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Synthesis and Properties of Fullerene-Containing *N*-Vinylpyrrolidone Copolymers

S. V. Kurmaz and A. N. Pyryaev

Institute of Chemical Physics Problems, Russian Academy of Sciences,
pr. Akademika Semenova 1, Chernogolovka, Moscow oblast, 142432 Russia
e-mail: skurmaz@icp.ac.ru

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Abstract—Branched copolymers containing covalently bonded fullerene C_{60} were synthesized by cross-linking radical copolymerization of *N*-vinylpyrrolidone with triethylene glycol dimethacrylate in toluene saturated with fullerene. Their composition was studied by elemental analysis and IR and electronic absorption spectroscopy. The concentration of double bonds, characteristic viscosity, and glass-transition temperature of the fullerene-containing copolymers were determined by ozonoliysis, viscosimetry, and differential scanning calorimetry. The parameters and thermal stability of the fullerene-containing copolymers were compared with those of their non-functionalized analogs.

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Poly(*N*-vinylpyrrolidone) (PVP) is widely used as carrier due to its ability to bind to various chemical compounds via different types of interactions [1]. Fullerene C_{60} is quite popular among such low-molecular-weight compounds; binding of C_{60} to water-soluble polymeric chains of PVP via covalent and non-covalent interactions gives rise to fullerene-containing polymers. Taking into account biological activity of fullerene (specifically its antiviral effect [2]), fullerene-containing polymers attract interest from the viewpoint of their medical applications.

Although non-covalent inclusion of fullerene into a polymer is a difficult problem because of its poor solubility in aromatic solvents and strong aggregation tendency in solvent–precipitant systems, PVP–C_{60} composites have been studied in most detail [3−5]. Poly(*N*-vinylpyrrolidone) containing covalently bound fullerene is obtained by conventional radical polymerization [6], as well as by low-temperature radiation-induced living radical polymerization [7]. As a rule, reaction of growing chains at fullerene double bonds gives products with different numbers of addition sites, and the resulting polymeric products are characterized by different concentrations of fullerene [8].

We previously found [9] that cross-linking radical copolymerization of *N*-vinylpyrrolidone with triethylene glycol dimethacrylate in toluene containing fullerene involves covalent binding of C_{60} to polymer chains. Branched architecture of fullerene-containing macromolecules, as well as of non-functionalized copolymers, arises from participation in the copolymerization process of pendant C=C bonds in side-chain dimethacrylate units. The architecture of fullerene-containing copolymers may be complicated as a result of chain termination at several centers in the fullerene core. Due to their specific topology, namely a large number of pendant chains in the peripheral layer, branched polymers are characterized by high solubility in various organic media and thermodynamic compatibility. The presence of excess free volume renders such polymers capable of sorbing low-molecular-weight compounds with formation of host–guest type complexes [10]. Covalent addition of fullerene could give rise to new hybrid materials possessing a combination of important properties intrinsic to closed molecular form of carbon and unusual properties of branched copolymers.

Fullerene may affect the chemical composition of polymerization products, structures of macromolecules, and parameters depending on the composition and structure of polymer chains. Inclusion of C_{60} in the polymer structure could radically alter optical, dielectric, and other properties of the latter [11].

Depending on the mode of binding to polymer matrix, fullerene differently affects thermal degradation of polymers. If fullerene is bound to a polymer via van der Waals forces, it acts as inhibitor which readily takes up radical species [12]. Fullerene as stabilizer is superior to such known antioxidants as amines, phenols, and sulfur- and phosphorus-containing compounds in thermooxidative degradation of poly (methyl methacrylate) and methyl methacrylate copolymers [13]. By contrast, covalent bonding of fullerene to polymer molecules could accelerate degradation processes due to formation of weak β-bonds [12]. For example, the formation of covalent bonds between C_{60} and polystyrene reduces the thermal stability of the latter by more than 100°C [12].

The goal of the present work was to synthesize fullerene-containing *N*-vinylpyrrolidone copolymers with triethylene glycol dimethacrylate and their non-functionalized analogs, determine their physico-chemical parameters, and estimate thermal stability of the obtained polymeric products.

Structural features of *N*-vinylpyrrolidone–triethylene glycol dimethacrylate copolymers containing covalently bound fullerene. *N*-Vinylpyrrolidone (VP) is an electron-rich monomer possessing a *π*–*p*–*π*-conjugation system (polar factor $e = -1.14$ [14]). It readily undergoes copolymerization with monomers containing electron-withdrawing substituents, in particular with methyl methacrylate (MMA, $e = +0.40$) [15]. Microstructure of copolymers is determined by the composition of the initial reaction mixture and considerably different copolymerization constants ($r_{\mathrm{VP}} = 0.16$, $r_{\mathrm{MMA}} = 1.30$) [1]. The reactivity of the methacryloyl fragment in methyl methacrylate is almost the same as in triethylene glycol dimethacrylate (TGM) [16], so that replacement of MMA by TGM should not affect the relative reactivity of the co-monomers. Therefore, copolymer enriched in TGM units should be formed in the initial copolymerization step. However, accumulation of less reactive VP in the mixture with rise in the conversion should lead to increase of its concentration in the copolymer. As a result, the final copolymer is compositionally non-uniform. This follows from the data obtained by studying the kinetics of copolymerization of VP with TGM and analyzing the composition of the copolymers [17].

