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MACROMOLECULAR COMPOUNDS AND POLYMERIC MATERIALS

Controlled Radical Polymerization of *N*-Vinylpyrrolidone and *N*-Vinylsuccinimide under the Conditions of Reversible Chain Transfer by the Addition–Fragmentation Mechanism

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Abstract—Regular trends in controlled radical polymerization of *N*-vinylpyrrolidone and *N*-vinylsuccinimide by the mechanism of reversible chain transfer in the presence of a series of dithiobenzoates and trithiocarbonates were studied. The possibility of preparing soluble poly-*N*-vinylsuccinimide in concentrated solutions using benzyl benzodithioate as reversible chain-transfer agent was demonstrated.

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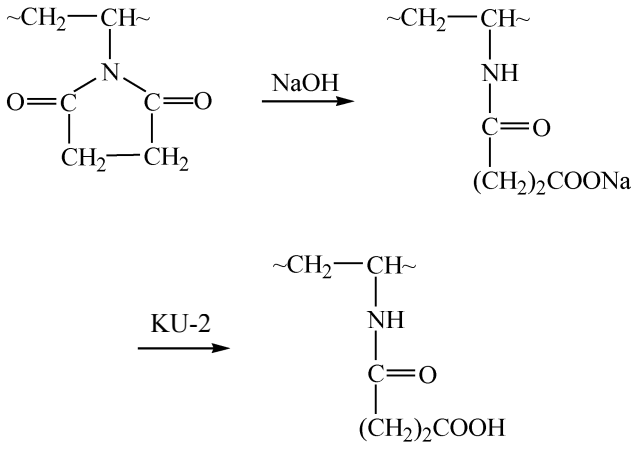
Polymers based on *N*-vinylpyrrolidone (VP) and *N*-vinylsuccinimide (VSI) find wide use as hydrophilic nontoxic materials in medicine and biology. They are permitted for use in contact with physiological media of a living body and can perform various functions as components of materials for medicobiological purpose [1–3]. Aqueous solutions of poly-*N*-vinylpyrrolidone (PVP) are used as blood substitute and as a base for infusion and peroral preparations exhibiting high sorption properties, binding toxic substances, and favoring their rapid elimination from the living body.

Scheme 1.

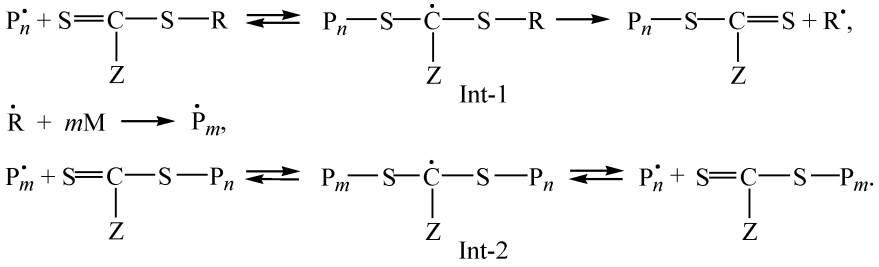


N-Vinylpyrrolidone copolymers act as auxiliary substances in the development of drug forms (thickeners for pastes and ointments, stabilizers for emulsions and suspensions, substitutes of fat bases and Vaseline, tablet shells, etc.). Complexes of poly-*N*-vinylpyrrolidone with iodine are used in antiseptic preparations. Polymers based on VP are used for modification of anionic surfactants exhibiting high bactericidal activity [4]. VP can be successfully used in the development of polymeric derivatives of antibiotics for decreasing their toxicity, improving the solubility and pharmacokinetics, and controlling the rate of supply into the living body [5]. A number of copolymers of VP with ionic comonomers exhibits intrinsic antimicrobial activity and exerts immunostimulating and immunomodulating effect.

VSI-based polymers also show promise for medicine [3, 6]. Base hydrolysis allows poly-VSI (PVSI) to be readily converted to poly(*N*-vinylamidosuccinic acid) salt, which, in turn, can be converted to the acid form with a cation exchanger (KU-2) (Scheme 1).

The thus modified homo- and copolymers of VSI are capable of ionic binding of antibiotic bases. Depending on the comonomer, they can be water-soluble or soluble only in organic media. In the first case, they are used as a polymeric matrix for prolonging the action of drugs [7],

Scheme 2.



and in the second case, for preparing elastic films [8–10], plasters, and adhesives [11]. Owing to incorporation of drugs which are gradually released from the swollen polymer, such materials, along with protection of a wound or burn from the action of the environment, fulfill anesthetic, antiseptic, and other functions [12].

Along with specific physiological activity and other particular properties, an important characteristic of polymers intended for introduction as components of drug forms into a living body is their molecular weight (MW) which, as a rule, should be in a relatively narrow range. Therefore, an urgent problem is the development of procedures for efficiently controlling the MW of polymers based on VP and VSI. In addition, in preparation of copolymers of VP and VSI with other monomers significantly differing in the relative activity, copolymers can become compositionally nonuniform at high conversions.

