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Dedicated to Prof. Edith A. Turi in recognition of her leadership in education

ANOMALIES OF GLASS TRANSITION
Manifestation in fullerene core polystyrene stars

V. A. Bershtein[1], *V. M. Egorov*[1], *V. N. Zgonnik*[2], *E. Yu. Melenevskaya*[2] *and L. V. Vinogradova*[2]

[1]A. F. Ioffe Physico-Technical Institute of the Russian Academy of Sciences, 194021 St. Petersburg
[2]Institute of Macromolecular Compounds of the Russian Academy of Sciences, 199004
St. Petersburg, Russia

Abstract

Segmental dynamics around T_g in the 4- and 6-arm fullerene (C_{60}) core star-like polystyrenes with different preset arm lengths was studied by DSC as compared to that in the linear PS and PS/C_{60} blend. The 'anomalies' in glass transition behavior were found for the stars including both suppression and facilitation of segmental motion, and pronounced dynamic heterogeneity within a transition range. The results are interpreted in terms of breakdown of intermolecular cooperativity of segmental motions and PS-C_{60} interactions.

Keywords: DSC, fullerene, glass transition, star-like polystyrene, segmental dynamics

Introduction

The fullerenes, C_{60} and others, as the large closed-cage molecules formed of carbon in the *sp*^{2}-hybridized state, may undergo a wide variety of reactions characteristic of alkenes (see, e.g. the review [1]); lesser attention has been devoted to polymeric C_{60} derivatives so far [2–12]. The latter are challenging since they allow the intriguing electrooptic, magnetic or conducting properties of C_{60} to be realized since they are processable [4, 5, 9]. 'Macromolecularization' of fullerene may be fulfilled via covalent linkage or by doping C_{60} into polymer matrix [8].

Samulsky *et al.* [2] have first prepared multi-substituted polystyrene (PS)-fullerene. Then, PS with C_{60} grafted to its side groups [4], and fullerene-end-capped PS [5] or fullerene core star-like PS (FSPS) [6, 7] have been synthesized. The most comprehensive work in PS covalent attachment to fullerene with formation of the well-defined PS stars was carried out by Ederle, Mathis and Melenevskaya *et al.* [10–12]. In the latter case, it was necessary not only to regulate and control the number of chains grafted to the fullerene but also to gain low polydispersities of the star arms that might assume experimental determination of fullerene functionality in the star structure. The authors above [10–12] have succeeded in that by using anionic polymerization which led to the products with the lowest polymolecularity [13].

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Attachment of the ‘living’ anionic oligomer or polymer to fullerene offered an opportunity to control both the number of chains grafted, and the molar mass and polymolecularity of the arms. As shown [12], regulation of the number of arms could be attained by varying the molar ratio of reagents, polystyryllithium to fullerene, and introducing a complex-forming agent. As a result, both research teams [10–12] prepared the fullerene core PS stars with narrow molecular weight distribution, M_w/M_n=1.01–1.09; moreover, the identical result has been obtained, viz.: in nonpolar solvents, the PS stars with up to six arms only could be prepared.

The physical properties of such star-like systems may be associated to large extent with segmental motion in the chains. In turn, a special dynamic behavior may be expected for C_{60}-bound polymer because of both covalent attachment of chains to ‘massive’ fullerene balls and possible non-chemical chain/C_{60} interactions.

It is known that polymer stars may manifest sometimes the peculiarities in relaxation properties, e.g. breakdown of time-temperature superposition with a slight increase in the activation energy for segmental motion [14]. Meanwhile, no such effects have been observed for star-like or branched PS (without fullerene) [15, 16]; in the work [17], that is considered for PS as an open question. There was no difference in glass transition temperatures of PS and C_{60}-end-capped PS [5]. When grafting C_{60} to PS benzene rings, T_g increased but still remained the usual narrow glass transition range, $\Delta T_g \leq 10$ K [4].