Copolymers formed as a [VP]–[TGM] ratio of more than 100 : 5 were network products. Copolymers obtained at a [VP]–[TGM] ratio of less than (or equal to) 100 : 5 were soluble in chloroform and acetone. In order to synthesize soluble polymeric products with a larger concentration of TGM, an equimolar amount of decane-1-thiol (DT) was added to restrict growth of polymer chains via chain transfer reaction [17]. In this case, shorter polymer molecules were formed, and the probability for cross-linking was reduced.

The chain-transfer coefficient C_s is determined by the structure of radical captured by decane-1-thiol. This follows from the C_s values calculated from the molecular weights of linear poly(methyl methacrylate) and PVP obtained by radical polymerization under the same conditions as for the VP–TGM copolymer. For this purpose, the dependences $1/R = f([\mathrm{DT}]/[\mathrm{M}])$ were plotted, where R is the degree of polymerization, and [DT] and [M] are the concentrations (mol/l) of the chain transfer agent and monomer, respectively; the slope of these dependences was equal to C_s. Chain transfer from methacrylate and vinylpyrrolidone radicals to decane-1-thiol was characterized by C_s values of ~0.4 and ~0.03, respectively. The former value is consistent with published data [18].

Copolymerization of VP with TGM in the presence of fullerene was accompanied by considerable variation of the kinetics of the process due to inhibitory effect of C_{60} [9]. The kinetic curves (conversion versus time) displayed an induction period whose duration depended on the ratio $[C_{60}]:[\text{initiator}]$ and concentration of TGM. The induction period shortened as the concentration of TGM rose, which indicated that the efficiency of fullerene as inhibitor of radical copolymerization decreased. As a result, the length of polymer chains and the concentration of pendant C=C bonds increased, thus enhancing the probability of cross-linking. In fact, fullerene-containing copolymers obtained at VP-to-TGM molar ratios of more than 100 : 5 were cross-linked. In order to obtain soluble fullerene-containing copolymers, decane-1-thiol was added. Thus copolymerization of VP with TGM at a ratio of ≤ 100 : 5 is controlled by fullerene which restricts the length of polymer chains owing to its inhibitory effect. Copolymerization at a VP–TGM ratio of ≥100 : 5 is controlled by fullerene and decane-1-thiol. Presumably, the resulting fullerene-containing polymers are even more compositionally non-uniform than their non-functionalized analogs.

From the reaction mixtures containing VP, TGM, and DT at ratios of 100 : 5 : 0, 100 : 5 : 5, 100 : 12 : 12, and 100 : 20 : 20 in toluene we obtained copolymers **Ia**–**Id**, respectively, while copolymerization of analogous mixtures with the same reactant ratios in toluene saturated with C_{60} gave fullerene-containing

Table 1. Elemental analyses of copolymers **I** and **II**

Copolymer no.	Molar ratio [VP]:[TGM]:[DT]	Fraction no.	Found, %		Calculated, %	
			N	S	N	S
Ib	100:5:5	1	10.2	0.5	10.4	1.2
		2	5.5	–	10.4	1.2
Ic	100:12:12	1	8.8	1.0	8.4	2.3
		2	4.6	–	8.4	2.3
Id	100:20:20	1	7.3	1.2	6.7	3.2
		2	4.2	–	6.7	3.2
IIa[a]	100:5:0	–	9.5	0	11.2	0
IIb	100:5:5	1	10.4	0.7	10.4	1.2
		2	5.6	–	10.4	1.2
IIc	100:12:12	1	8.9	1.0	8.4	2.3
		2	4.4	–	8.4	2.3
IId	100:20:20	1	7.3	1.4	6.7	3.2
		2	4.3	–	6.7	3.2

[a] Non-fractionated copolymer.

copolymers **IIa–IId**, respectively. When the reaction both in the presence and in the absence of fullerene was complete (reactant molar ratio 100:5:0), the mixture divided into two phases. After chain-transfer copolymerization in the presence and in the absence of fullerene, the reaction mixtures remained homogeneous, regardless of the reactant ratio. Fractions *1* of copolymers **I** and **II** (**I**-*1* and **II**-*1*) were precipitated from those mixtures and were isolated as amorphous powders. Polymers **II** were brown due to the presence of fullerene. The yield of copolymers **I** almost did not depend on the reactant ratio and was no less than 80%. The yield in the presence of fullerene was lower, ~75%. After removal of the precipitant (hexane), fractions *2* of copolymers **I** and **II** (**I**-*2* and **II**-*2*) were isolated as colorless or colored viscous liquids.

Composition of copolymers I and II. The nitrogen and sulfur content of copolymers **I** and **II** obtained at high conversions (Table 1) depended on the composition of the reaction mixtures. The nitrogen content and hence the relative number of VP units in fractions *1* decreases as the concentration of TGM increases. Copolymers **II**-*1* contained approximately the same number of VP units as in copolymers **I**. Quite satisfactory agreement is observed between the experimental and theoretical nitrogen contents of **I**-*1*. It should be noted that the nitrogen content of fractions *2* is approximately twice as low as that in the corresponding fraction *1* copolymers. This means that fractions *2* contain less VP units, presumably due to different reactivities of the comonomers and chain transfer coefficients C_s. The same is typical of copolymers **II**.

The sulfur content of the examined copolymers is lower than the theoretical value. However, these data are relative and semiquantitative; nevertheless, they indicate that decane-1-thiol residues ($C_{10}H_{21}S$) are included in polymer chains. The absolute consumption of DT followed from the analytical data for **Ic**-*1*, according to which the sulfur content (1.55%) was lower than the theoretical value by a factor of ~1.5. This means that only a part of DT (~70%) is involved in chain transfer.

