

MACROMOLECULAR CHEMISTRY
AND POLYMERIC MATERIALS

Thermal Desorption of Covalently Bound Fullerene C₆₀ from Poly-*N*-vinylpyrrolidone Films

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Abstract—Kinetics of formation of thermolysis products in heating of thin films of poly-*N*-vinylpyrrolidone and of poly-*N*-vinylpyrrolidone with covalently bound fullerene C₆₀ was studied by thermal desorption mass spectrometry.

Since fullerene C₆₀ (C₆₀) exhibits biological activity, synthesis of its water-soluble forms and, in particular, polymer–C₆₀ systems, is a topical task [1–4]. These are two types of fullerene-containing polymers in which C₆₀ is bound to water-soluble macromolecules by covalent or noncovalent bonds. Poly-*N*-vinylpyrrolidone (PVP) is a nonionic water-soluble amphiphilic polymer that can form complexes with molecules of diverse structures and polarities [5]. Poly-*N*-vinylpyrrolidone is produced commercially and is widely used in medicine [6]. Fullerene C₆₀ supported by this polymer can be used in biological studies [7]. Some features of the interaction between C₆₀ and PVP are known. A radical ion donor–acceptor complex in the PVP–C₆₀ system has been detected by ESR spectroscopy [8]. The formation of donor–acceptor bonds between C₆₀ and the carbonyl groups of PVP has been confirmed by ¹³C NMR studies [9].

The structure and properties of solutions of PVP–C₆₀ systems are determined by the type of the PVP–C₆₀ interaction and the nature of a solvent. As determined by the method of Rayleigh scattering, solutions of PVP–C₆₀ complexes contain domains whose size is determined by the balance of the attractive forces between C₆₀ molecules and repulsive force between the macromolecules [10]. It should be noted that the degree of heterogeneity of composite and nanocomposite polymer systems is an important parameter affecting their properties. However, there are only a few methods for measuring this parameter. At the same time, this parameter is required to correlate the structure and the properties of these systems and to develop techniques for their synthesis.

The high sensitivity of mass spectrometry and thermal desorption mass spectrometry (TDMS) to a molecule flow in the gas phase allows determination of the weight loss by the polymer–C₆₀ system in the course of C₆₀ desorption. The sensitivity of other common methods of thermal analysis (e.g., thermogravimetry) is substantially lower, and these methods are unsuitable for this purpose. The type of polymer–fullerene bonding and the structural state of C₆₀ (X-ray-amorphous or crystalline) were determined by TDMS from the curves of thermal desorption of C₆₀ and the thermolysis products of the polymeric matrix [11–15]. In this study we examined thermal desorption of fullerene C₆₀ from PVP–C₆₀ systems prepared by different procedures and analyzed the thermolysis products of PVP.

EXPERIMENTAL

Samples of PVP and PVP containing C₆₀ bound by covalent bonds (PVP–cov-C₆₀) were prepared by radical polymerization in toluene, using azobis(isobutyronitrile) (AIBN) of pure grade [TU (Technical Specification) 6-09-3840–74]. Trace amount of water were removed from AIBN in a vacuum [16]. *N*-Vinylpyrrolidone (N-VP) was dried over KOH and distilled under reduced pressure. The middle fraction was degassed. A fullerene powder with 98% C₆₀ was kept in a vacuum at 100°C. The toluene solutions of C₆₀ were prepared by the procedure described in our previous study [17]. Copolymerization of N-VP and C₆₀ was performed in toluene at 60°C in the presence of AIBN as an initiator.

Properties of PVP and its complex with C₆₀*

Properties	Sample	
	PVP	PVP-cov-C ₆₀
C ₆₀ content, wt %	—	1.6
MW _{peak} (MEC)	>90 × 10 ³	6 × 10 ³
MW _{LS} in water	—	10 × 10 ³
MWD	4.9	2.2
MW _{SD}	—	10 ³

* MW_{peak} is the number-average molecular weight corresponding to the maximum content of macromolecules in the molecular-weight distribution (MWD) determined by exclusion chromatography; MW_{LS} is the weight-average molecular weight determined from light scattering; and MW_{SD} is the number-average molecular weight determined by the sedimentation procedure.