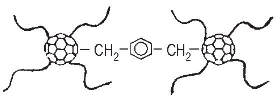
In this communication, we report on the peculiarities in segmental dynamics around T_g in fullerene-containing polymers, namely, in well-defined FSPS.

Experimental

Samples and their characterization

The samples studied and their molecular mass (MM) characteristics are given in Table 1. Linear oligo- or polystyrenes with narrow MM distribution, $M_w/M_n \approx 1.03–1.04$, and the values of $M_w \approx 4 \cdot 10^2$, $1.5 \cdot 10^3$, $5 \cdot 10^3$ and $7 \cdot 10^3$ were synthesized by anionic polymerization as described in [18]. The fullerenes C_{60} (99%) and C_{60}/C_{70} (4:1) were used for preparing the stars and blend. The molecular LF blend was obtained by mixing both components in toluene solution and holding it in vacuum. The FSPS samples were synthesized by joining of ‘living’ poly(styryllithium) (PSL) chains with the indicated preset lengths to the fullerene as it has been reported previously [6, 7, 12]. At the PSL/C_{60} ratio of 7:1 or 4:1, the 6- or 4-arm FSPS samples have been obtained, respectively. Thus, in both the synthesized stars and their linear precursors the lengths of arms and free chains were identical, i.e. equaled about one-half or two, or 6-9 Kuhn statistical segments, respectively, since the longitudinal size of this segment for PS is equal to 2 nm and corresponds to $M_w \approx 800$ [19]. All the experiments were carried out under the high purity conditions required for anionic polymerization [13].

In addition, the anisometric molecules (S15AM) were prepared by reaction of two FSPS15 stars with $Br–CH_2–C_6H_4–CH_2–Br$:



The powdery samples obtained were dried at 40°C in vacuum to constant weight. Covalent attachment of PS chains to the fullerene was corroborated by the ^{13}C NMR spectra whereas the light scattering and birefringence experiments indicated multiple substitution at C_{60} in the FSPS samples. The branching degree in the stars, i.e. the number of their arms, was estimated by comparison of the diffusion coefficients for the star-like PS and its linear analog having the same MM [12].

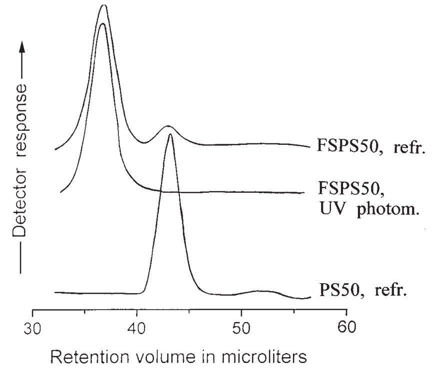


Fig. 1 GPC plots for PS50 and FSPS50 samples obtained with the refractometer and UV photometer (λ=330 nm) detectors

Gel Permeation Chromatography (GPC), with ultrastyrogel 1000 column and chloroform as an eluent, and using the refractive index and light scattering UV photometer (λ=330 nm) detectors, was utilized for characterization the stars. GPC analysis manifested predominance of the main product in an each of the stars but indicated also their complicated compositions. Thus, the chromatograms in Fig. 1 show that the FSPS50 sample retained the narrow molecular-weight distribution but incorporated ca. 10% linear PS. The FSPS15 sample consisted of about 70% main product and also included PS15 and mono-substituted PS-C_{60}. The most complex composition was found for the S15AM sample, viz. 35% S15AM, 40% FSPS15, and 25% PS15 and mono-substituted PS-C_{60}. Of importance, nevertheless, that PS chains, both grafted and free, retained invariable in length within an each sample.

DSC analysis

The DSC curves were measured over the range from 200 K to 400 K by using the Perkin Elmer DSC-2 apparatus that was calibrated with water (273.1 K), cyclohexane (279.6 K) and indium (429.8 K). The heat capacity scale was calibrated using sapphire. The experiments were carried out under nitrogen or helium atmosphere with the rate v=10 K min^{-1} at scan I, and then with v=2.5, 5, 10 or 20 K min^{-1} at the subsequent scans. Cooling from 400 K to 200 K was carried out every time with v=320 K min^{-1}.

