ISSN 1070-4272, Russian Journal of Applied Chemistry, 2009, Vol. 82, No. 7, pp. 1281−1287. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © E.V. Sivtsov, A.I. Gostev, N.A. Lavrov, 2009, published in Zhurnal Prikladnoi Khimii, 2009, Vol. 82, No. 7, pp. 1186−1191.

MACROMOLECULAR COMPOUNDS AND POLYMERIC MATERIALS

Copolymerization of *N*-Vinylsuccinimide with Butyl Acrylate in an Electron-Donor Medium of Tertiary Aminese

E. V. Sivtsov, A. I. Gostev, and N. A. Lavrov

St. Petersburg State Institute of Technology, St. Petersburg, Russia

Received January 15, 2009

Abstract—The effect of electron-donor solvents on the parameters of the NMR signals of vinyl protons in *N*-vinylsuccinimide and butyl acrylate was examined. The kinetics of copolymerization of *N*-vinylsuccinimide with butyl acrylate in triethylamine and tributylamine was studied by monitoring the running concentrations of the monomers in the course of the reaction. The copolymerization constants were calculated. The diad and triad composition of the copolymers formed in the medium of tertiary amines was predicted, and their microstructural nonuniformity was evaluated.

DOI: 10.1134/S1070427209070222

Copolymers of *N*-vinylsuccinimide (VSI) with *n*-butyl acrylate (BA) are of practical interest as materials for preparing films [1–3] and adhesives [4] for medical purpose. Base hydrolysis of such copolymers leads to succinimide ring opening with the formation of *N*-vinylamidosuccinic acid (VASA) units containing a carboxy group to which low-molecular-weight physiologically active substances of basic character can be linked by ionic bonding. The BA units act as an internal plasticizer.

Previously we studied the copolymerization of VSI with BA in dimethyl sulfoxide (DMSO) [5, 6], acetic anhydride (AA) [7, 8], and pyridine [9]. The reaction kinetics was studied by a combination of the gravimetric method (to determine conversion) with elemental analysis and IR spectroscopy (to determine the copolymer composition). In [6] we used a new procedure for studying copolymerization kinetics, based on monitoring of the reaction mixture by intermittently measuring the ^{1}H NMR spectra. The results of previous studies suggest that proper choice of the reaction medium can solve the problem of compositional nonuniformity of the copolymers obtained, caused by the large difference between the relative activities of VSI and BA. Encouraging results showing that the monomer activities can be made closer were obtained when the copolymerization was performed in pyridine [9] and AA [7, 8]. The copolymerization constants of VSI with BA in these solvents, and also the solvent parameters characterizing their donor–acceptor power {donor (DN) and acceptor (AN) numbers [10], ionization potential, proton affinity (taken from NIST database)} are given in Table 1.

The need for using several different parameters for describing donor–acceptor properties of solvents is caused by their ambiguous sense when applied to systems other than those for which these parameters were developed. For example, the Gutmann donor number DN objectively characterizes the capability of molecules of a given substance to donate electrons for participation in donor–acceptor interaction with Sb(V) chloride taken as standard electron acceptor.

Another parameter suggested by Gutmann an coworkers, acceptor number, characterizes the electrophilic properties of a solvent in its interaction with triethylphosphine oxide. In this case, the same Sb(V) chloride is taken as reference. This approach does not take into account significant difference between compounds having low-lying unoccupied orbitals [Sb(V) chloride] and compounds in which such orbitals are lacking (e.g., pyridine) and the lowest unoccupied molecular orbital has so high energy that the interaction with the majority of electron-donor compounds is energetically unfavorable.

