J Therm Anal Calorim (2012) 109:1033–1038
DOI 10.1007/s10973-011-1936-4

DSC investigation of the polystyrene films filled with fullerene

**Olga V. Alekseeva · Vladimir P. Barannikov ·
Nadezhda A. Bagrovskaya · Andrew V. Noskov**

Received: 18 April 2011 / Accepted: 19 September 2011 / Published online: 12 October 2011

Abstract Polystyrene composite films with different content of $C_{60} + C_{70}$ fullerene mix have been obtained from *o*-xylene solutions. The mass fraction of fullerene was varied from 0.01 to 0.1 mass%. The glass transition temperatures and specific heat capacities in range of 293–423 K have been determined for the films by DSC method. The plasticization of the polymer is observed in thermal properties of the films under influence of small fullerene additions. The values of T_g and C_P decrease and thermal coefficient of heat capacity b increase as fullerene content increases up to 0.02 mass%. The effect of interaction between polymer and fullerene molecules on thermal properties becomes evident at higher fullerene content in range from 0.02 to 0.1 mass%. At this the values of T_g and C_P increase and b coefficient decrease with increasing content of fullerene. Concentration dependence of C_P and b values is less steep for polymer composite films in elastic state at temperatures above T_g. Molecular interactions in the composites are discussed in view of our-self and literature data.

Keywords Polystyrene · Fullerene · Glass transition temperature · Specific heat capacity · Plasticization · Molecular interaction

Introduction

Composite materials consisting of polymer matrix and fullerenes are of interest for electronics, optics, sensors, medicine, biology, etc. [1]. It was ascertained that incorporation of fullerene improves physical and chemical properties of polymer materials. Polystyrene (PS) is widely used as polymer that can immobilize nano-carbon particles. There are two ways to include nano-carbon particles into the polymer matrix: through covalent attachment of fullerene molecules with polymer chains [2] or by the formation of polymer–fullerene complexes [2, 3]. The synthesis standard methods of fullerene–PS materials are well known [4, 5]. A mixing of solutions of fullerene and polymer in certain ratio is often used to produce the composites as some organic solvents can readily dissolve both components. Whereas synthesis of the composites, their optical properties and some features of interaction of fullerene with PS are already known [5, 6], thermal, thermodynamic, and structural properties of the composites are studied insufficiently. Weng et al. [7] came to conclusion that 5–20 mass% addition of C_{60} results in an increase of glass transition temperature of PS but effect of smaller additives was not investigated. A change in some physical and chemical parameters of polymer materials influenced by small additions of fullerene (significant increase in tensile strength and elasticity) has been also shown by Potalitsin et al. [6]. Noticeable interaction of fullerene with PS in composite materials of different content was shown by IR data [8, 9]. The aim of this study is to produce fullerene–PS composite films and to study effect of small additives on thermal and thermodynamic properties of polymer.

Experimental

Atactic PS (Aldrich, US; molecular mass is 140,000, polydispersity is $M_w/M_n = 1.64$) and fullerene mix

---

O. V. Alekseeva (✉) · V. P. Barannikov ·
N. A. Bagrovskaya · A. V. Noskov
Institute of Solution Chemistry, Russian Academy of Sciences,
Academicheskaya Str. 1, Ivanovo 153045, Russian Federation
e-mail: ova@isc-ras.ru

$C_{60} + C_{70}$ (Fullerene Technologies Ltd., Russia) were used. A solvent casting of perspective components from solutions was employed for preparing the mixtures of $C_{60} + C_{70}$ with polymer. Preliminary purification of organic solvent (*o*-xylene) and fullerenes was made by standard techniques [10, 11].

We produced the PS films as follows. PS batch was dissolved in *o*-xylene (17 mass% of PS) and the solution was stirred for about 1 day before being cast into thin films. After casting the solvent was slowly evaporated over several days to produce the PS films.

Fullerene–PS composition films have been produced as follows. Fullerene batches were dissolved in *o*-xylene. Concentrations of fullerenes in solutions were equal to 0.018, 0.036, 0.063, and 0.180 kg m^{-3}. Then PS batches were dissolved in all obtained solutions (17 mass% of PS) and the mixed solutions were stirred for about 1 day before being cast into thin films. After casting the solvent was slowly evaporated over several days to produce the composite films. By this technique, we prepared four samples of fullerene–PS composites with different fullerene percentage, x (0.010, 0.020, 0.035, and 0.100 mass%) in the form of film.