Additional information on the composition of copolymers **I** and **II** was obtained by IR spectroscopy. The dependences $D = f([\text{copolymer}])$ were linear within the examined concentration range (Fig. 1), indicating that the Bouguer–Lambert–Beer law is fulfilled and that various intermolecular interactions do not affect the molar absorption coefficient of the lactam carbonyl band. The slope of the dependence $D = f([\textbf{I}\text{-}1])$ decreases as the number of TGM units increases (correspondingly, the number of VP units decreases) (Fig. 1a; curves *2*–*4*). The same applies to copolymers **II**-*1* and is consistent with the analytical data. The $D = f([\text{copolymer}])$ dependences for **Ib** and **IIb** completely coincided with each other (Fig. 1a; *2*, *2*′).

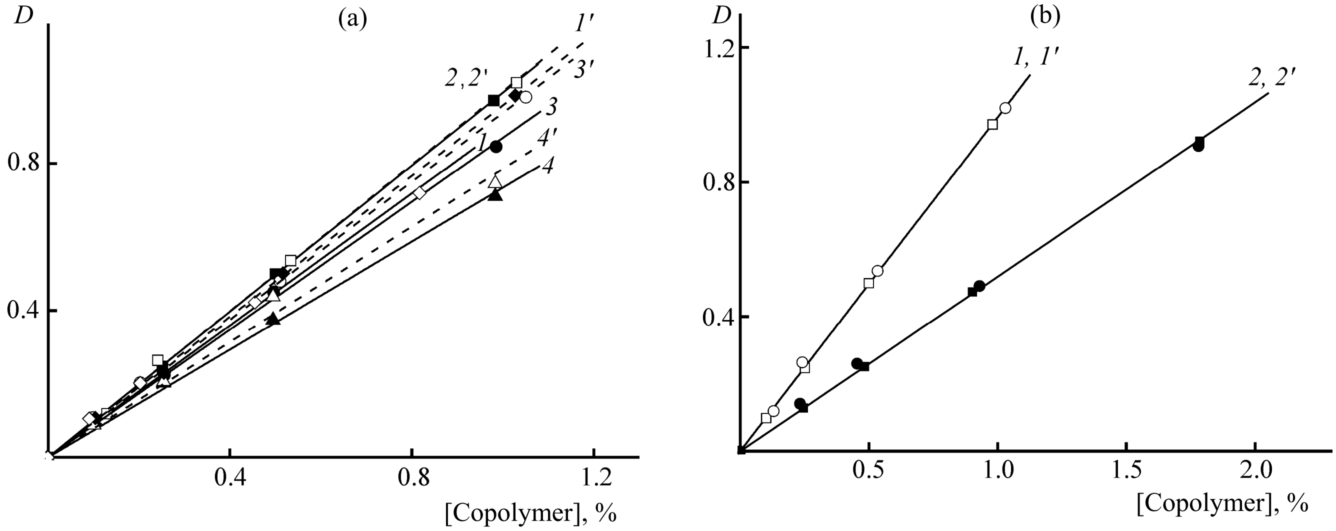

Fig. 1. Concentration dependences of the optical density at the C=O stretching vibration band. in the IR spectra of copolymers **I** and **II** in chloroform (cell path length 0.13 mm). (a) Copolymers (*1–4*) **Ia**–**Id** and (*1′–4′*) **IIa**–**IId**; (b) fractions (*1*, *1′*) *1* and (*2*, *2′*) *2* of (*1*, *2*) **Ib** and (*1′*, *2′*) **IIb**.

A different pattern is observed for copolymers **I** and **II** obtained at other reactant ratios. Judging by curves *1* and *1′*, *3* and *3′*, and *4* and *4′* in Fig. 1a, copolymers **II** contain a larger number of VP units as compared to **I**. Presumably, this results from variation of the copolymer composition toward increase of fraction *2* enriched in methacrylate units, which is removed upon precipitation with hexane. The dependences $D = f([\text{copolymer}])$ for copolymers **II** obtained in the absence and in the presence of DT attract attention. As follows from curves *1′* and *2′*, copolymers **IIa** and **IIb** are characterized by fairly similar concentrations of VP units in polymer chains, i.e., their composition is determined mainly by the VP–TGM ratio.

Figure 1b shows the dependences $D = f([\text{copolymer}])$ for copolymers **Ib** and **IIb** of both fractions. Comparison of these dependences confirms their nitrogen content determined experimentally. The dependences for fractions *2* are characterized by a considerably lower slope than those for fractions *1*, the concentrations of VP units in both fractions being similar. The ratio D_{1725}/D_{1680} in the IR spectra of **I** and **II** (films) increases as the concentration of TMG in the reaction mixture rose.

The complex composition of fractions *1* of copolymers **II** followed from the data on their solubility in chlorobenzene (~6−8 g/100 ml). These copolymers dissolved only partly to form intensely brown solutions, indicating a high concentration of C_{60}. The IR spectra of the soluble components of the copolymers obtained by chain transfer polymerization contained an absorption band at 1725 cm^{-1} due to stretching vibrations of carbonyl groups in methacryloyl units, so that these components were identified as copolymers. The undissolved part was weakly colored since the concentration of fullerene therein was low. According to the IR data, the insoluble products consist of copolymers with the little methacrylate groups, presumably with an impurity of linear polymer. The presence of a small amount of linear PVP in copolymerization products was detected by us previously [17]. The insoluble part amounted to ~20−30% (gravimetric data). On the other hand, the major part (~85%) of **IIa** obtained in the absence of DT, was insoluble in chlorobenzene, probably because of higher molecular weight and poor compatibility with the solvent. As followed from the IR data, the weakly colored soluble product was copolymer of *N*-vinylpyrrolidone and TGM.