The T_g values were recorded at the half-height of heat capacity step ΔC_p; the onset, T'_g, and completion, T''_g, temperatures of glass transition range $\Delta T_g = T''_g - T'_g$, and heat capacity $C_p(T)$ were also measured. By displacement of the temperatures , T'_g, T_g or T''_g when varying the heating rate, with subsequent using the linear ln$v$ *vs.* T^{-1} (K^{-1}) dependencies obtained and the formula [19]:

$$Q = -R\,\mathrm{d}(\ln v)/\mathrm{d}(T^{-1}) \tag{1}$$

the effective activation energy of segmental motion Q and its dispersion within glass transition were estimated. Moreover, in case the Q value remained practically invariable, as determined from T_g, T'_g and T''_g, the volume V_{coop} of polymer participating in the motional unit event (‘the cooperatively rearranging region volume’) could be determined by Donth’s formula [20]:

$$V_{coop} = kT_g^2 \Delta C_p^{-1}/\rho(\delta T)^2 \tag{2}$$

where $\Delta C_p^{-1} = \Delta C_p/[C_p(T<T_g)C_p(T>T_g)]$, ρ is a polymer density, $C_p(T<T_g)$ and $C_p(T>T_g)$ are heat capacities just before and after the heat capacity step at T_g, and $\delta T = \Delta T_g/2$ as measured on cooling from well above T_g with the rate v=5 K min^{-1}. The accuracy of Q and V_{coop} estimations were of ca. 10% and 20%, respectively. These both characteristics are of special significance for evaluation of the cooperativity degree of segmental motion in glass transition.

Results and discussion

For all star-like and blend samples, anomalous behavior of the glass transition, as compared to that for linear PS, was found, and Fig. 2a shows how the ΔT_g range broadens, from 6 K to 20 K, in the samples FSPS50, FSPS50* and LF blend with the longest chains. However, the difference is that this broadening takes place towards the lower temperature for the blend but to higher temperature for the stars. As the glass transition range deviates from its ‘usual’ temperature position, the Q values decrease to some extent, from ca.450 kJ mol^{-1} to 250–350 kJ mol^{-1}. Moreover, a two-stage ΔC_p step could be observed. At the same time, the heat capacity step remains at approximately the same magnitude as for the linear PS precursor.

The same effect of high-temperature displacement and broadening of glass transition was also observed for the stars with the shorter PS chains (Fig. 2b). In this case, however, ΔC_p step at T_g, substantially decreased, i.e. a partial suppression of segmental motion occurred.

Interestingly, the S15AM sample manifested a special thermal behavior: the doublet endothermic peak, at ‘usual’ and increased glass transition temperatures, was observed at scan I but at scan II, i.e. at heating after fast cooling this sample from 400 K, ΔT_g range

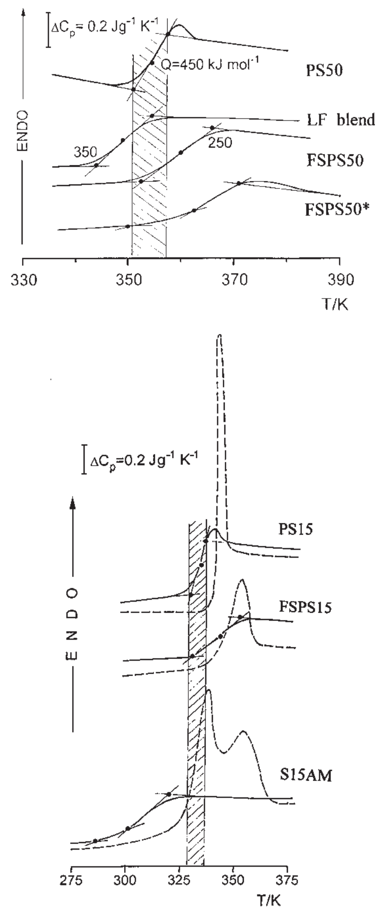


Fig. 2 DSC curves obtained at heating rate v=10 K min^{-1} for (a) PS50, LF blend, FSPS50 and FSPS50* samples, and (b) PS15, FSPS15 and S15AM samples. Dashed lines- scan I, solid lines- scan II, after cooling from 400 K to 200 K with v=320 K min^{-1}. The hatched stripe designates the glass transition range for linear PS. The energies Q estimated at indicated temperatures are given in Fig. 2a