Fullerene C₆₀ traps free radicals and inhibits copolymerization. This leads to termination of in the early stages in the case of simultaneous component mixing. The monomer conversion is about 20%. To increase the copolymer yield, AIBN was introduced in two steps. Half of the whole amount of AIBN was added at room temperature and the reaction mixture was stirred for 1 h. Then a toluene solution of C₆₀ was added, and the reaction mixture was heated at 60°C for 100 h. After that, the remaining portion of AIBN was added, and the copolymerization was continued for the same time. Then PVP-cov-C₆₀ was isolated.

The copolymer, formed in 70–90% yield was reprecipitated from diethyl ether, dissolved in distilled water, and lyophilically dried. Polyvinylpyrrolidone prepared by copolymerization in toluene in the presence of AIBN and commercial fractionated PVP with molecular weight (MW) of about (10–12) × 10³ were used as references. The PVP fraction with MW = 12 × 10³ was additionally dried in a vacuum (residual pres-

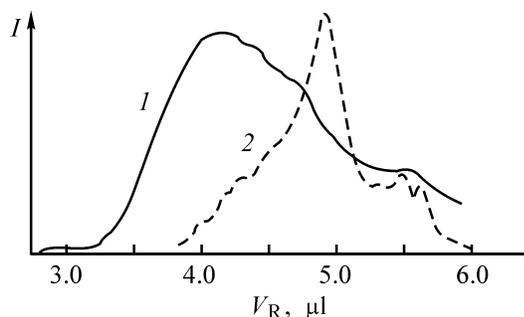


Fig. 1. HPLC pattern of PVP-cov-C₆₀ solution in chloroform measured with (1) refractometric detection and (2) photometric detection ($\lambda = 260$ nm, 0.5 × 400-mm Ultrastrogel 1000 column, chloroform as an eluent, elution rate 3 $\mu\text{l min}^{-1}$). (I) Intensity and (V_R) retention volume.

sure 10⁻⁶ mm Hg) at 140°C for 10–15 h. The molecular weights of PVP and PVP-cov-C₆₀ copolymer were determined by microcolumn exclusion chromatography (MEC) and by the method of Rayleigh scattering (see table).

The glass transition point of PVP $T \sim 180^\circ\text{C}$ [18].

Complexes of PVP with C₆₀, in which PVP is bound to C₆₀ by noncovalent bonds (PVP-C₆₀) were prepared from a benzene solution of these components [19]. The fullerene content in the complex thus obtained may be higher than 1%. In this study, we used the complex containing about 1.7% C₆₀.

Samples of PVP, PVP-cov-C₆₀, and PVP-C₆₀ were studied by TDMS. Thin films with a definite thickness were prepared as follows. An aliquot of a dilute solution of PVP-cov-C₆₀ or PVP-C₆₀ in distilled water or toluene was applied to an oxidized tantalum support-heater equipped with a thermocouple. To minimize the contact of the polymer with water, dried PVP was applied by hatching a support with a sample. The coated support was dried for 5 min at room temperature under a reduced pressure (~ 700 mm Hg) in a VT6060T vacuum oven (Kendro Laboratory Products) and then placed in a vacuum chamber of MKh-1320 magnetic mass spectrometer (energy of ionizing electrons 75 eV). Thermal desorption experiments were performed in a vacuum with residual pressure of $\sim 10^{-7}$ mm Hg.

The composition of PVP complexes with C₆₀ was examined in our previous study by thin-layer chromatography (THC) using toluene as an eluent [16]. The presence of free fullerene was detected only in pure C₆₀ and PVP-C₆₀. The absence of free C₆₀ in PVP-cov-C₆₀ was confirmed by UV spectra of solutions of C₆₀ and PVP-cov-C₆₀ in chloroform [16]. Naturally, PVP-cov-C₆₀ contains large amounts of C₆₀ bound to the initiator radicals formed after the second addition of AIBN.