The film samples were dried in vacuum at 383 K for 24 h before experiments.

DSC measurements were performed using DSC 204 F 1 apparatus (Netzsch, Germany) in argon atmosphere (15 cm^3 min^{-1}). A stack of films with a diameter of 5 mm was placed in a press-fitted aluminum crucible covered the pierced lid. Mass of samples was from 4 to 10 mg. The samples were undergone first heating up to 410 K to remove volatile substances from the polymer and cooled down to 283 K with a scan rate of 10 K min^{-1} by means of liquid nitrogen. Second heating of the simples was carried out according to the following sequence: heating up to 293 K; isothermal mode at 293 K for 10 min; and heating up to 423 K with a scan rate of 10 K min^{-1}. The glass transition temperatures and specific heat capacities were determined from data of the second heating. The reference aluminum crucible was empty. Sapphire disk with a mass of 12.5 mg was used as standard of specific heat capacity. All measurements were performed relative to the base line obtained with two empty crucibles. Three measurements required for each composite (base line, sample, and standard) were carried out on the same day. Calibration of the calorimeter was performed by measuring the temperatures and heat effects of phase transitions for the 11 standard substances in the temperature range from 187 to 749 K [12].

The content of volatile substances in the samples studied was determined by thermogravimetry method using Netzsch microthermobalance TG 209 F 1 under similar conditions of experiment, i.e., heating up to 423 K with a scan rate of 10 K min^{-1}. A mass loss about 2% is observed due to evaporation of volatile substances (styrene oligomers and solvent traces) from the films. The error in determination of the mass loss was 1×10^{-3} mg. Thermogravimetric data were taken into account to correct the mass of samples at second heating in DSC experiments.

IR-spectra of films were recorded by Avatar 360 FT-IR ESP spectrometer (Termo Nicolet, US).

Each DSC measurement was repeated three times and the results were given as mean values ± standard deviations. Reproducibility for value of the glass transition temperature was 0.5 K, and for value of the change of the specific heat capacity during phase transition—0.02 J g^{-1} K^{-1}.

Results and discussion

By above described technique, we prepared one sample of PS film and four samples of fullerene–PS composite films with different $C_{60} + C_{70}$ percentage. A thickness of the films amounts from 60 to 80 μm as measured by micrometer with uncertainty of 5 μm. The samples obtained have been examined by optical microscope «Boetius» (Germany). We found both PS films and fullerene–PS composite films transparent, that is, the films are homogeneous on the optical level. Unmodified PS samples were colorless, whereas the fullerene–PS composite films were light purple. The intensity of color depended on the content of fullerene in the composite.

Typical DSC curves for the films of original PS and filled composite with fullerene are shown in Fig. 1. It is seen that for all examined polymeric materials there is a reversible phase transition from the glassy state to elastic one, which manifests itself as a step of heat flow in endothermic direction. We have been characterized this phase transition by the following parameters: the extrapolated temperatures for onset, T_{onset}, end, T_{end}, and middle of phase transition, T_{mid}; the glass transition temperature, T_g, which corresponds to inflection point on the DSC curve; the change of the specific heat capacity during phase transition, ΔC_P. Three DSC curves were obtained for each film sample. Repeatability of measured values amounted to 0.2 K for T_g and 0.04 J g^{-1} K^{-1} for ΔC_P. The average characteristics of the glass transition obtained from tree experiments for each polymer films are presented in Table 1. It was found that the $C_{60} + C_{70}$ addition affects all characteristic temperatures and temperature range of phase transition, $\Delta T = T_{\text{end}} - T_{\text{onset}}$, for the composite materials.

The concentration dependence of ratio of T_g values for original and filled PS is given in Fig. 2. Small additions of fullerene sharply reduce the glass transition temperature of the composite in comparison with original polymer film.