The UV spectra of fullerene-free copolymers **I**-*1* in chloroform are shown in Fig. 2a. Copolymers **Ib**-*1* and **Id**-1 displayed an absorption band in the region λ 250−270 nm (curves *1*, *3*), which was a superposition of bands with their maxima at ~256, ~263, and ~270 nm. The same pattern in that region was typical of the linear polymer. The observed band is likely to arise from $n \rightarrow \pi^*$ transition in the lactam carbonyl group in VP units [19]. Curve *7* in Fig. 2b corresponds to the electronic spectrum of C_{60} in chloroform in the region λ 250−400 nm, where ρ-bands were present at $\lambda_{\max}$

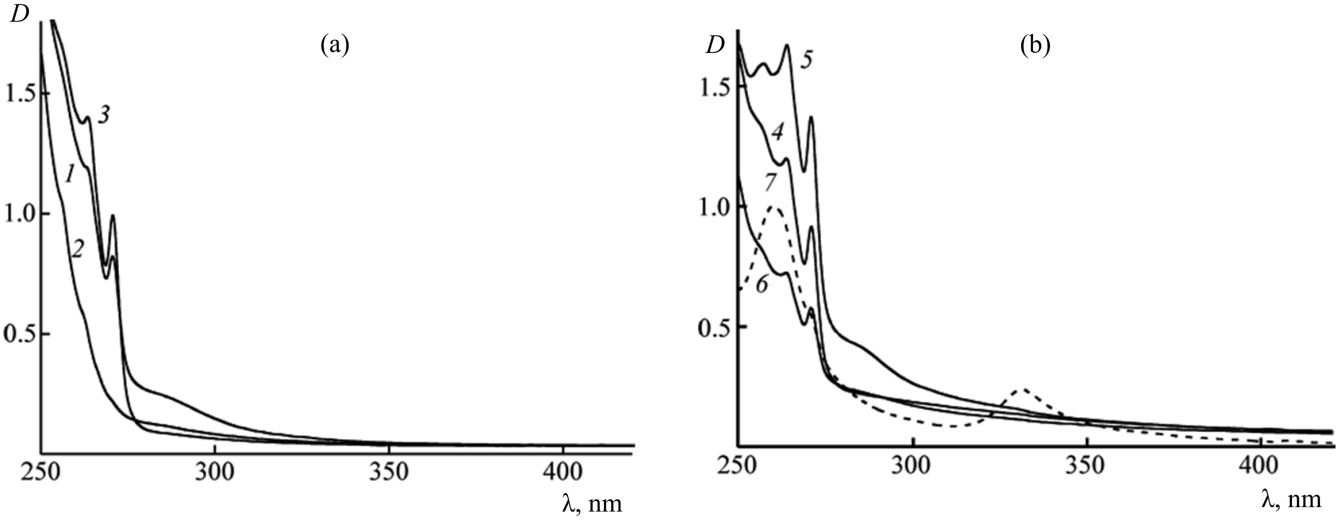

Fig. 2. UV spectra of copolymers (a, *1–3*) **Ib–Id** and (b, *4–6*) **IIb–IId** and (b, *7*) C_{60} in chloroform (cell path length 1 cm).

330 and 407 nm; in addition, a broad structureless absorption band was present at λ_{max} ~260 nm [20]. The UV spectra of copolymers **IIb–IId** in the region λ 250−300 nm also contained a broad absorption band as superposition of several bands at λ_{max} ~257, 263.7, and 271 nm (Fig. 2b; *4−6*). As in the spectra of **I**, this absorption originates from $n \rightarrow \pi^*$ transition in VP carbonyl groups. Insofar as it is overlapped by the C_{60} band at λ_{max} 260 nm, the state of fullerene in the copolymers cannot be determined unambiguously. On the other hand, the lack of another band intrinsic to C_{60} (λ_{max} 330 nm), as well as additional specific absorption in the region λ 300−700 nm, indicated variation of the electronic state of fullerene as a result of its participation in radical reactions. Thus, copolymers **IIb–IId** contain no free fullerene, and copolymer **IIa** also includes fullerene in a bound state.

Physicochemical parameters of copolymers I and II. Both fractions of copolymers **I** and **II** contain double bonds (Table 2), and their number in fractions *2* is larger. Special studies have shown that ozonolysis of fullerene involves no more than 20% of C=C bonds in its molecule. Therefore, the C=C bonds in **II**, as well as in **I**, are those in pendant methacrylate units. Their number increases in parallel with the concentration of TGM in copolymers due to increased concentration of DT which restricts growth of polymer chains as a result of chain transfer reaction. The presence of fullerene appreciably affects the concentration of C=C bonds in **IIb** and **IIc**.

Molecular weight distribution in the examined copolymers was qualitatively estimated by gel permeation chromatography (GPC) using a refractive index detector (Fig. 3). The chromatograms gave complete graphical representation of the molecular weight distribution in the copolymers with relatively low molecular weights. It should be noted that the data obtained using a light scattering detector were characterized by a larger error in analogous measurements. Figures 3a and 3b show chromatograms of both fractions of copolymers **I** and **II** obtained in the presence of DT. Fractions *1* have higher molecular weights. Increase in the concentration of the branching agent (TGM) and DT is accompanied by broadening of the chromatographic curves for copolymers **I**-*1* and **II**-*1* and their shift toward lower molecular weights. The shape of the curves for high-molecular-weight components of **II** resembles that observed for copolymers **I**. The main differences, namely better peak resolution and change of their intensity ratio, concerned fractions *2* of copolymers **I** and **II**.