Table 1. Copolymerization constants of VSI (M_1) with BA (M_2) in electron-donor solvents

Solvent	Solvent properties				Constants calculated by indicated method			
	DN, kJ mol^{-1}	AN	ionization potential I, eV	proton affinity PA, kJ mol^{-1}	EBR		KT	
DMSO	124.7	19.3	9.1	884.4	0.07	2.76	0.07	2.78
AA	43.9	–	10.0	–	0.05	0.94	0.04	0.97
Pyridine	138.5	14.2	9.34	930.0	0.26	1.86	0.29	1.86
TEA	132.6	1.4	7.53	981.8	0.07	2.67	0.07	2.67
TBA	–	–	7.86	998.5	0.02	1.61	0.05	1.61

Therefore, when considering solvents from the viewpoint of these parameters, a contradictory situation often arises. For example, it is difficult to determine whether DMSO should be classed with donor or acceptor solvents. Usually it is considered as an electron-donor solvent, as indicated by its high DN (Table 1). As compared to DMSO, AA is rather an acceptor: Its DN is three times lower. At the same time, the S atom in DMSO has vacant orbitals capable of formation of donor–acceptor complexes, whereas AA has no such orbitals. In other words, under similar conditions, in interaction with a donor compound bearing a lone electron pair, DMSO rather than AA will act as an acceptor.

The ionization potential and proton affinity depend on the medium in which the electron is detached or the proton is added. The effect of the medium is very difficult to take into account in practice. Therefore, when finding correlations of any properties with the donor–acceptor power of a solvent, it is necessary to take into account all the above-mentioned characteristics and specific conditions of interaction of solvents with components of the reaction system. As applied to radical copolymerization of VSI with BA, all the solvents given in Table 1 can be considered as electron-donor solvents.

The accumulated experimental data suggest that an increase in the electron-donor power of a solvent decreases the difference in the relative activities of VSI and BA. Therefore, we chose in this study tertiary amines (triethylamine, TEA; tributylamine, TBA), which are typical electron-donor solvents (Table 1), as solvents for copolymerization of VSI with BA. Previously they were not used as solvents for radical polymerization, despite wide use of TEA as solvent in organic synthesis.

EXPERIMENTAL

N-Vinylsuccinimide was synthesized by the procedure described in [11] and recrystallized three times from a solution in isopropyl alcohol (mp 48.5°C, n_D^{50} 1.5020). BA and TBA were vacuum-distilled just before use. Triethylamine was distilled two times at atmospheric pressure. Azobis(isobutyronitrile) (AIBN) was recrystallized two times from ethanol at 50 ±2°C and vacuum-dried at 20°C (mp 104°C).

Samples for copolymerization of VSI with BA were prepared by dissolving the calculated amounts of AIBN, VSI, and BA in appropriate amine. At certain monomer ratios, short heating to 40°C is required for complete dissolution of the components. The solutions were placed in ampules. After making an argon atmosphere over the solutions by repeated freezing–pumping–thawing–filling with argon, the ampules were sealed. The polymerization was performed at 60°C. The total concentration of the monomers was 0.7, and that of AIBN, 0.0165 M. Reaction mixture samples were taken with a syringe through a rubber stopper and immediately frozen. The ^{1}H NMR spectra were recorded in deuterated $CDCl_3$ at 25°C (operation frequency 500 MHz, internal reference TMS).

Interaction of reaction system components. The solvent effect on the relative activity of the monomers in copolymerization of VSI with other vinyl monomers was observed previously [12]. In this study we evaluated the effect of TEA and TBA on the electron density distribution in VSI and BA molecules by ^{1}H NMR spectroscopy, namely, by measuring the chemical shifts and coupling constants of the vinyl protons of the monomers.

To this end, we examined the proton spectra of several systems: pure monomers in deuterated chloroform and DMSO and samples of reaction mixtures prepared

Table 2. ^{1}H NMR parameters of systems containing VSI, BA, and the solvents

System	Chemical shifts of vinyl protons, ppm						Coupling constants, Hz			
	VSI			BA			VSI		BA	
	$\beta(H^1)$	$\beta(H^2)$	$\beta(H^3)$	$\beta(H^1)$	$\beta(H^2)$	$\beta(H^3)$	$^3J_{H^1H^2}$	$^3J_{H^1H^3}$	$^3J_{H^1H^2}$	$^3J_{H^1H^3}$
VSI or BA (in DMSO-d_6)	6.63	4.99	5.96	6.10	5.88	6.30	9.58	16.45	10.83	16.74
VSI–BA–DMSO (in DMSO-d_6)	6.62	4.97	5.97	6.08	5.87	6.30	9.85	16.74	9.84	16.74
VSI or BA (in $CDCl_3$)	6.66	5.04	6.05	6.10	5.80	6.38	9.56	16.18	10.30	16.91
VSI–BA–TEA (in $CDCl_3$)	6.63	4.99	6.03	6.03	5.72	6.30	9.85	16.74	10.83	17.72
VSI–BA–TBA (in $CDCl_3$)	6.70	5.06	6.09	6.09	5.78	6.36	10.18	16.65	10.18	16.65

for copolymerization in DMSO, TEA, and TBA, with the same composition (monomers and initiator) but different solvents. The spectra of mixtures in the case of copolymerization in TEA and TBA were recorded in $CDCl_3$, and in the case of copolymerization in DMSO, in deuterated DMSO.