The most promising way to overcome these difficulties is the use of a new kind of controlled radical polymerization, polymerization with reversible chain transfer (RCT) occurring by the addition–fragmentation mechanism [13–15]. In a typical RCT polymerization process, sulfur-containing compounds of the general formula Z–C(=S)–S–R are used, where Z is a stabilizing group and R is a leaving group. The most frequently used RCT agents are dithiobenzoates (Z = Ph), trithiocarbonates (Z = S–R), dithiocarbamates (Z = NRR'), and xanthates (Z = OR) [15].

The mechanism of the RCT polymerization, along with elementary reactions of chain initiation and propagation, common for radical polymerization, includes specific reversible chain-transfer reactions whose occurrence ensures control of the molecular weight and formation of polymers with narrow molecular-weight distribution [15] (Scheme 2).

Studies dealing with VP polymerization by the RCT mechanism are few. Fragmentary data have been obtained with the most common classes of RCT agents: dithio esters [16], trithiocarbonates [17], xanthates [17–20], and dithiocarbamates [21]. However, systematic data on regular trends of RCT polymerization of VP were lacking.

In this study we examined polymerization of VP in the presence of dithiobenzoates and trithiocarbonates differing in the structure of the stabilizing and leaving groups. We also performed for the first time the VSI polymerization by the mechanism of radical RCT polymerization.

EXPERIMENTAL

VP was vacuum-distilled before use. VSI was prepared according to [22] and recrystallized three times from isopropyl alcohol (mp 48.5°C, n_D^{50} = 1.5020). Azobis(isobutyronitrile) (AIBN) was recrystallized two times from ethanol at 60 ± 2°C and vacuum-dried at 20°C (mp 104°C). Dithiobenzoates of the general formula PhC(=S)–S–R {benzyl benzodithioate (BB, R = $–CH_2Ph$), *tert*-butyl benzodithioate [TB, R = $–C(CH_3)_3$], 1-(2-carboxyethyl)-1-cyanoethyl benzodithioate [CB, R = $–C(CH_3)(CN)CH_2CH_2COOH$]} and trithiocarbonates of the general formula R–S–C(=S)–S–R {dibenzyl carbonotrithioate (BC, R = $–CH_2Ph$), di-*tert*-butyl carbonotrithioate [TC, R = $–C(CH_3)_3$]} were prepared by published procedures [23].

Samples for VP polymerization were prepared by dissolving calculated amounts of the RCT agent and initiator (AIBN) in the monomer. The solutions were placed in ampoules, which after degassing by repeated freezing–pumping–thawing were sealed off. Polymerization was performed at 60 and 80°C. The polymers were isolated from benzene by freeze drying.

Samples for VSI polymerization were prepared by dissolving calculated amounts of BB and AIBN in an equimolar mixture of the monomer and DMSO. The

subsequent procedures were similar to those with VP.

The polymerization kinetics was monitored calorimetrically with a DAK-1-1a differential automatic microcalorimeter in the mode of direct recording of the heat release rate under isothermal conditions at 60 and 80°C. From the calorimetric data, we calculated the kinetic parameters of the polymerization using programs developed at the Chair of Macromolecular Compounds of the Lomonosov Moscow State University.

The MW characteristics of polymer samples were determined by GPC in THF at 35°C with a Waters liquid chromatograph equipped with refractometric and UV detectors, using columns packed with Ultrastyrogel with a pore size of 10^3 and 10^5 Å and a linear column. The device was calibrated using polystyrene references.

The ^{1}H NMR analysis was performed at the Max-Planck Institute for Polymer Research (Mainz, Germany) at room temperature in a CD_2Cl_2 solution with a Bruker DRX 300 spectrometer operating at 300 MHz. The scale was calibrated (ppm) against the residual proton signal of the solvent.

The ESR spectra were recorded with an RE-1307 spectrometer. Samples were thermostated by pumping air heated to 90°C through a Teflon tube passing through the cavity. The temperature was monitored at the point of sample location. The amount of radicals was determined by double integration using EPR program (version 2.3). As a reference we used a calibrated sample of sugar charcoal containing 6×10^{15} spins.

Polymerization of *N*-vinylpyrrolidone by the reversible chain-transfer mechanism. Introduction of RCT agents into the reaction mixture of VP polymerization leads to a noticeable decrease in the polymerization rate, characteristic of RCT polymerization. The rate of this decrease is determined not only by the concentration of the RCT agent but also by the nature of the stabilizing and leaving groups.