The chromatogram of **IIa** synthesized in the absence of DT (Fig. 3c, curve *1*), is displaced toward higher molecular weights relative to the chromatogram of **IIb** obtained in the presence of DT (curve *2*). The chromatogram of the water-soluble fraction of **IIa** displayed a clearly defined shoulder at low molecular weights (curve *3*). The chromatogram of the insoluble part of **IIa** (curve *4*) was similar to that of unfractionated copolymer **IIa**.

The most characteristic parameter of highly nonuniform branched polymers is weight-average molecular weight M_w. The absolute values of M_w for copolymers **I** and **II** are given in Table 2. Increase in

Table 2. Physicochemical parameters of copolymers **I** and **II**

Copolymer no.	Ratio [VP]:[TGM]:[DT]	$[C=C] \times 10^3$, mol/g		$M_w \times 10^{-3}$	[η], dl/g	k'	T_g, °C
		fraction *1*	fraction *2*				
Ia	100:5:0	–	–	62.3	–	–	–
Ib	100:5:5	0.15	1.53	23.6	0.10	1.4	75.6
Ic	100:12:12	0.56	4.4	21.1	0.09	1.54	63.3
Id	100:20:20	0.73	2.6	22.7	0.06	2.44	54.9
IIa	100:5:0	–	–	89.2	0.14	0.81	126.3
IIb	100:5:5	0.27	2.94	52.5	0.11	1.52	55.3
IIc	100:12:12	0.29	2.47	49.1	0.08	2.28	75.6
IId	100:20:20	0.72	2.5	50.0	0.06	3.13	48.3

the concentrations of TGM and DT in the reaction mixture did not affect M_w values of **I** to an appreciable extent. The M_w value of **Ib** (obtained in the presence of DT) is lower by a factor of >2.5 than that of **Ia** (in the absence of DT), which is due to effective chain transfer to DT. Copolymers **II** are characterized by higher M_w values than **I**. However, the data given in Table 2 are likely to be regarded as approximate. Aggregation of fullerene-containing macromolecules in a polar eluent [21], as well as absorption of a part of incident light by fullerene molecule, may induce errors in measurement of molecular weights by gel permeation chromatography using a light scattering detector.

The behavior of fractions *1* of branched copolymers **I** and **II** in solution was described by their intrinsic viscosities and Huggins constants. Despite fairly similar values of M_w for copolymers **I** with different compositions, their parameters [η] and k' were different (Table 2). The largest differences were observed for copolymers **Ib** and **Id**. Obviously, the difference in the [η] values is determined by difference in the Mark–Houwink–Kuhn exponent α. Copolymer **Id** enriched in TGM units is characterized by the lowest intrinsic viscosity [η] among copolymers **I** and by the most compact conformation of macromolecules in isopropyl alcohol. High concentration of methacrylate units and DT residues in polymer chains leads to reduced thermodynamic affinity for the solvent and poor swelling of polymer globules therein. Reduction of α is likely to be determined by higher degree of branching of copolymer **Id**.

Copolymers **I** and **II** with similar compositions are characterized by quite similar [η] values (Table 2). On the other hand, copolymers **II** revealed stronger $\eta_{sp}/c = f(c)$ dependence (Fig. 4, curves *1′–3′*) and higher k' values. Different [η] values of copolymers **IIa** and **IIb** are related primarily to their different molecular weights. The higher value of k' for copolymer **IIb** synthesized in the presence of DT indicates its lower thermodynamic affinity for isopropyl alcohol.

Linear PVP obtained by radical polymerization in ethanol under the same conditions as for the examined copolymers had a glass transition temperature T_g of 150°C. Branched copolymers are characterized by lower T_s values and hence higher segmental molecular mobility (Table 2). The glass transition temperature of copolymers **I** decreases as the concentration of TGM increases. The reason is increased number of end chains as a result of branching [22]. Inclusion of C_{60} in the structure of copolymer may affect their segmental molecular mobility and T_g. On the one hand, hydrophobic fullerene molecules incorporated into polymer chains could weaken intermolecular interactions between polar polymer chains; on the other hand, intermolecular interactions between carbonyl groups in VP units and fullerene fragments exert the opposite effect [20]. Increased non-uniformity of fullerene-containing macromolecules with respect to their composition and molecular weight also favors variation of T_g. The glass transition temperature of **Ib** is higher by ~20°C than the T_g value of **IIb** (Table 2). The opposite relation is observed for copolymers **Ic** and **IIc**: the T_g value of the latter is higher by ~10°C. The glass transition temperature of **IId** is lower than that of **Id**, and copolymer **IIa** obtained in the absence of DT is characterized by a T_g value exceeding T_g of **IIb** almost twofold. Thus the glass transition temperature of copolymers **I** and **II** depends on their composition and molecular weight; the presence of covalently bound fullerene could both reduce and increase T_g value.

Thermal stability of copolymers I and II. Figure 5a shows weight loss curves and variation of the weight loss rate for linear PVP and copolymers **Ib–Id** which were synthesized by chain transfer polymerization.