Of prime interest are vinyl proton signals, because specifically these signals reflect the polarization and electron density distribution of the double bond in the monomer. The chemical shifts and coupling constants for the examined systems are given in Table 2. We used the following numbering for vinyl protons: 1, α-proton bonded to the carbon atom bearing the substituent; 2, β-*cis* proton; and 3, β-*trans* proton. In DMSO-d_6, the signals of all the vinyl protons are readily identified and do not overlap with each other. In $CDCl_3$, the H^1 signal of BA overlaps with the H^3 signal of VSI, but the signals can be readily distinguished.

On adding TEA and TBA, the signals of vinyl protons of BA are shifted upfield, which may be due to an increase in the electron density on the BA double bound. Similar trend is observed in the VSI spectra in the presence of TEA, whereas TBA shifts the signals downfield, increasing the difference in the electron density on the double bond of the monomers. The coupling constants are usually insensitive to a solvent, but in the systems under consideration they vary significantly. However, we failed to reveal any regular trend.

Kinetic features of copolymerization of VSI with BA in tertiary amines. In the course of the synthesis, we took samples of the reaction mixture. The ^{1}H NMR spectra of these samples furnished data on the running

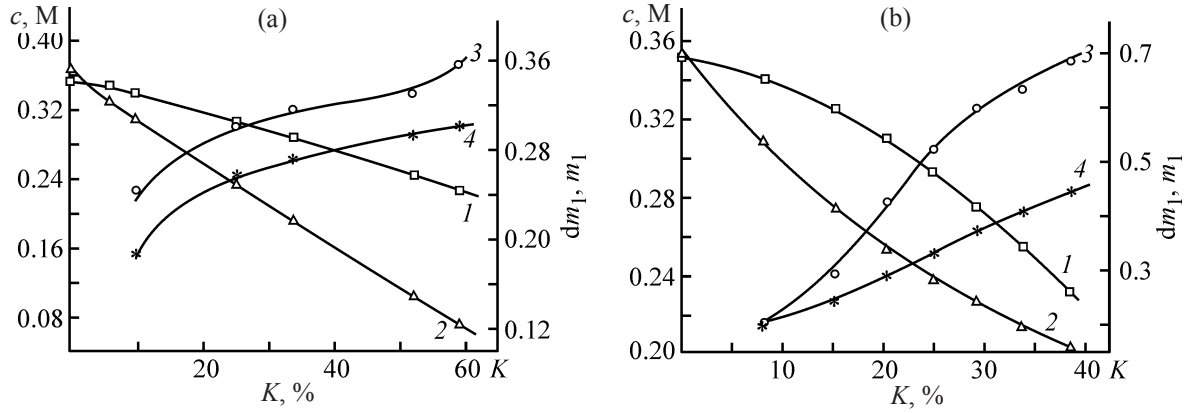
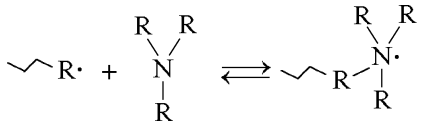


Fig. 1. Concentration c of (*1*) VSI and (*2*) BA, and (*3*) instantaneous (dm_1) and (*4*) overall (m_1) compositions (VSI mole fraction) of VSI–BA copolymers prepared in (a) TEA and (b) TBA from an equimolar mixture of the monomers, as functions of the conversion *K*.

concentrations of both monomers. From these data, we determined the composition of separate fractions of the polymer, formed in the period between the two successive measurements ("instantaneous" copolymer composition), the overall composition of the polymer, and the monomer conversion. The results obtained for equimolar monomer mixtures are plotted in Fig. 1.