additionally broadened and much shifted to lower temperatures, nearly to the β-relaxation temperature region.

Figures 3–5 demonstrate the peculiarities of glass transition kinetics and pronounced heterogeneity of segmental dynamics within the ΔT_g range found for the 4-arm stars. As seen in Fig. 3, the parallel shift of the ΔC_P step with heating rate was observed for linear PS whereas different T_g', T_g and T_g'' displacements were observed for the star-like sample. It resulted in quite different slopes of the ln$v$ *vs.* T^{-1} plots (Fig. 4). Calculations of the activation energies showed an absence of noticeable Q dispersion within narrow glass transition range for linear PS where Q = 350–400 kJ mol^{-1} ; moreover, the

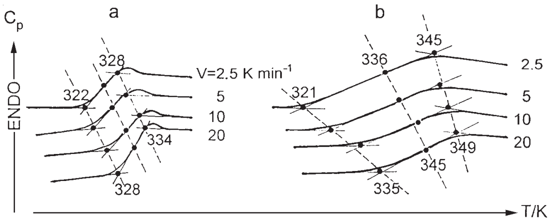


Fig. 3 DSC curves obtained at scan II and indicated heating rates for (a) PS15 and (b) FSPS15 samples

high value of V_{coop}= 5 nm^3, typical of cooperative segmental relaxations in polymers [19], was observed. At the same time, for the relevant FSPS15 star, the pronounced dispersion of Q values, from 140 kJ mol^{-1} up to 600 kJ mol^{-1}, within the temperature region of glass transition was observed.

In the case of the quenched S15AM sample with the star-like but anisotropic molecules , a new effect was found: besides decreasing T_g, the parameters Q and V_{coop} dropped by three folds, to 150–180 kJ mol^{-1} and 1.7 nm^3, respectively (Fig. 5).

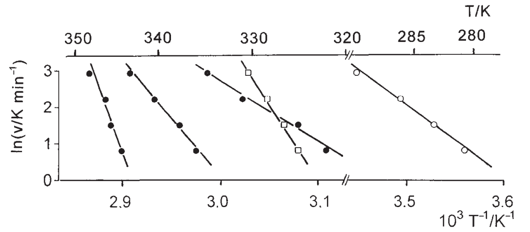


Fig. 4 Glass transition temperatures *vs*. ln$v$ dependencies obtained for FSPS15 (T_g, T_g', T_g''), PS15 and S15AM (T_g) samples. ● – FSPS15; □ – PS15 o – S15 AM

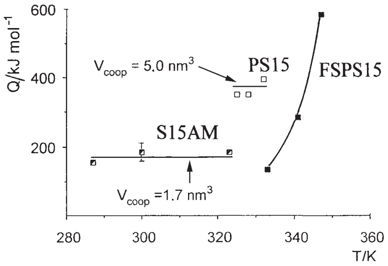


Fig. 5 Distribution of the activation energies for segmental motion within glass transition range in PS15, FSPS15 and S15AM samples. The V_{coop} values estimated are also given

Finally, if the shortest linear oligomer (PS4) was characterized by the increased value of ΔC_P=0.4 J g^{-1} K^{-1} and T_g=246 K, for the relevant star-like FSPS4 sample, the glass transition disappeared on the DSC curve, i.e. total suppression of segmental motion took place due to grafting the oligomer chains to the fullerene (this DSC curve is not given here).