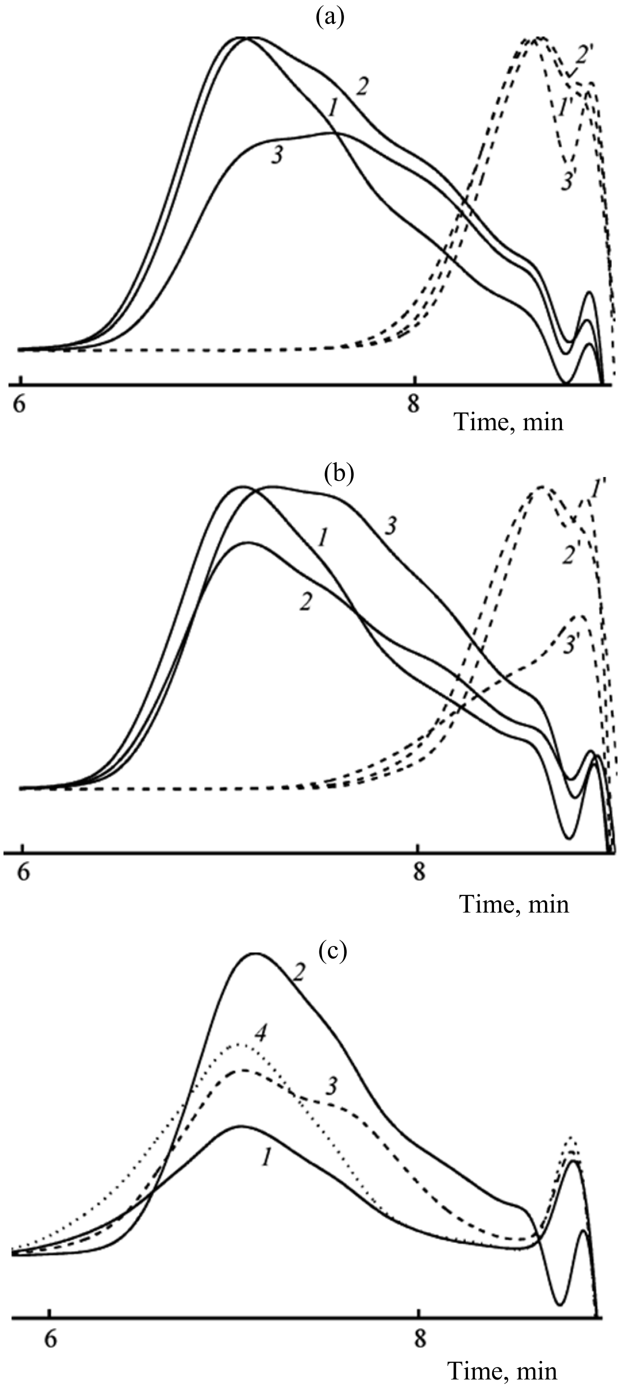

Fig. 3. Gel permeation chromatograms of fractions (*1–3*) *1* and (*1′–3′*) *2* of copolymers (a) **Ib**–**Id** and (b) **IIb**–**IId** and (c) copolymers (*1*) **IIa**, (*2*) **IIb**, and (*3*) water-soluble and (*4*) water insoluble fractions of **IIb**.

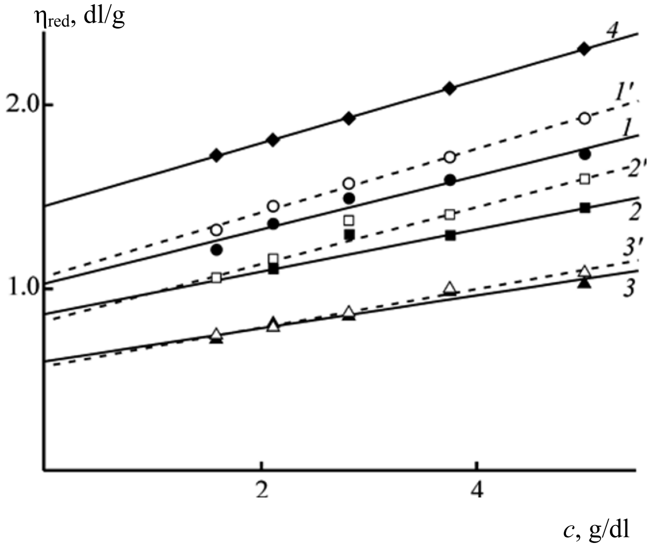

Fig. 4. Concentration dependences of the reduced viscosity of copolymers (*1–3*) **Ib**–**Id**, (*1′–3′*) **IIb**–**IId**, and (*4*) **IIa** in isopropyl alcohol. Temperature 20°C.

Thermal degradation of linear PVP (curve *1*) starts above 350°C and includes only one step; the maximal weight loss rate is observed at 430°C. Copolymers containing TGM units and DT residues are characterized by a different shape of the weight loss curves, mainly in the low-temperature region. Copolymer **Ib** containing the minimal amount of TGM and DT displayed a low-temperature weight loss maximum at 150°C, and the second maximum was observed at the same temperature as for the linear polymer. The first maximum may be related to decomposition of polymethacrylate fragments [12, 13]. Copolymers with a higher concentration of TGM and DT start to decompose even at lower temperature, and the corresponding second maxima on the weight loss rate curves (*3′*, *4′*) are also displaced toward lower temperature. In this case, weight loss in the low-temperature region is likely to result from elimination of water which is weakly bound to the polymer matrix [23]. On the whole, increase in the concentration of TGM in copolymers **Ib–Id** is accompanied by decrease of their thermal stability.

Decomposition of copolymers **IIb–IId** begins even at low temperature, presumably as a result of elimination of water molecules (Fig. 5b). The weight loss below 200°C amounts to ~3−5%; further rise in temperature leads to increase in the rate of decomposition of the copolymer with a high concentration of TGM, which attains its maximal value at 412°C (curve *7′*). Copolymers containing less TGM units displayed maxima on the temperature dependences of the weight loss rate at 418 and 426°C. We can conclude that the thermal stability series of copolymers **IIb–IId**, as well as of **Ib–Id**, is determined mainly by the concentration of TGM units in polymer chains.