The copolymerization in the tertiary amines occurs considerably more slowly than in DMSO (Fig. 2), which may be due to complexation of the propagating macroradicals with amines. Assuming that the complex of the propagating radical with the amine is inactive in the polymerization, the concentration of the active centers is given by the equilibrium



In the case of the more basic TBA, the equilibrium is shifted to the right more strongly, the complex with the radical is more stable, and the polymerization deceleration is the most pronounced.

The results we obtained were used for calculating the copolymerization constants of VSI (M_1) with BA (M_2), using a specially developed program and a procedure described in [13]. The constants determined by the modified Ezrielev–Brokhina–Roskin (EBR) [14] and Kelen–Tüdös (KT) [15] methods are given in Table 1. It was shown previously [13, 16] that the EBR method allows more reliable determination of the copolymerization constants, because the equations for the copolymer composition are symmetrical with respect to r_1 and r_2. Therefore, we chose the EBR data for the subsequent calculations of the effect of unit alternation in copolymer macromolecules.

In the examined range of conversions (up to 60%), with the progress of the reaction, the copolymer gets enriched with units of the less active VSI (Fig. 1, curve *4*). In both diagrams, the rate of BA consumption is higher than that of VSI consumption (Fig. 1, curves *1, 2*), which leads to faster exhaustion of BA and variation of the monomer ratio in favor of VSI. As a result, the polymer formed in each subsequent step of the polymerization is enriched in VSI units relative to the polymer formed in the previous step (Fig. 1, curves *3*). It can be seen that the "instantaneous" composition of the copolymer changes by tens of mole percents, and, as a result, the product obtained is extremely nonuniform in the composition.

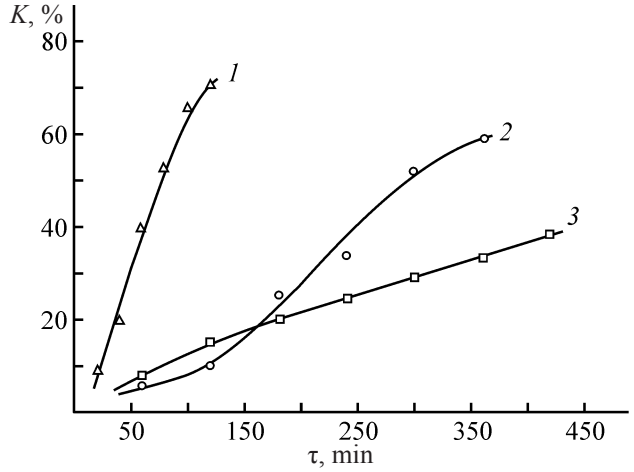


Fig. 2. Monomer conversion K as a function of time τ in copolymerization of an equimolar mixture of VSI and BA in (*1*) DMSO, (*2*) TEA, and (*3*) TBA.

Microstructure of VSI–BA copolymers prepared in tertiary amines. From the copolymerization constants r_1 and r_2 calculated by the EBR method (Table 1), we predicted the character of unit alternation in macromolecules of VSI–BA copolymers prepared at various compositions of the initial monomeric mixtures. The probabilities of formation of various types of structures were calculated using known procedures [17] and the specially developed Kinetika program [18]. The calculation results are given in Table 3. The Medvedev's method allows prediction of the probabilities of formation of structures consisting of n series-connected units of each type, F_{1n} and F_{2n} (Fig. 3) [17], and the M. Izu and K.F. O'Driscoll's method allows calculation of the probabilities of formation of diads and triads of various compositions (Fig. 4). Data in Table 3 show that, in a wide range of compositions of the monomer mixture, there is a trend toward formation of long sequences of BA units, whereas VSI, even when in a large excess, is mainly incorporated in the polymer chain in the form of separate units surrounded by BA units.