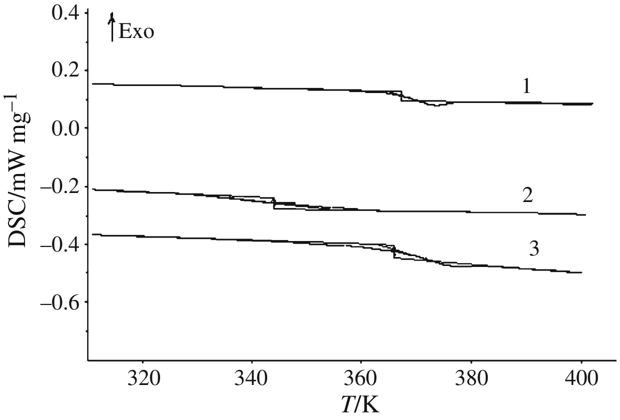

Fig. 1 DSC curves of PS films: *1* without fullerene, *2* composite with 0.01 mass% of fullerene, *3* composite with 0.1 mass% of fullerene

Table 1 Parameters of phase transition from glassy state to elastic one for the original and filled PS films with different content of $C_{60} + C_{70}$

x/mass%	T_{onset}/K	T_{mid}/K	T_g/K	T_{end}/K	ΔT/K	ΔC_P/J g^{-1} K^{-1}
0	357.0	361.5	363.8	365.8	8.8	0.30
0.010	328.1	343.8	335.8	355.1	27.0	0.23
0.020	341.6	348.6	345.0	359.3	17.7	0.25
0.035	347.0	358.4	357.4	366.5	19.5	0.26
0.100	365.3	369.1	371.6	373.5	8.2	0.29

The minimum value of T_g is observed at the concentration equal to 0.01 mass%. Apparently, in this case, there is the plasticization of PS with the fullerene [7, 13]. Molecules of $C_{60} + C_{70}$ embed between the chains and weaken interchain interactions in the PS. It results in increasing mobility of polymer chain segments and reducing value of T_g. The noticeable extension of the temperature range for phase transition, $\Delta T = T_{end} - T_{onset}$, at low concentration of fullerene (Table 1) confirms an evident plasticization effect of these additives on thermal properties of the composite. The glass transition temperature increases with further increase in the $C_{60} + C_{70}$ content. When the fraction of fullerene is equal to 0.1 mass%, the T_g value for the composite exceeds that for the original PS.

It is known that fullerene molecules are capable of strong intermolecular interaction due to the large number of conjugated double bonds [13]. Intermolecular interactions of PS and fullerene are emerged on the values of T_g in the films with additions of more than 0.01 mass%. When the concentration of fullerenes is equal to 0.1 mass% and above, the effect of intermolecular interactions is dominant, the probability of interaction between fullerene molecules in the composite increases, that is manifested in increasing glass transition temperature as compared with the original PS and, apparently, can lead to the physical cross-linking of PS chains. Vice versa, at extremely low concentration (less then 0.01 mass%) the probability of interaction between fullerene and PS molecules is very small because of there is one fullerene molecule per 55–60 PS macromolecules (or one fullerene molecule per 70,000–80,000 monomeric unit) in the composite material. In this regime, weakening of interchain interactions in the PS is dominant.

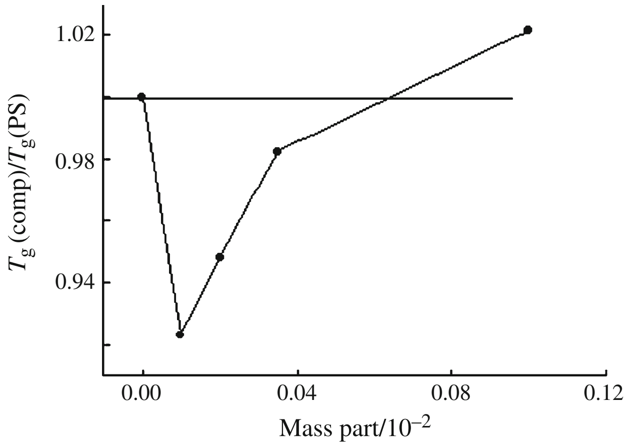

Fig. 2 Ratio of glass transition temperatures for composite films, T_g(comp), to one of original PS film, T_g(PS), versus fullerene content

In [8], we used electron microscopy and X-ray diffraction to study the influence of the fullerene additives on structure of the PS films formed by evaporation of the solvent. We concluded in films without fullerenes, packing of straightened chains parallel to each other predominated. This shows that a PS molecule, which had the shape of a coil in solution, straightened and stretched itself along the surface of an aggregate when attached to it. At $x = 0.035$ mass% (one fullerene per 7–10 PS macromolecules), attachment to aggregates occurred similarly. However, at such concentrations the intermolecular interactions between PS and fullerene are appreciable and under the influence of fullerene molecules, PS molecules straightened with the formation of ordering elements in the arrangement of chains [8].