It should be noted that, in these systems, C₆₀ is bound to radicals of the initiator and polymer by covalent bonds; their number may range from 1 to 3–4 [16]. We suggest that products are formed with both polymer and initiator radicals, initiator radicals only, and polymer radicals only. A study of PVP-cov-C₆₀ solution by two-detector exclusion chromatography confirmed its nonuniformity (Fig. 1). As seen from the chromatogram, the C₆₀ content in the low-molecular-weight fractions is high. Apparently, PVP with higher molecular weight is formed after the second addition of the initiator, since the contribution of chain termination reaction decreases owing to the lowering

of the activity of C₆₀ that reacted in the first polymerization step. Thus, our chromatographic study demonstrated that the polymerization product is not uniform and contains PVP homopolymer, a series of fullerene-containing PVPs with different numbers of macromolecules with different molecular weights, and structures containing radicals of both the polymer and initiator or only initiator radicals.

The mass spectrum of volatile thermolysis products (VTP) contains signals of vinylpyrrolidone VP ($m/z = 56_{100\%}, 111_{50\%}, 28_{47\%}, 27_{25\%}, 41_{18\%}$), pyrrolidone Pr ($m/z = 85_{100\%}, 42_{42\%}, 41_{36\%}, 28_{32\%}, 30_{29\%}, 56_{16\%}$) and trace amounts of water ($m/z = 18_{100\%}$). The main lines of these compounds and their relative intensities (lower index) are in parentheses. The ratios of VP and Pr formed in thermolysis of PVP and PVP-cov-C₆₀ differ in a wide temperature range. A typical mass spectrum of VTP of these samples is shown in Figs. 2a and 2b, respectively. The intensity of the Pr lines in the spectrum of VTP of PVP is the highest, which indicates that elimination of side pyrrolidone groups prevails. On the contrary, PVP-cov-C₆₀ is mainly thermolyzed by depolymerization to form VP monomer.

To gain deeper insight into thermolysis of these samples, we recorded the temperature dependences of the rate of formation of the VP monomer $dN_{VP}/d\tau$, pyrrolidone ring $dN_{Pr}/d\tau$, and C₆₀ molecules $dN_{C_{60}}/d\tau$ (N_i is the current amount of product liberated from the sample; τ is the time). The kinetics of formation of the thermolysis products was monitored by the line of their molecular ions M⁺ 111, 85, and 720, respectively. The samples were heated at a rate of about 7 deg s⁻¹.

The temperature dependences of the rate of liberation of VP $dN_{VP}/d\tau$ from predried PVP and PVP-cov-C₆₀ are shown in Fig. 3. It should be noted that, since different radicals are grafted to PVP-cov-C₆₀, only a shift of T_{max} of thermal desorption steps, but not their contribution, can be interpreted. In the case of PVP-cov-C₆₀, the low-temperature peak at $T_{max} \sim 290^\circ\text{C}$ is observed along with a high-temperature peak at $T_{max} \sim 480^\circ\text{C}$.

The low-temperature peak is due to rupture of the PVP-C₆₀ covalent bond in PVP-cov-C₆₀. This bond is located at the β -position with respect to the double bond of C₆₀ and is weak. A similar low-temperature peak has been observed in thermolysis of polystyrene with grafted C₆₀ groups [13]. The activation energy of rupture of this bond, calculated from the temperature dependence of the rate of monomer desorption in the low-temperature step ($T_{max} \sim 290^\circ\text{C}$), is about 80 kJ mol⁻¹. The total activation energy of VP for-

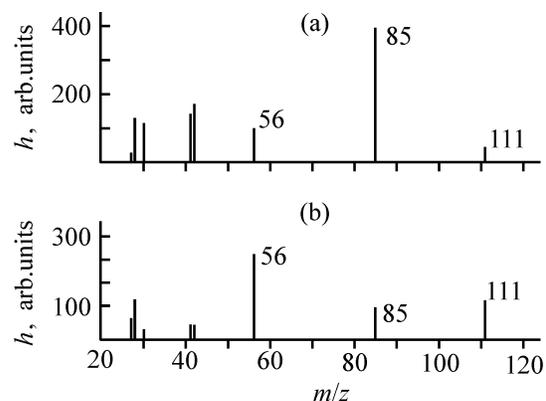


Fig. 2. Fragment of mass-spectrum obtained after thermal treatment of (a) PVP and (b) PVP-cov-C₆₀ at $\sim 320^\circ\text{C}$. (h) Relative peak intensity and (m/z) molecular weight to charge ratio.