Figure 1a shows the kinetic curves of VP polymerization with BB as example. These curves are typical for all the examined dithiobenzoates. Irrespective of the structure of the leaving group in the dithiobenzoate (BB, TB, CB), the polymerization is virtually fully inhibited at [RCT] > 3×10^{-3} M. At lower concentrations of the RCT agent, the polymerization rate appears to be appreciably lower than the rate of the classical radical polymerization of VP. Even at the ratio $[RCT]_0/[AIBN]_0 = 0.3$, the rate of the RCT polymerization decreases by a factor of approximately 2

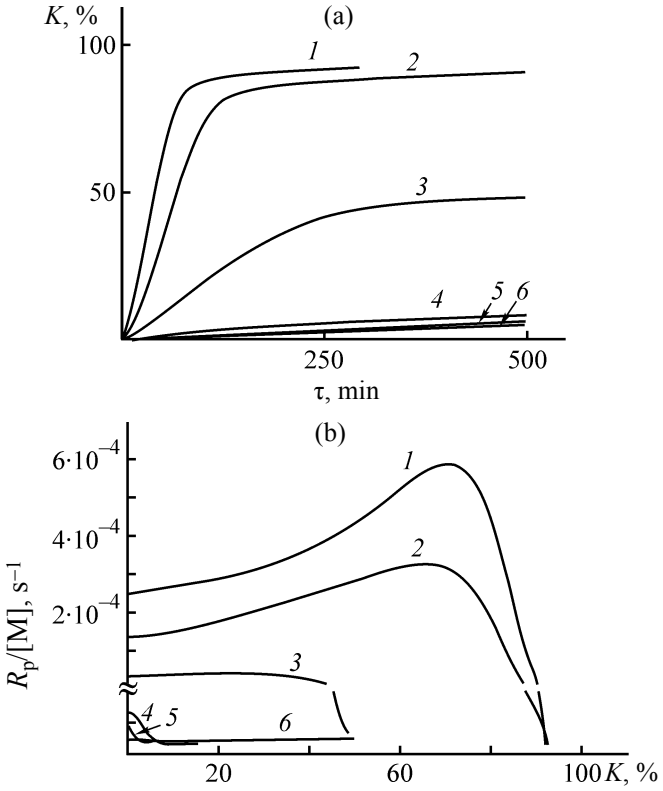


Fig. 1. (a) Conversion K as a function of time τ and (b) reduced rate $R_p/[M]$ as a function of conversion K in polymerization of VP in the bulk at 80°C in the presence of AIBN (10^{-3} M) and various concentrations of BB. c_{BB}, M: (*1*) 0, (*2*) 3×10^{-4}, (*3*) 10^{-3}, (*4*) 3×10^{-3}, (*5*) 10^{-2}, and (*6*) 3×10^{-2}.

compared to the classical radical polymerization.

Classical polymerization of VP occurs with pronounced autoacceleration of the reaction, which is manifested already at low conversions (Fig. 1b). However, on adding an RCT agent to the polymerization system the reduced rate (i.e., the rate divided by the running concentration of the monomer) at both low and high conversions decreases, and at $[RCT]_0 > 10^{-3}$ M the autoacceleration fully vanishes.

With trithiocarbonates, an increase in the concentration of the RCT agent also leads to a decrease in the reaction rate, but the polymerization deceleration is less pronounced (Figs. 2a, 2b). It should be noted that the extent to which the RCT agent affects the reaction kinetics in these systems depends on the nature of the leaving group. For example, with BC the polymerization is inhibited at $[BC]_0 \sim 3 \times 10^{-1}$ M, and with TC, at $[TC]_0 \sim 10^{-1}$ M. The gel effect in these systems fully vanishes at higher concentrations of RCT agents compared to dithiobenzoates ([RCT] > 10^{-2} M).