Based on the results of DSC studies we identified specific heat capacities, C_P, for the films of original PS and PS doped additive mixture $C_{60} + C_{70}$ (0.01–0.1 mass%), in the range of 290–420 K. The specific heat capacity values for original PS are equal to 1.23 ± 0.03 and 1.95 ± 0.03 J g^{-1} K^{-1} at 298 and 398 K, respectively. These results agree well with reference data which amount to 1.224 and 1.924 J g^{-1} K^{-1}, respectively [12]. The repeatability of C_P values for the composite films amounted to 0.03 J g^{-1} K^{-1} also as determined from tree measurements for each sample. As seen from Fig. 3, the dependence of the specific heat capacity of the composite on the fullerene

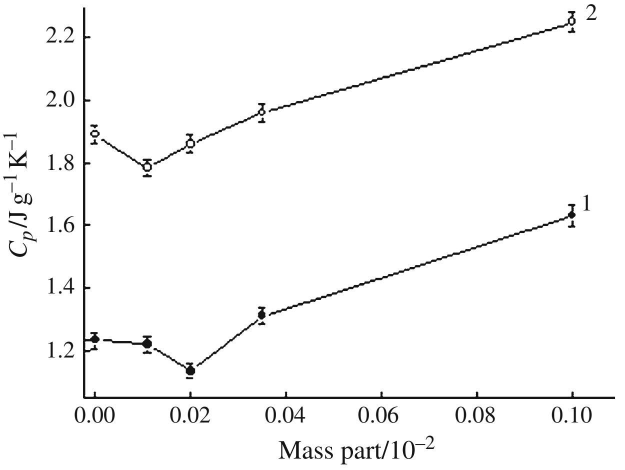

Fig. 3 Dependence of specific heat capacity of PS films on fullerene content: *1* glassy state at 298 K, *2* elastic state at 398 K

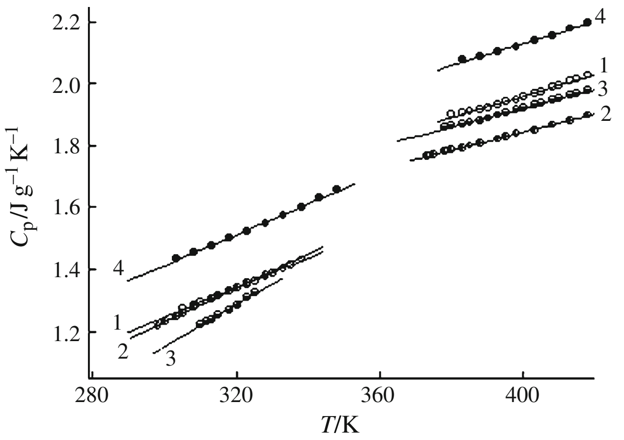

Fig. 4 Temperature dependence of specific heat capacity for PS films with various content of fullerene: *1* 0.0, *2* 0.010, *3* 0.020, *4* 0.035 mass%

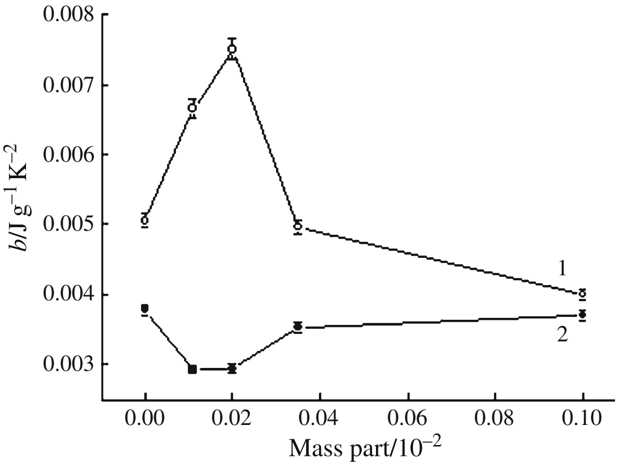

Fig. 5 Coefficient of temperature dependence of specific heat capacity for PS films with various content of fullerene: *1* glassy state in temperature range of 298–328 K, *2* elastic state in range of 368–423 K

content is non-monotone. Specific heat capacity at 298 K slightly decreases from 1.23 to 1.12 J g^{-1} K^{-1} when the content of C_{60} + C_{70} increases up to 0.02 mass%. Further enhancement of fullerene content leads to the considerable increase in heat capacity to 1.40 J g^{-1} K^{-1} (curve 1).