In both solvents examined, $r_1 < 1$ and $r_2 > 1$ (Table 1), i.e., $k_{11} < k_{12}$ and $k_{22} > k_{12}$. This means that the propagating macroradical always adds more readily to BA. In going from TEA to TBA, r_1 decreases by a factor of 3.5, i.e., the probability of addition of the macroradical with the VSI terminal unit to BA increases by a factor of 3.5, and r_2 decreases by a factor of 1.7, which enhances a trend toward addition of VSI to the "foreign" radical. Therefore,

Table 3. Probability of diad formation f and statistical average length *Z* of blocks of VSI (M_1) and BA (M_2) units in chains of VSI–BA copolymers prepared in TEA and TBA

VSI content in initial monomer mixture, mol %	f_{11}		f_{22}		$f_{11} = f_{12}$		Z_1		Z_2	
	TEA	TBA	TEA	TBA	TEA	TBA	TEA	TBA	TEA	TBA
10	0	0	0.923	0.879	0.038	0.061	1.01	1.00	25.03	15.49
20	0.001	0.001	0.841	0.763	0.079	0.118	1.02	1.00	11.68	7.44
30	0.004	0.002	0.754	0.652	0.121	0.174	1.03	1.01	7.23	4.76
40	0.008	0.003	0.662	0.545	0.165	0.226	1.05	1.01	5.00	3.42
50	0.015	0.006	0.563	0.444	0.211	0.276	1.07	1.02	3.67	2.61
60	0.027	0.010	0.458	0.346	0.257	0.322	1.10	1.03	2.78	2.07
70	0.049	0.017	0.346	0.252	0.302	0.365	1.16	1.05	2.14	1.69
80	0.095	0.032	0.226	0.162	0.339	0.403	1.28	1.08	1.67	1.40
90	0.215	0.076	0.101	0.076	0.342	0.424	1.63	1.18	1.30	1.18

the overall effect is that the incorporation of BA into the polymer chain becomes more probable, but BA adds with a higher probability to the radical with the VSI terminal unit, which leads to better alternation of units and smaller length of sequences of BA units (Table 3).

A specific feature of copolymers prepared at a high content of BA in the initial monomer mixture is broad length distribution of the sequences of BA units (Fig. 3, curves *2, 3*). With an increase in the VSI content in the monomer mixture, the probability of formation of short BA blocks increases (Fig. 3, curves *1*), and the tendency to alternation of VSI and BA units increases.

The unit alternation, which can be judged from the probability of formation of triads M_1–M_2–M_1 and M_2–M_1–M_2, is illustrated by the dependences of the probabilities of formation of various triads (M_1–M_1–M_1, M_1–M_1–M_2 or M_2–M_1–M_1, M_1–M_2–M_1, M_1–M_2–M_2 or M_2–M_2–M_1, M_2–M_1–M_2, and M_2–M_2–M_2) on the composition of the monomer mixture (Fig. 4). The tendency to alternation can be illustrated more clearly by the dependence of the probability of formation of single monomeric units (F_{12}, F_{21}) on the composition of the monomer mixture (Fig. 5). It can be readily seen that the maximal alternation is observed only at 80–90 mol % content of VSI in the monomer mixture. At such monomer ratios, the probability of formation of single units is maximal (Fig. 5, curves *1, 2*), and the total

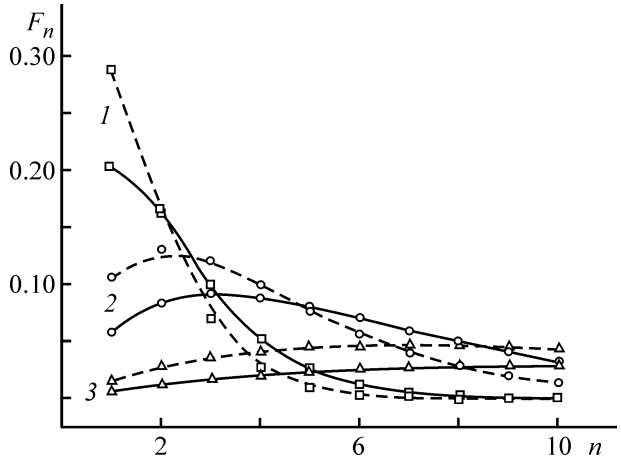


Fig. 3. Probability of formation of structures consisting of *n* series-connected BA units, F_n, in VSI–BA copolymers prepared in TEA (solid lines) and TBA (dashed lines). Initial monomer ratio, VSI : BA, mol %: (*1*) 80 : 20, (*2*) 50 : 50, and (*3*) 20 : 80.