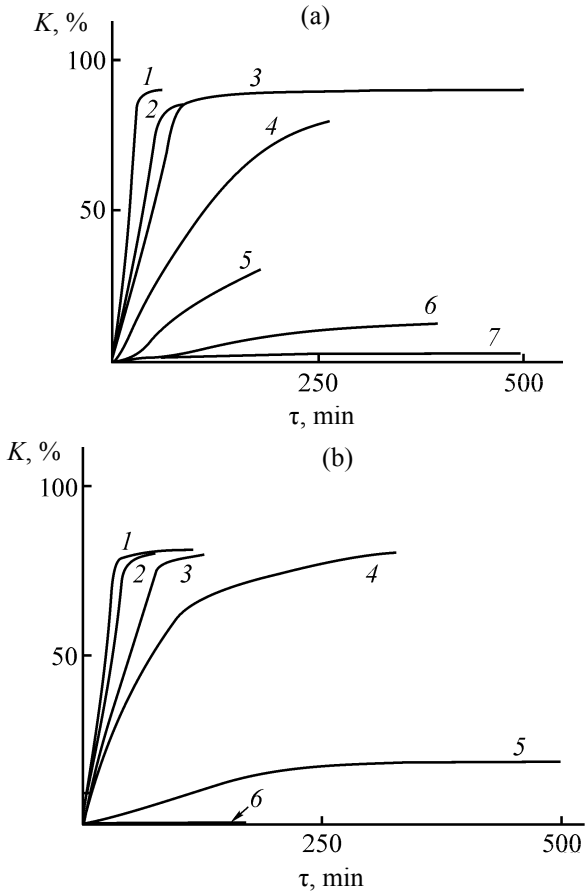


Fig. 2. Conversion K as a function of time τ in polymerization of VP in the bulk at 80°C in the presence of 10^{-3} M AIBN and various concentrations c of (a) BC and (b) TC. c, M: (a) (*1*) 0, (*2*) 10^{-3}, (*3*) 3×10^{-3}, (*4*) 10^{-2}, (*5*) 3×10^{-2}, (*6*) 10^{-1}, and (*7*) 3×10^{-1}; (b): (*1*) 3×10^{-4}, (*2*) 10^{-3}, (*3*) 3×10^{-3}, (*4*) 10^{-2}, (*5*) 3×10^{-2}, and (*6*) 10^{-1}.

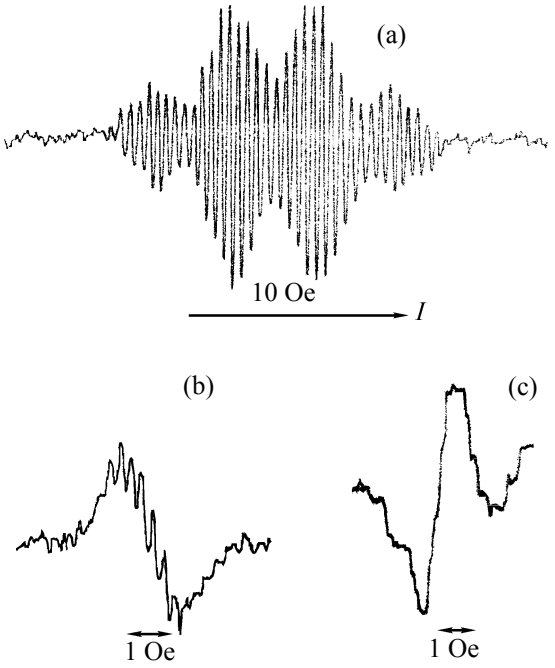


Fig. 3. ESR spectra recorded in the course of polymerization of N-vinylpyrrolidone in the bulk in the presence of (a) TB ([AIBN] = 0.5, [TB] = 0.1 M), (b) TC ([AIBN] = 0.5, [TC] = 1 M), and (c) BC ([AIBN] = 0.9, [BC] = 2.5 M). (*I*) Field intensity.

The kinetic effect of RCT agents is directly or indirectly caused by formation of radical intermediates Int-1 [reaction (I)] and Int-2 [reaction (II)]. The polymerization inhibition may be due to fairly high stability of the intermediates, or, in other words, to their slow fragmentation [reactions (I) and (II)]. The same reasoning can be applied to rationalizing a decrease in the overall polymerization rate.

To check this assumption, we examined formation of radical intermediates in the systems VP–TB–AIBN and VP–TC–AIBN. These RCT agents contain the same leaving *tert*-butyl group and differ in the chemical structure of the stabilizing group. At commonly used concentrations of the RCT agent and AIBN, we failed to detect ESR signals of the intermediates. Therefore, we studied by ESR model systems in which the concentrations of the RCT agent and initiator were appreciably increased.

When VP is heated in the presence of TB, a multiplet ESR spectrum (Fig. 3a) appears already within 15–20 s after the start of heating. Its intensity grows in the course of 10 min, after which it slowly decreases. The spectrum consists of four major components of the hyperfine structure with the intensity ratio of 1 : 3 : 3 : 1, each of which, in turn, is split into no less than 14 components. A similar spectrum was observed previously in polymerization of butyl acrylate, vinyl acetate, and styrene in the presence of TB [24]. It was shown that this spectrum corresponds to intermediate Int-1 formed by the reaction of the propagating radical with TB. In the course of the reaction, the Int-1 concentration gradually decreases and reaches a constant and relatively high value in ~30 min (Fig. 4a). Thus, inhibition of the VP polymerization in the presence of TB is apparently associated with the formation of a stable radical intermediate.

With BB or CB, differing in the structure of the leaving group, taken instead of TB, we failed to observe intermediate Int-1. Presumably, these intermediates are more active and rapidly undergo fragmentation. Thus, the structure of the leaving group exerts a decisive effect on

the stability of intermediate Int-1.

A strange, at first glance, fact, stronger hyperfine interaction of the unpaired electron of intermediate Int-1 with protons of the more remote *tert*-butyl group (compared to closer protons of the polymeric substituent), can be attributed to conformational folding of intermediate Int-1, because direct interaction through three or four single bonds is virtually impossible. A calculation, using the Chem 3D Ultra 7.0 program, of the most stable conformation (i.e., corresponding to the energy minimum) of this intermediate confirms this assumption. Apparently, because of the conformational folding of molecules of the intermediate, orbitals of *tert*-butyl protons can overlap with the *p* orbital of the unpaired electron and participate in the formation of the hyperfine structure of the ESR spectrum of this intermediate. In this case, the formally closer γ-proton of the polymeric substituent appears to be more remote sterically. It lies closer to the nodal plane of the *p* orbital and does not make a noticeable contribution to the hyperfine structure, which is typical of γ-protons of alicyclic substituents.

