with *n*-butyl methacrylate and *n*-butyl acrylate in pyridine with an error factor of 0.0001–0.001.

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