The dependence of the heat capacity on the content of C_{60} + C_{70} for filled polymer materials in the elastic state at 398 K passes through a minimum also at a concentration of fullerenes equal to 0.01 mass% (curve 2). The observed changes in the specific heat capacity confirm the conclusion indicated above about the plasticization of PS by small additions of fullerene. The increase in heat capacity at the content of fullerene more than 0.02 mass% can be associated with the manifestation of the PS–fullerene interactions that is consistent with the regularities in change of the glass transition temperatures [7].

As seen in Fig. 4, specific heat capacity of the composites monotonically increases with temperature and increases abruptly at the phase transition. The dependence “measured values of C_P versus temperature” was described by a linear equation.

$$C_P = a + bT$$

The temperature dependence coefficients of the specific heat capacity, *b*, for the composites at different contents of fullerenes are presented in Fig. 5. It can be seen that value of *b* for samples in the glassy state in the temperature range 298–328 K increases sharply with increasing fullerene content up to 0.02 mass% and decreases with further increase in the concentration of additives (curve 1). The observed dependences of C_p and *b* values reflect the competing effects of two factors. Namely, the plasticizing effect of fullerenes manifests itself with small additions. At this the values of C_p decrease (Fig. 3) and *b* increase (Fig. 5). The effect of interactions between fullerene and polymer molecules dominates at concentrations more than 0.02 mass%. At this the values of C_p increase (Fig. 3) and *b* decrease (Fig. 5). The concentration dependence of *b* values for the samples in the elastic state for the range 368–423 K is weak (Fig. 5, curve 2).

Note an analogous non-monotone dependence of physical and chemical parameters of composites on the fullerene concentration was found for crystallinity degree of some polymer materials [14].

Interactions between fullerene and PS can be seen in IR spectra. IR-spectra of PS films and fullerene doped PS films possess some distinctions [8, 9]. In the transmission spectrum of the modified film, one can see that contour of a 1,380–1,190 cm^{-1} band changes compared to the unmodified one. There is some change in intensity for bands which are related to phenyl ring. In the IR spectrum of the

Table 2 Spectral characteristics of PS films modified by the incorporation of fullerenes and unmodified ones

x/mass%	D_{1601}/D_{908}
0.0	2.13
0.010	2.08
0.035	2.28
0.100	2.31

fullerene molecules, there are four active variations of the absorption bands at 527, 577, 1183, and 1429 cm^{-1} [15]. We performed semiquantitative analysis of IR-spectra of the studied films with application of a method of a base line and internal standard [16]. The absorption band of C–H bond in ring with maximum at 908 cm^{-1} has been chosen as internal standard. The ratios of optical densities of a characteristic band, D_{1601}, to optical densities of internal standard, D_{908}, are presented in the Table 2. From tabular data follows there is a change of relative intensity of bands at maximum 1,601 cm^{-1} in spectra of PS films modified by the incorporation of fullerene. Most likely changes in spectra of modified films are caused by interaction of aromatic rings of a polymer macromolecule with π-electronic system of fullerene. Note that dependence of the absorption band relative intensity, D_{1601}/D_{908}, on the $C_{60} + C_{70}$ concentration is non-monotone. The minimum of D_{1601}/D_{908} ratio is observed at the concentration equal to 0.01 mass%. It agrees with results obtained by DSC and in our opinion reflects the competing effects of two factors mentioned above, i.e., plasticizing action of fullerenes, and their interaction with polymer macromolecules.

Conclusions

The fullerene–PS composite films have been successfully prepared by evaporating of *o*-xylene solvent. It was found that the glass transition temperature, specific heat capacity and its temperature coefficient were influenced by the fullerene content. Concentration dependences of these values are non-monotone in range of small additives of fullerene (lesser than 0.1 mass%) in contrast to them for the composites with higher content of fullerene [7]. The values of T_g and C_P decrease and thermal coefficient of heat capacity b increase as fullerene content increases up to 0.01–0.02 mass%. At higher fullerene content (up to 0.1 mass%) the values of T_g and C_P increase and b coefficient decrease with increasing content of fullerene. The observed dependences reflect the competing effects of two factors. The plasticizing effect of fullerenes on thermal properties of composites dominates in range of small additions. The effect of interactions between fullerene and polymer molecules becomes evident at concentrations more than 0.01–0.02 mass%.

Highlights

PS composite films with small content of fullerene from 0.01 to 0.1 mass% have been prepared from *o*-xylene solutions.

The glass transition temperatures and specific heat capacities of the composite films are measured by DSC.