In the course of heating of VP in the presence of TC and AIBN, taken in higher concentrations compared to TB, we recorded a multiplet ESR spectrum shown in Fig. 3b. In this spectrum there are 11 resolved components of the hyperfine structure. Apparently, some of components in the spectrum wings are lost because of incomplete resolution and insufficient spectrum intensity. The ESR spectrum also arises immediately after switching on the sample heating, reaches the maximal concentration of 2.4×10^{-5} M within several minutes, and then slowly decreases to the level of noise of the ESR spectrometer (Fig. 4b).

The hyperfine structure of this spectrum is not associated with α-protons of propagating radicals added to TC in the course of the process. It arises only from

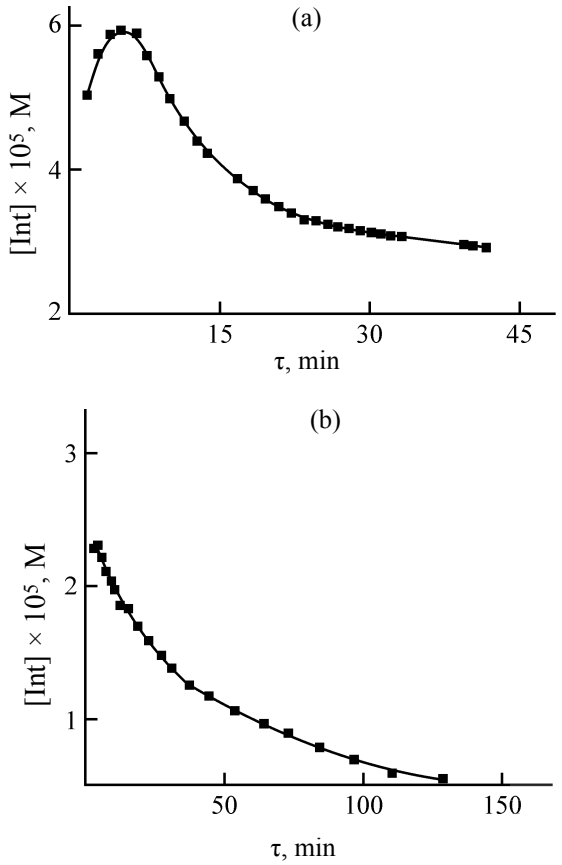
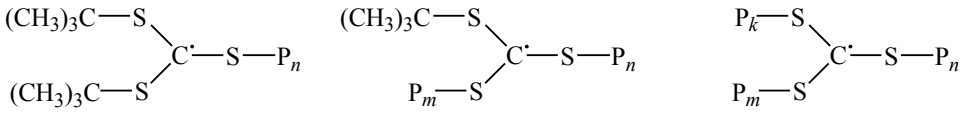


Fig. 4. Concentration of intermediates Int as a function of time τ in polymerization of N-vinylpyrrolidone in the bulk in the presence of (a) TB ([AIBN] = 0.5, [TB] = 0.1 M) and (b) TC ([AIBN] = 0.5, [TC] = 1 M).

interaction of an unpaired electron with δ-protons of the leaving *tert*-butyl groups. The possibility of this long-range interaction was also confirmed by simulating the conformation corresponding to the energy minimum of the molecule.

In the presence of TC, formation of three kinds of radical intermediates is possible:



The spectrum of intermediate Int-1 should contain 19 lines from 18 equivalent protons of two *tert*-butyl groups, and the spectrum of intermediate Int-2, 10 lines from 9 protons of one *tert*-butyl group. The spectrum of intermediate Int-3 should be singlet. Because the spectrum we obtained consists of more than 10 lines, it can belong only to intermediate Int-1. Actually some of the 19 lines are not observed, because at binomial distribution the intensities of the extreme lines are lower by several orders of magnitude than those of the central lines. We never observed ESR spectra corresponding to intermediates Int-2 and Int-3. This apparently means

that, in contrast to relatively stable intermediate Int-1, intermediates Int-2 and Int-3 are less stable, and their steady-state concentration at any concentrations of components of the reaction system is below the sensitivity threshold of the spectrometer.

With the *tert*-butyl leaving group replaced by the benzyl group, we detected radical intermediates at still higher concentrations of AIBN and RCT agent (Fig. 3c); their concentration appeared to be lower than in the case of TC, and we failed to reliably identify the intermediate in this case.

Thus, the presence of the *tert*-butyl leaving group is a stabilizing factor for intermediate Int-1, and it creates prerequisites for an appreciable increase in its concentration irrespective of the structure of the stabilizing group. Intermediates with the other leaving groups are more reactive, their steady-state concentration in polymerization is low, and they often cannot be detected by ESR.