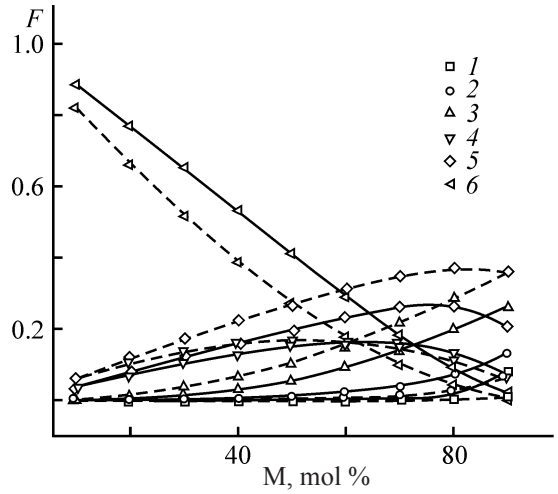


Fig. 4. Probability of triad formation F as a function of the VSI content in the initial monomer mixture M in copolymerization of VSI with BA in TEA (solid lines) and TBA (dashed lines). (*1*) M_1–M_1–M_1, (*2*) M_1–M_1–M_2 (M_2–M_1–M_1), (*3*) M_1–M_2–M_1, (*4*) M_1–M_2–M_2 (M_2–M_2–M_1), (*5*) M_2–M_1–M_2, and (*6*) M_2–M_2–M_2.

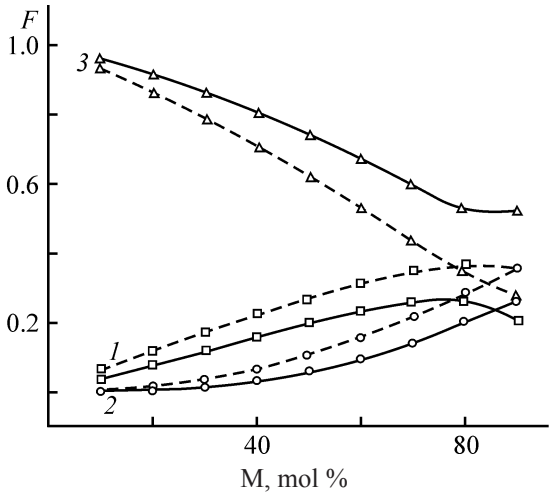


Fig. 5. Probability F of formation of single units of (*1*) VSI and (*2*) BA and (*3*) of sequences of several like units as a function of the VSI content M in the initial monomer mixture in copolymerization of VSI with BA in TEA (solid lines) and TBA (dashed lines).

probability of formation of series-connected units, given by the equation

$$(F_{1n} + F_{2n}) = (100 - F_{11} - F_{21}),$$

where $n \geq 2$, is the lowest (Fig. 5, curve *3*).

The dependences shown in Figs. 3–5 are indicative of stronger tendency to unit alternation in the copolymers prepared in TBA. In both solvents, the maximum of the unit alternation is observed at ~80% content of VSI in the monomer mixture. In this case, the total probability of formation of sequences of several like units is 0.54 and 0.34; the probability of formation of single VSI units, 0.26 and 0.37; and the probability of formation of single BA units, 0.20 and 0.29 for the copolymers prepared in TEA and TBA, respectively, i.e., under similar conditions the copolymers prepared in TBA have a more regular microstructure.

CONCLUSIONS

(1) In the solvent series dimethyl sulfoxide–triethylamine–tributylamine, the vinyl proton signals of *N*-vinylsuccinimide and butyl acrylate in the ^{1}H NMR spectra are shifted, suggesting variation of the electron density on the double bond of the monomers under the action of tertiary amines.

(2) Copolymerization of *N*-vinylsuccinimide with butyl acrylate in tertiary amines occurs more slowly than in dimethyl sulfoxide, which is accounted for by formation of stable complexes of the macroradicals with amines, incapable of participation in chain propagation.

(3) The copolymerization constants were calculated by two different methods from data on the reaction mixture composition, obtained by ^{1}H NMR spectroscopy.

(4) The maximal alternation of units in the polymer chains can be attained at ~80 mol % content of *N*-vinylsuccinimide in the monomer mixture.