Non-monotone concentration dependence of the thermal properties of the composites evidences competition effects of plasticizing and fullerene–polymer interaction.

References

1. Vinogradova LV, Melenevskaya EYu, Khachaturov AS, Kever EE, Litvinova LS, Novokreshchenova AV, Sushko MA, Klenin SI, Zgonnik VN. Water-soluble complexes of C_{60} fullerene with poly(*n*-vinylpyrrolidone). Polym Sci A. 1998;40:1152–9. English translation of Vysokomolekulyarnye Soedineniya A. 1998;40: 1854–62.
2. Krakovyak MG, Nekrasova TN, Anan'eva TD, Anufrieva EV. Noncovalent interactions between polymers and fullerene C_{60} in organic solvents. Polym Sci B. 2002;44:271–4. English translation of Vysokomolekulyarnye Soedineniya B. 2002;44:1853–7.
3. Yamakoshi YN, Yagami T, Fukuhara K, Sueyoshi S, Miyata N. Solubilization of fullerenes into water with polyvinylpyrrolidone applicable to biological tests. J Chem Soc Chem Commun. 1994;4:517–8.
4. Okamyra H, Ide N, Minoda M, Komatsu K, Fukuda T. Solubility and micellization behavior of C_{60} fullerenes with two well-defined polymer arms. Macromolecules. 1998;31:1859–65.
5. Yevlampieva NP, Zaitseva II, Ryumtsev EI, Dmitrieva TS, Melenevskaya EYu. Interaction of polystyrene and fullerene C_{60} in benzene: composition and molecular properties of the product. Polym Sci A. 2007;49:284–91. English translation of Vysokomolekulyarnye Soedineniya A. 2007;49:447–55.
6. Potalitsin MG, Babenko AA, Alekhin OA, Alekseev NI, Arapov OV, Charykov NA, Nekrasov KV, Gerasimov VI, Semenov KN. Caprolons modified with fullerenes and fulleroid materials. Russ J Appl Chem. 2006;79:306–9. English translation of Zhurnal Prikladnoi Khimii. 2006;79:308–11.
7. Weng D, Lee HK, Levon K, Mao J, Scrivens WA, Stephens EB, Tour JM. The influence of Buckminsterfullerenes and their derivatives on polymer properties. Eur Polym J. 1999;35:867–78.
8. Alekseeva OV, Bagrovskaya NA, Kuzmin SM, Noskov AV, Melikhov IV, Rudin VN. The influence of fullerene additives on the structure of polystyrene films. Russ J Phys Chem A. 2009;83:1170–75. English translation of Zhurnal Fizicheskoi Khimii. 2009;83:1320–6.
9. Alekseeva OV, Bagrovskaya NA, Kuzmin SM, Noskov AV. Study of structural properties of polystyrene–fullerene composites. J Balk Tribol Assoc. 2010;16:558–63.
10. Vinogradova LV, Melenevskaya EYu, Kever EE, Shibaev LA, Antonova TA, Zgonnik VN. Synthesis of fullerene-containing poly(ethylene oxide)s. Polym Sci A. 1997;39:1149–54. English translation of Vysokomolekulyarnye Soedineniya A. 1997;39: 1733–9.
11. Coetzee JF, editor. Recommended methods for purification of solvents and tests for impurities. Oxford: Pergamon Press; 1982.
12. Sabban JR, Xu-Wu A, Chichos JS, Planas Leitão ML, Roux MV, Torres LA. Reference materials for calorimetry and differential thermal analysis. Thermochim Acta. 1999;331:93–204.

13. Gladchenko SV, Polotskaya GA, Gribanov AV, Zgonnik VN. The study of polystyrene–fullerene solid-phase composites. Tech Phys Russ J Appl Phys. 2002;47:102–6. English translation of Zhurnal Tekhnicheskoi Fiziki. 2002;72:105–9.
14. Badamshina ER, Gafurova MP. Characteristics of fullerene C_{60}-doped polymers. Polym Sci B. 2008;50:215–25. English translation of Vysokomolekulyarnye Soedineniya B. 2008;50: 1572–84.
15. Konarev DV, Lyubovskaya GN. Donor–acceptor complexes and radical ionic salts based on fullerenes. Russ Chem Rev. 1999;68:19–38. English translation of Uspekhi Khimii. 1999;68: 22–44.
16. Smith AL. Applied infrared spectroscopy. Fundamentals, techniques, and analytical problem-solving. New York: Wiley; 1979.