The observed formation of radical intermediates and the polymerization deceleration caused by them indicate that the polymerization occurs by the pseudoliving RCT mechanism. However, the more reliable evidence of the pseudoliving character of the process is linear increase in MW of the forming polymers with conversion.

Because the polymerization deceleration in the VP–AIBN–BC system is the least pronounced, i.e., at fairly high concentrations of the RCT agent (10^{-1} M) it is possible to attain ~40–50% conversion of the monomer, we chose this system for studying MW characteristics of the forming PVP. Preliminary studies (by viscometry and light scattering) showed that, in contrast to commercial PVP, for the polymer prepared by the RCT mechanism macromolecules are noticeably aggregated in aqueous-salt and alcoholic solutions, which may be due to the presence in the chain of hydrophobic terminal benzyl and central trithiocarbonate groups [25]. Thus, M_n was determined by NMR in CD_2Cl_2 from the content of terminal groups. The results are given in the table.

MW characteristics of PVP prepared by polymerization of VP in the bulk in the presence of BC and AIBN ([BC] = 10^{-1}, [AIBN] = 10^{-2} M)

T, °C	Time, h	Conversion, %	M_n	M_n(theor)
60	3.2	4.8	–	790
	4	7.2	–	1040
	5	8.4	1400	1200
	6.2	30.3	3600	3500
	20.4	45.4	4000	5000
80	19.5	0.8	5200	2300
	38.4	2	8200	4300
	55	3	8600	6000
	62	6	10800	6800

It can be seen that M_n increases with conversion. The experimental values are in reasonable agreement with the theoretical values calculated by the equation

$$M_n = M_{RCT} + \frac{q[M]_0}{[RCT]_0} M_M,$$

where M_{RCT} and M_M are the molecular weights of the RCT agent and monomer, and $[RCT]_0$ and $[M]_0$, their molar concentrations, respectively; q is the monomer conversion.

Hence, it can be assumed that BC is an effective RCT agent for VP polymerization.

Polymerization of *N*-vinylsuccinimide by the mechanism of reversible chain transfer. The double bond in VSI, as in VP, is electron-rich, as indicated by negative values of the parameter e (–0.34 and –1.14, respectively). Appearance of the second acceptor carbonyl group in the VSI molecule leads to a considerable decrease in the negative value of e. Therefore, the VSI radicals destabilized by such shift of the electron density are more reactive than VP radicals (in copolymerization of VSI with VP, VSI is more active: $r_{VSI} = 1.54$, $r_{VP} = 0.30$ [3]), and it can be assumed that VSI radicals will also participate in chain transfer to RCT agents effective in polymerization of VP. Performing controlled polymerization of VSI by the RCT mechanism is an important practical problem. In classical radical polymerization in the bulk, the actively occurring chain transfer to methylene protons of the succinimide ring leads to the formation of the polymer insoluble in organic solvents and only swelling in chlorinated aliphatic hydrocarbons, pyridine, and acetic, trichloroacetic, and formic acids. Soluble PVSI can be prepared only in dilute (≤10%) solutions in such solvents as dichloroethane, acetic acid, acetic anhydride, benzene, DMSO, and pyridine.

Based on the data we obtained for VP polymerization and on structural similarity of the VP and VSI monomers, we chose as an RCT agent BB which forms unstable radical intermediates with propagating PVP radicals.

As expected, introduction of BB leads to drastic deceleration of the VSI polymerization at 60°C, which is clearly seen from the curves of conversion vs. reaction

time (Fig. 5a). Under the chosen reaction conditions, with an increase in the BB concentration not only the polymerization rate decreases, but also the gel effect is suppressed. It follows from the curves of the reduced rate vs. conversion (Fig. 5b) that, without BB, sharp autoacceleration is observed already in early steps of the process, so that virtually 100% conversion of the monomer is rapidly attained. The resulting PVSI is cross-linked; it neither dissolves nor noticeably swells in any solvents. Addition of even a small amount of BB (10^{-3} M) decreases the polymerization rate by an order of magnitude (Fig. 5b, curve 2) and shifts the onset and maximum of the autoacceleration toward higher conversions. The effect is enhanced with a further increase in the concentration, and at [BB] = 10^{-2} M the process is fully inhibited (Fig. 5b, curve *4*).

An increase in the temperature (to 80°C) makes considerably shorter the time in which high conversions are attained, and with an excess of BB relative to AIBN one can expect preservation of the observed kinetic relationships and formation of the non-cross-linked polymer. Under these conditions, at various synthesis times, we prepared oligomeric soluble samples of PVSI. Their MW characteristics were determined by GPC (Fig. 6a). It can be seen that the GPC curves of all the polymers are unimodal, and with an increase in the polymerization time they are shifted toward higher molecular weights. The number-average MW of the polymers linearly increases with the polymerization time, and the polymers are characterized by relatively low polydispersity coefficients M_w/M_n ~1.3, which unambiguously proves the occurrence of the polymerization by the pseudoliving mechanism (Fig. 6b).