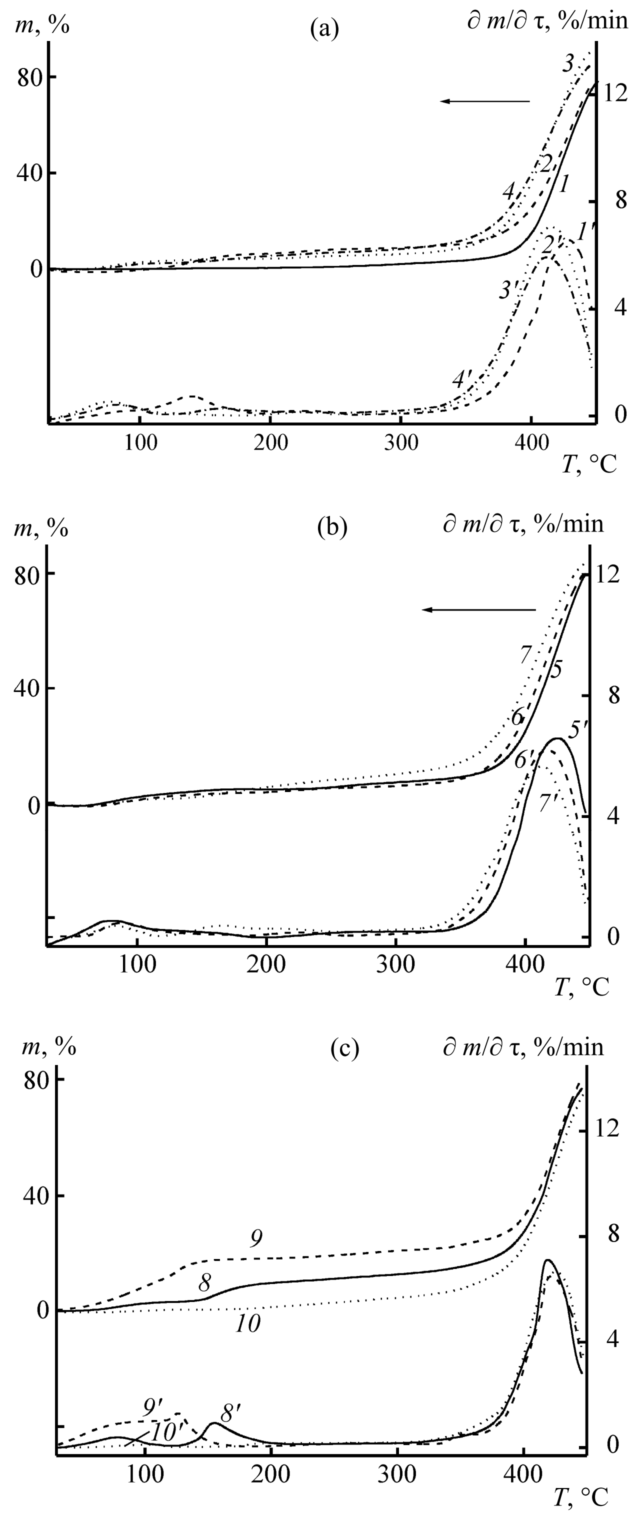

Fig. 5. (*1*–*10*) Weight loss and (*1*′–*10*′) weight loss rate curves for (a) (*1*, *1*′) linear poly(*N*-vinylpyrrolidone) and (*2*–*4*, *2*′–*4*′) copolymers **Ib**–**Id**, (b, *5*–*7*, *5*′–*7*′) copolymers **IIb**–**IId**, and (c) (*8*, *8*′) copolymer **IIa** and its (*9*, *9*′) water-soluble and (*10*, *10*′) water-insoluble fractions.

The weight loss of copolymer **IIb** in the temperature range from 50 to 150°C is larger than that observed for **Ib**. This may be related to increased fraction of weakly bound water in **IIb** whose macromolecules are more hydrophobic due to the presence of fullerene fragments. In the temperature range from 200 to 400°C, the rate of decomposition of copolymer **Ib** increases, whereas decomposition of **IIb** slows down. The weight loss maxima at 140 and 220°C, typical of copolymer **Ib**, are not pronounced in the thermal decomposition of **IIb**.

In the range 70−200°C copolymer **Ic** loses a larger weight than **IIc**, and then thermal degradation patterns of **Ic** and **IIc** are similar up to 330°C. However, further raising the temperature leads to a greater weight loss from **Ic** as compared to **IIc**. The rate of weight loss for the fullerene-containing copolymer is lower; by the end of the process it loses by about 10% less weight than **Ic**. Copolymers **Id** and **IId** were characterized by identical weight loss curves, i.e., their thermal stabilities are almost similar.

Thermal decomposition of copolymer **IIa** and its fractions occurred in a way different from copolymer **IIb** obtained in the presence of DT (cf. Figs. 5b and 5c). Several steps can be distinguished on the weight loss curves of **IIa**. Comparison of curves *8* and *9* shows that thermal decomposition of copolymer **IIa** is determined mainly by decomposition of its water-soluble fraction. Presumably, the low thermal stability of the latter is related to the presence of water involved in hydrogen bonds with the lactam carbonyl groups. Hydrogen bonding makes the C–N bonds weaker thus facilitating its rupture [23] with liberation of pyrrolidone. The insoluble fraction of **IIa** is stable up to 300°C.