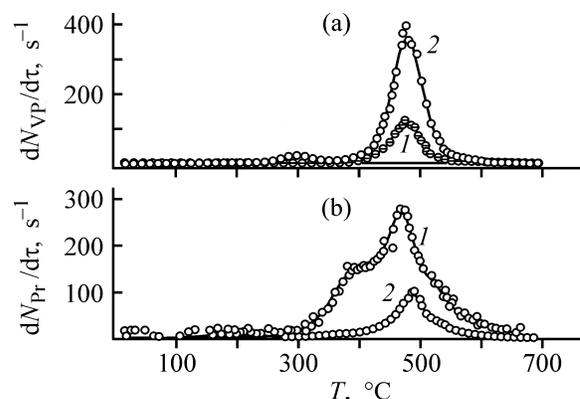


Fig. 3. Rate of formation of (a) VP $dN_{VP}/d\tau$ and (b) Pr $dN_{Pr}/d\tau$ vs. the temperature T of thermal treatment of predried films of (1) PVP and (2) PVP-cov-C₆₀.

mation in thermolysis of dry PVP is ~ 170 kJ mol⁻¹. It is difficult to calculate the activation energy of PV formation in the high-temperature step of PVP-cov-C₆₀ thermolysis, since this step overlaps with the low-temperature step.

The temperature dependence of the rate of Pr formation, $dN_{Pr}/d\tau$, in the course of thermolysis of PVP-cov-C₆₀ films and predried PVP are shown in Fig. 3. As can be seen from Fig. 3, Pr is formed in a wider temperature range (100–700°C) than VP. It should be noted that, at low temperatures, liberation of Pr from PVP predried in a vacuum and applied by the dry procedure is less intense. Poly-*N*-vinylpyrrolidone contains trace amounts of *N*-VP and 2-pyrrolidone, which are mainly removed by prolonged heating in a vacuum [20]. It is natural to assume that pyrrolidone is released from dry PVP owing to the presence of strongly bound water in the polymer [18]. We suggest that liberated VP undergoes acidic hydrolysis, since the pH of the aqueous PVP solution is ~ 5.5 . The hy-

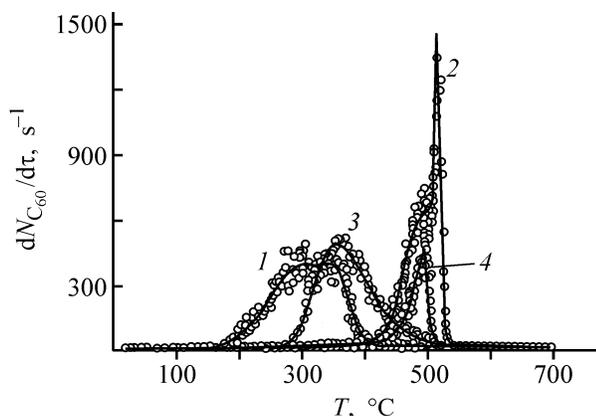


Fig. 4. Rate of C_{60} desorption, $dN_{C_{60}}/dt$, vs. the temperature T of thermal treatment of (1) 20-nm films of pure C_{60} , applied from a toluene solution to the metal surface, PVP-cov- C_{60} films applied from (2) aqueous and (3) toluene solutions, and (4) PVP- C_{60} film.

drolysis continues until water is present in the system. Water molecules form strong hydrogen bonds with the oxygen atoms of the carbonyl groups and are, apparently, retained in the polymer up to its complete degradation.