CONCLUSIONS

(1) Conditions were found for controlled synthesis of poly-*N*-vinylpyrrolidone with the molecular weight not exceeding 10 000.

(2) Relationship was revealed between the stability of radical intermediates formed in polymerization of *N*-vinylpyrrolidone and kinetic features of the process.

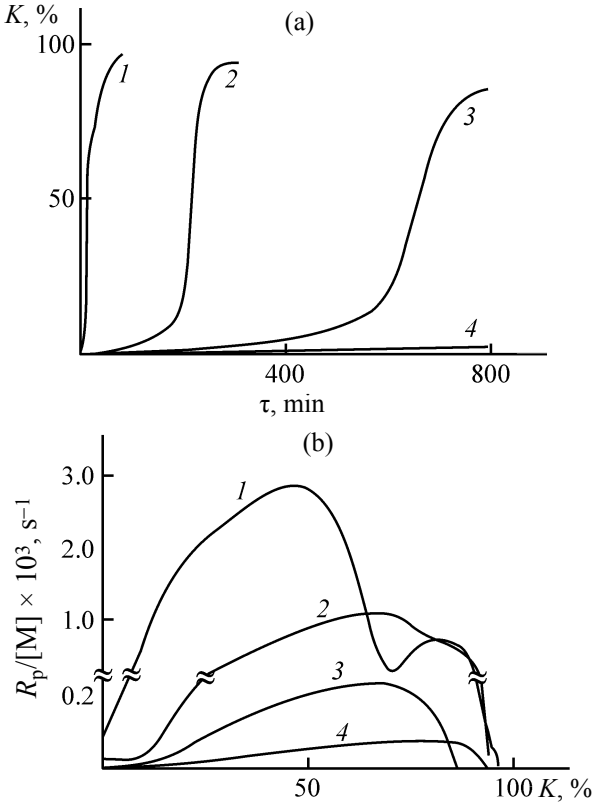


Fig. 5. (a) Conversion K as a function of time τ and (b) reduced rate $R_p/[M]$ as a function of conversion K in polymerization of VSI in DMSO (VSI : DMSO = 1 : 1) at 60°C in the presence of 10^{-2} M AIBN and various concentrations of BB. c_{BB}, M: (*1*) 0, (*2*) 10^{-3}, (*3*) 3×10^{-3}, and (*4*) 10^{-2}.

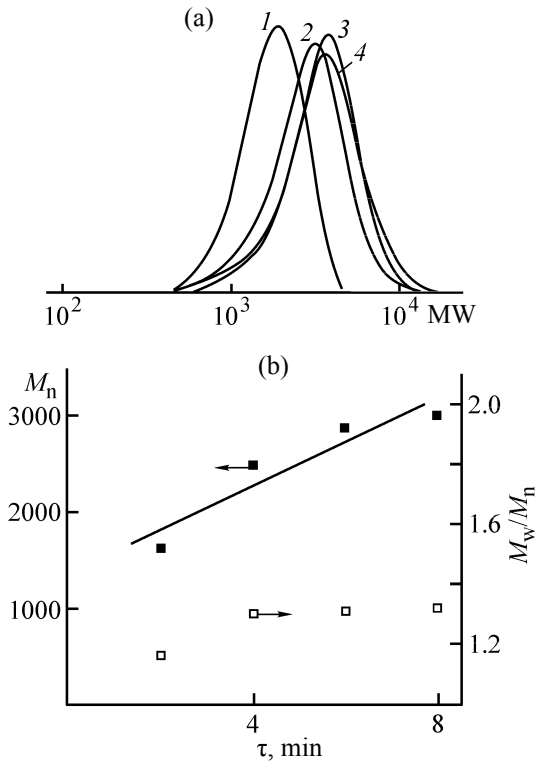


Fig. 6. MW characteristics of poly-*N*-vinylsuccinimide prepared by polymerization of VSI in DMSO (VSI : DMSO = 1 : 1) at 80°C in the presence of 10^{-2} M AIBN and 3×10^{-3} M BB: (a) GPC patterns of polymers isolated after polymerization for (*1*) 2, (*2*) 4, (*3*) 6, and (*4*) 8 h; (b) number-average molecular weight M_n and polydispersity coefficient M_w/M_n of polymers as a function of reaction time τ.

(3) Soluble poly-*N*-vinylsuccinimide with narrow molecular-weight distribution and molecular weight of 1600–3000 was prepared by polymerization by the reversible chain-transfer mechanism in concentrated dimethyl sulfoxide solutions.