REFERENCES

1. Shal'nova, L.I., Chudnova, V.M., and Trofimova, E.A., *Plast. Massy*, 1989, no. 11, pp. 29–34.
2. Lavrov, N.A., Shal'nova, L.I., and Nikolaev, A.F., *Zh. Prikl. Khim.*, 1997, vol. 70, no. 8, pp. 1356–1363.
3. Lavrov, N.A. and Shal'nova, L.I., *Klei. Germet. Tekhnol.*, 2008, no. 9, pp. 2–6.
4. Sivtsov, E.V. and Lavrov, N.A., *Klei. Germet. Tekhnol.*, 2007, no. 3, pp. 13–19.
5. Lavrov, N.A., Sivtsov, E.V., and Nikolaev, A.F., *Zh. Prikl. Khim*., 1998, vol. 71, no. 12, pp. 2055–2058.
6. Sivtsov, E.V., Gostev, A.I., and Lavrov, N.A., *Zh. Prikl. Khim.*, 2007, vol. 80, no. 10, pp. 1679–1682.
7. Lavrov, N.A., Sivtsov, E.V., and Nikolaev, A.F., *Zh. Prikl. Khim*., 2000, vol. 73, no. 4, pp. 683–686.
8. Lavrov, N.A., Sivtsov, E.V., and Nikolaev, A.F., *Plast. Massy*, 2001, no. 10, pp. 43–45.
9. Lavrov, N.A., Sivtsov, E.V., and Pisarev, A.G., *Zh. Prikl. Khim*., 2003, vol. 76, no. 7, pp. 1154–1159.
10. Reichardt, C., *Solvents and Solvent Effects in Organic Chemistry*, Weinheim: VCH, 1988, 2nd ed.
11. Chudnova, V.M., Lavrov, N.A., and Shal'nova, L.I., *Poluchenie polimerov i sopolimerov N-vinilimidov yantarnoi i ftalevoi kislot: Metodicheskie ukazaniya* (Preparation of Polymers and Copolymers of N-Vinylimides of Succinic and Phthalic Acids: Methodical Instructions), Leningrad: Leningr. Tekhnol. Inst. im. Lensoveta, 1989.
12. Lavrov, N.A., Sivtsov, E.V., and Nikolaev, A.F., *Reaktsionnaya sreda i kinetika polimerizatsionnykh protsessov* (Reaction Medium and Kinetics of Polymerization Processes), St. Petersburg: Sintez, 2001.
13. Lavrov, N.A. and Krasil'nikova, Yu.O., in *Khimicheskaya tekhnologiya, svoistva i primenenie plastmass: Mezhvuzovskii sbornik nauchnykh trudov* (Chemical Technology, Properties, and Use of Plastics: Intercollegiate Coll. of Scientific Papers), St. Petersburg: Sankt-Peterb. Tekhnol. Inst., 1992, pp. 24–29.

14. Ezrielev, A.I., Brokhina, E.L., and Roskin, E.S., *Vysokomol. Soedin., Ser. A*, 1969, vol. 11, no. 8, pp. 1670–1680.
15. Tüdös, F., Kelen, T., Földes-Berezhnykh, T., and Turcsányi, B., *React. Kinet. Catal. Lett.*, 1975, vol. 2, no. 4, pp. 439–447.
16. Sautin, S.N., Lavrov, N.A., Punin, A.E., and Hartman, K., *Metody rascheta otnositel'nykh aktivnostei monomerov pri sopolimerizatsii: Uchebnoe posobie* (Methods for Calculating Relative Activities of Monomers in Copolymerization: Textbook), Leningrad: Leningr. Tekhnol. Inst. im. Lensoveta, 1986.
17. Lavrov, N.A., *Raschet cheredovanii zven'ev v sopolimerakh: Metodicheskie ukazaniya* (Calculation of Unit Alternations in Copolymers: Methodical Instructions), Leningrad: Leningr. Tekhnol. Inst. im. Lensoveta, 1988.
18. Sivtsov, E.V., Lavrov, N.A., and Kulinskii, R.A., *Konstanty sopolimerizatsii i mikrostruktura sopolimerov: Uchebnoe posobie* (Copolymerization Constants and Microstructure of Copolymers: Textbook), St. Petersburg: Sankt-Peterb. Gos. Tekhnol. Inst., 2007.