The temperature dependences of the rate of C_{60} desorption, $dN_{C_{60}}/dt$, from films applied from an aqueous solution of PVP- C_{60} , PVP-cov- C_{60} films applied from aqueous and toluene solutions, and 200-Å films of C_{60} applied from saturated toluene solution of C_{60} to the metal support are shown in Fig. 4. The film of pure C_{60} was studied for comparison, since thermal desorption of C_{60} is not complicated in this case by C_{60} diffusion in the polymeric matrix. The thermogram of thermal desorption of C_{60} from PVP-cov- C_{60} contains a dome-shaped peak at 380–500°C and a sharp peak at 500–530°C. Low-temperature desorption of C_{60} is accompanied by degradation of the macromolecules to form VP and Pr (Figs. 3 and 4). In addition, a comparative kinetic study of C_{60} desorption from a film of pure C_{60} on a metallic support and from PVP-cov- C_{60} film demonstrated that C_{60} molecules are firmly retained by the PVP matrix until they diffuse to the polymer-vacuum interface. The total activation energy of low-temperature (380–500°C) desorption of C_{60} ($\sim 110 \text{ kJ mol}^{-1}$) is close to that for other polymer- C_{60} complexes bound by covalent bonds [21]. If the low-temperature desorption of C_{60} is caused by rupture of the covalent bonds, the lower activation energy of C_{60} desorption as compared to that of PVP degradation should be due to the fact that the PVP- C_{60} covalent bond is weaker than the C-C bonds in a PVP macromolecule. The high-temperature peak (500–530°C) of C_{60} desorption is absent in the thermogram of PVP-cov- C_{60} films applied from

a toluene solution. In this case, C_{60} desorption starts at temperatures lower than those of the onset of PVP depolymerization (Fig. 3a). These data confirm that the mechanisms of high- and low-temperature desorption of C_{60} differ.

The difference in the mechanisms of high- and low-temperature desorption may be due to formation of donor-acceptor bonds of the fullerene both with the macromolecule grafted to it and with free PVP present in the sample. In addition, as we shown previously [19], donor-acceptor bonds and radical ions [8] are formed after exhaustive removal of the solvent (toluene) from the PVP- C_{60} system. Occurrence of these processes in the course of PVP-cov- C_{60} thermolysis cannot be ruled out *a priori*.

In concentrated aqueous solutions of PVP- C_{60} complexes, aggregation to form fractal structures was revealed by small-angle neutron scattering [22, 23]. At relatively high fullerene content in the complex (more than 1%), phase separation occurs and micellar structures composed of fullerene agglomerates with a polymer shell are formed. At the same time, in toluene, which is bad solvent for PVP, its macromolecules are contracted, which prevents contact between the components. Hence, the probability of formation of PVP- C_{60} donor-acceptor bonds in toluene is very low, and the thermal desorption of C_{60} from a PVP- C_{60} film applied from toluene solutions should be similar to that from other polymers, e.g., poly(methylmethacrylate).

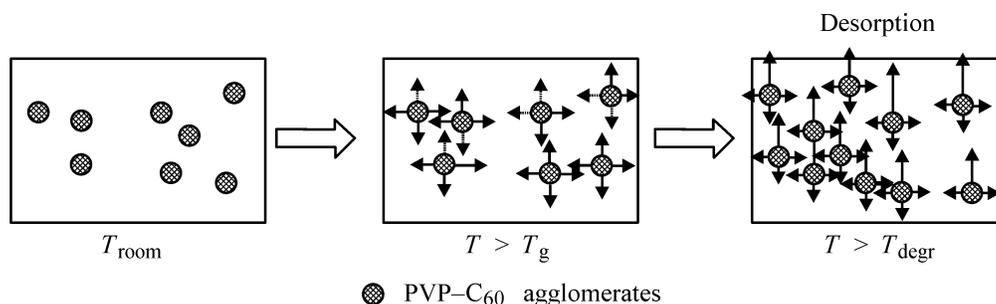
In this stage of the study, we suggest that the difference between the thermal desorption of C_{60} from PVP-cov- C_{60} films prepared from toluene and aqueous solutions is due both to different strengths of interaction of these components and different degrees of fullerene aggregation. The high-temperature peak at 500–530°C can be assigned to desorption of C_{60} molecules bound by donor-acceptor bonds or forming radical ions with appreciable charge transfer from the carbonyl oxygen of PVP to C_{60} (negative charge on C_{60} prevents its desorption from the polymer). The content of these C_{60} molecules, roughly estimated by integration of the desorption rate in the high-temperature step, is about 10% of the total fullerene amount in the sample.