According to the mass spectrometric data, volatile products formed by thermal degradation of linear PVP and branched copolymers **I** and **II** included those with molecular ions *m*/*z* 18, 85, and 111; they were assigned to water, pyrrolidone, and vinylpyrrolidone, respectively. In addition, the mass spectra contained other peaks with *m*/*z* 17 (OH^+), 90, and 96. The qualitative composition of the volatile decomposition products did not depend on the concentration of TGM and fullerene in the copolymer.

EXPERIMENTAL

N-Vinylpyrrolidone (Alfa Aesar) containing 0.1 wt % of sodium hydroxide was purified by vacuum distillation. Triethylene glycol dimethacrylate (Aldrich, 95%) and decane-1-thiol (Alfa Aesar, 96%) were used without additional purification. 2,2′-Azobis(isobutyronitrile) (AIBN) used as initiator was purified by recrystallization from ethanol. Toluene was distilled prior to use. Fullerene C_{60} contained ~99.95% of the main substance.

Copolymers **I** were synthesized according to the procedure described in [17]. Triethylene glycol dimethacrylate was the branching agent, and decane-1-thiol, chain transfer agent; AIBN concentration 0.02 M, molar ratio C_{60}–AIBN 1:20, overall reactant concentration in toluene ~20%, temperature 80°C. For the synthesis of copolymers **II**, a solution of C_{60} in toluene (0.7 g/l) was preliminarily prepared; it was kept for several days at 5°C to ensure complete dissolution, the required reactant mixture was added, and the reaction was carried out under the same conditions as in the synthesis of copolymers **I**.

When the reaction was complete (5.5 h), the mixture was cooled and poured into a 10-fold volume of hexane (precipitant). The precipitate (fraction *1*) was filtered off, washed with hexane, and dried first in air and then under reduced pressure at 20°C. The filtrate was evaporated to isolate fraction *2*.

Copolymer **IIa** was dissolved in chloroform, a double volume of water was added, and the mixture was stirred for 50 min using a magnetic stirrer. The mixture was allowed to settle down, the aqueous and organic phases were separated and evaporated, and the products (water-soluble and water-insoluble fractions) were dried until constant weight.

The nitrogen content of copolymers **I** and **II** was determined by elemental analysis. The sulfur content was determined with the aid of an X-ray fluorescent spectrometer using copolymer **Ic** as reference; the sulfur content of the latter was determined by chemical analysis.

The concentration of VP units in copolymers **I** and **II** was determined by IR spectroscopy. For this purpose, the IR spectra of **I** and **II** as films or dilute solutions in chloroform were recorded. In the first case (films), the intensity ratio of absorption bands due to stretching vibrations of carbonyl groups in methacrylate and pyrrolidone units at 1725 and 1680 cm^{-1} (D_{1725}/D_{1680}) was measured; in the second case ($CHCl_3$ solution), the dependences of the optical density at 1674 cm^{-1} (lactam C=O group in VP units) upon copolymer concentration $\{D = f([\text{copolymer}])\}$ were analyzed.

The concentration of residual C=C bonds in branched copolymers was determined by ozonolysis using an ADS-4M double bond analyzer. Copolymer **I** or **II**, was dissolved in chloroform, and ozone absorption curves were recorded using stilbene as standard. The concentration of C=C bond was calculated according to the procedure described in [17].

Gel permeation chromatography was performed on a Waters GPCV 2000 instrument equipped with refractive index and Wyatt DAWN HELEOS II (λ 658 nm) light scattering detectors (two 300×7.5 mm PL-gel columns, 5 μm MIXED-C); refractive index increment $\partial n/\partial c = 0.06-0.07$ ml/g; *N*-methylpyrrolidone containing 1% of LiCl (to suppress aggregation of polar macromolecules) was used as eluent, flow rate 1 ml/min; temperature 70°C. The absolute molecular weights were determined by processing the light scattering detector data with the aid of Astra 5.3.2.20 software.

The intrinsic viscosities [η] of fractions *1* of copolymers **I** and **II** were determined with a VPZh-2 viscometer (0.56-mm capillary) in isopropyl alcohol at 20°C. The concentration dependence of the reduced viscosity was extrapolated to zero concentration. The slope of that dependence was measured, and the Huggins constant k' characterizing interaction of macromolecules with a solvent was calculated by the Huggins equation $\eta_{red} = [\eta] + k'[\eta]^2c$ from the [η] values.

The glass transition temperatures (T_g) of fractions *1* of copolymers **I** and **II** were measured using a Mettler Toledo differential scanning calorimeter at a heating rate of 5 deg/min for the second or third heating−cooling cycle (0–150°C).

The electronic absorption spectra of fractions *1* of copolymers **I** and **II** were recorded from solutions in chloroform on a Specord M40 spectrophotometer (cell path length 0.5–1 cm). The IR spectra of **I**-*1* and **II**-*1* as films prepared from chloroform solution were measured on a Bruker ALPHA FTIR spectrometer equipped with an ALPHA-T module. The IR spectra of solutions of **I**-*1* and **II**-*1* in chloroform were recorded on a Specord 75-IR spectrometer using 0.13-mm cells.

The thermal stability of fractions *1* of copolymers **I** and **II** was analyzed by thermogravimetry using an STA 409C LUXX NETZSCH synchronous thermal analyser (Germany, 2006). Volatile products formed as a result of thermolysis of the copolymers were analyzed by mass spectrometry using a quadrupole mass spectrometer coupled with the thermal analyzer.

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