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REFERENCES

1. Sidel'kovskaya, F.P., *Khimiya N-vinilpirrolidona i ego polimerov* (Chemistry of N-Vinylpyrrolidone and Its Polymers), Moscow: Nauka, 1970.
2. Kirsh, Yu.E., *Poli-N-vinilpirrolidon i drugie poli-N-vinilamidy: Sintez i fiziko-khimicheskie svoistva* (Poly-*N*-vinylpyrrolidone and Other Poly-*N*-vinylamides: Synthesis and Physicochemical Properties), Moscow: Nauka, 1988.
3. Lavrov, N.A., Shal'nova, L.I., and Nikolaev, A.F., *Zh. Prikl. Khim*., 1997, vol. 70, no. 8, pp. 1356–1363.
4. Afinogenov, G.E. and Panarin, E.F., *Antimikrobnye polimery* (Antimicrobial Polymers), St. Petersburg: Gippokrat, 1993.
5. Vasil'ev, A.E. and Davydov, A.B., *Zh. Vses. Khim. O–va. im. D.I. Mendeleeva*, 1985, vol. 30, no. 4, pp. 395–402.
6. Shal'nova, L.I. and Nikolaev, A.F., *Plast. Massy*, 2000, no. 3, pp. 42–45.
7. RF Patent 2071323.
8. Shal'nova, L.I., Chudnova, V.M., and Trofimova, E.A., *Plast. Massy*, 1989, no. 11, pp. 29–34.
9. Chudnova, V.M., Shal'nova, L.I., and Trofimova, E.A., in *Khimicheskaya tekhnologiya, svoistva i primenenie plastmass: Mezhvuzovskii sbornik nauchnykh trudov* (Chemical Technology, Properties, and Applications of Plastics: Intercollegiate Coll. of Scientific Works, Leningrad: Leningr. Tekhnol. Inst. im. Lensoveta, 1986, pp. 120–126.
10. Shal'nova, L.I., Chudnova, V.M., Trofimova, E.A., and Popova, A.V., in *Khimicheskaya tekhnologiya, svoistva i primenenie plastmass: Mezhvuzovskii sbornik nauchnykh trudov* (Chemical Technology, Properties, and Applications of Plastics: Intercollegiate Coll. of Scientific Works, Leningrad: Leningr. Tekhnol. Inst. im. Lensoveta, 1987, pp. 83–87.
11. Sivtsov, E.V. and Lavrov, N.A., *Klei. Germet. Tekhnol*., 2007, no. 3, pp. 13–19.
12. Shal'nova, L.I., Trofimova, E.A., Chudnova, V.M., and Andreeva, E.D., in *Khimicheskaya tekhnologiya, svoistva i primenenie plastmass: Mezhvuzovskii sbornik nauchnykh trudov* (Chemical Technology, Properties, and Applications of Plastics: Intercollegiate Coll. of Scientific Works, Leningrad: Leningr. Tekhnol. Inst. im. Lensoveta, 1988, pp. 89–98.
13. Chiefari, J., Chong, Y.K., Ercole, F., et al., *Macromolecules*, 1998, vol. 31, no. 16, pp. 5559–5562.
14. Barner-Kowollik, C., Quinn, J.F., Morsley, D.R., and Davis, T.P., *J. Polym. Sci*., 2001, vol. 39, p. 1353.
15. *Handbook of RAFT Polymerization, Barner-Kowollik*, C., Ed., Weinheim: Wiley, 2008.
16. Wan, D., Satoh, K., Kamigaito, M., and Okamoto, Y., *Macromolecules*, 2005, vol. 38, pp. 10397–10405.
17. Postma, A., Davis, T.P., Li, G., et al., *Macromolecules*, 2006, vol. 39, pp. 5307–5318.
18. Nguyen, T.L.U., Eagles, K., Davis, T.P., et al., J. *Polym. Sci., Polym. Chem*., 2006, vol. 44, pp. 4372–4383.
19. Moad, G., Rizzardo, E., and Thang, S.H., *Aust. J. Chem*., 2005, vol. 58, no. 6, pp. 379–410.
20. Devasia, R., Bindu, R.L., Mougin, N., and Gnanou, Y., *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.),* 2005, vol. 46, pp. 195–196.
21. Devasia, R., Bindu, R.L., Borsali, R., et al., *Macromol. Symp*., 2005, vol. 229, pp. 8–17.
22. *Poluchenie polimerov i sopolimerov N-vinilimidov yantarnoi i ftalevoi kislot: Metodicheskie ukazaniya* (Preparation of Polymers and Copolymers of *N*-Vinylamides of Succinic and Phthalic Acids: Methodical Instructions), Chudnova, V.M., Lavrov, N.A., and Shal'nova, L.I., Compilers, Leningrad: Leningr. Tekhnol. Inst. im. Lensoveta, 1989.
23. Moad, G., Rizzardo, E., and Thang, S.H., *Polymer,* 2008, vol. 49, pp. 1079–1131.
24. Golubev, V.B., Chernikova, E.V., Leonova, E.A., and Morozov, A.V., *Vysokomol. Soedin., Ser. A,* 2005, vol. 47, no. 7, pp. 1115–1124.
25. Terpugova, P., Chernikova, E., Golubev, V., et al., Abstracts of Papers, *European Polymer Congr*., Moscow, 2005, pp. 14–51.