The fact that the temperature dependence of C_{60} formation in the course of thermolysis of PVP- C_{60} film (Fig. 4, curve 4) shows only the high-temperature peak (T_{\max} is slightly lower than that for PVP-cov- C_{60}) and does not contain the dome-shaped peak at 380–500°C, which is present in the thermogram of PVP-cov- C_{60} , confirms our assumption that the high-

temperature step is caused by rupture of donor-acceptor bonds between C₆₀ and the polymer. The fullerene content in the complex is about 1.7%, i.e., is higher than the critical concentration (1%) at which, in accordance with the data of small-angle neutron scattering [22, 23], dense micellar structures can be formed. It should be noted that, at the temperatures of desorption of the fullerene from PVP-C₆₀ film applied from an aqueous solution [22, 23], the PVP-C₆₀ co-

valent bonds are ruptured and the degree of heterogeneity of the film is determined by the C₆₀ content in the system.

Although chemical transformations in solutions that contain PVP and C₆₀ and in films applied from these solutions are complex, we suggest the following simplified scheme describing the heterogeneous structure of PVP-cov-C₆₀ and PVP-C₆₀ films, as well as the temperature transformations of this structure.



Fullerene desorption from PVP-C₆₀ agglomerates is difficult, since they are encapsulated in the PVP matrix, which is preserved up to complete thermolysis of the polymer. As a result, the high-temperature peak of C₆₀ desorption appears at 500–530°C (Fig. 4). The low-temperature peak (380–500°C) in the thermogram of PVP-cov-C₆₀ is caused both by rupture of C₆₀-PVP covalent bonds and desorption of separate nonbonded C₆₀ molecules or C₆₀ molecules present in loose agglomerates. If the initial system becomes heterogeneous after formation from solution on the support, complex competitive processes determined by the reactivity and interdiffusion of the components will occur on further heating. The diffusion can be accelerated at temperatures higher than the glass transition point T_g . The TDMS data discussed above suggest heterogeneous structure of the examined films is caused by agglomeration in the initial solutions is retained up to the temperature of PVP thermal degradation, T_{degr} . The heterogeneous structure of these systems will be studied in more detail in our further works.

CONCLUSIONS

(1) Curves of thermal desorption of fullerene C₆₀ from poly-*N*-vinylpyrrolidone bound to C₆₀ by covalent bonds were recorded, as well as the curves of formation of thermolysis products of poly-*N*-vinylpyrrolidone films applied from different solvents.

(2) In the sample applied from an aqueous solution, fullerene is firmly retained in the poly-*N*-vi-

nylpyrrolidone matrix up to the decomposition temperature of poly-*N*-vinylpyrrolidone. This interaction is independent of the bonding type in the initial poly-*N*-vinylpyrrolidone-C₆₀ system.

(3) The unusual high-temperature peak of C₆₀ desorption is due to rupture of the donor-acceptor bonds between the fullerene and the carbonyl oxygen of the pyrrolidone ring in the poly-*N*-vinylpyrrolidone matrix.

(4) The mechanism of thermolysis of the systems examined and the mechanism of thermal desorption of C₆₀ from them is determined both by the type of poly-*N*-vinylpyrrolidone-C₆₀ bonds and the solvent used for film preparation. The degree of aggregation of C₆₀ and its derivatives increases when water is used as the solvent.

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