The above results may be understood proceeding from (a) the concept of common segmental nature of glass (α-) and β-relaxations in flexible chain polymers, and (b) the idea about two different kinds, covalent and non-chemical, of PS-fullerene interactions.

As proved experimentally [19, 21–23], the unit events of α- and β-relaxations might be considered as the intermolecularly cooperative or independent rotatory motions, respectively, in chain sections equal in length to Kuhn statistical segment. At low frequencies, the degree of motional cooperativity in the glass transition, Z, turned out to be equal, for different flexible chain polymers, to $Z=Q_\alpha/Q_\beta \approx V_{\mathrm{coop}}/V_s \approx 4\pm1$ where V_s is a Kuhn segment volume. Thus, for linear PS, $Z\approx4$, $Q_\alpha=(420\pm40)$ kJ mol^{-1} and $Q_\beta=(100–110)$ kJ mol^{-1} [19].

Table 1 The studied linear and fullerene core star-like polystyrenes

Sample	Structure	M_w	M_w/M_n
PS4	linear PS	400	1.04
PS15	linear PS	1500	1.03
PS50	linear PS	5000	1.03
LF blend	linear PS/C_{60} molecular blend [a]	7000	1.01
FSPS4	4-arm C_{60}–core star PS[b]	400[c]	1.04
FSPS15	4-arm C_{60}–core star PS[b]	1500[c]	1.03
S15AM	Anisometric molecule including two FSPS15 stars	1500[c]	
FSPS50	6-arm C_{60}–core star PS[b]	5000[c]	1.03
FSPS50*	6-arm C_{60}/C_{70}–core star PS[b]	5000[c]	1.03

[a] With 6.7 wt.-% C_{60} in 100 g of blend

[b] Star-like PS samples contained, besides a main product, also some quantities of linear PS and monosubstituted PS-C_{60} (see text); however, both grafted and free PS chains were of the same preset length in each sample

[c] M_w values for the stars relate to one arm

Loosened chain packing or the presence of foreign molecules in a polymer system may result in a partial or total breakdown of intermolecular cooperativity of segmental motions, i.e. in a drop in Q, V_{coop} and T_g values. Then, in a common case, the β-relaxation parameters, Q_β and T_β, have to be considered as the lowest limits for the parameters of such ‘anomalous’ glass transition. At the same time, if the foreign molecules are introduced into a polymer, and they are characterized by the substantially larger value of a solubility parameter $\delta=(E_C/V_M)^{1/2}$ [E_C is a cohesion energy, V_M is a molar volume] as compared to that for a main polymer, reduction of Q and V_{coop} values may also be accompanied with T_g increasing [19, 24, 25]. It is just our case since E_C=196 kJ mol^{-1} [26] and δ=21 (J cm^{-3})$^{1/2}$ for C_{60} whereas δ=18.6 (J cm^{-3})$^{1/2}$ for PS [19].

Thus, such effects as displacement of the glass transition to lower or higher temperatures, with decreasing the Q values (Fig. 2) or simultaneous drop in T_g , Q and

V_{coop} values, for the quenched S15AM sample (Fig. 5), entirely correspond to the above considerations. The latter case is especially demonstrative: owing to anisometric form of the molecules and rapid cooling of the S15AM sample from well above T_g, loosened molecular packing and collapse of intermolecular cooperativity of segmental motion in the grafted oligostyrene chains occurred. Therefore, the values of T_g, Q and V_{coop} turned out to be rather close to the β-relaxation parameters for the relevant linear oligostyrene [19].

On the other hand, the covalent attaching of PS chains to the fullerene may result in another effect. First, unlike the PS/C_{60} blends where microphase separation with fullerene crystallization takes place, a totally homogeneous nanometer-scale structure is formed on grafting the PS chains to the fullerene [5]. The direct influence of grafting is some suppression of movement in the star arms, at least for the first attached chain segment. This condition obviously increases the activation energy of cooperative segmental motion in the FSPS15 sample up to 600 kJ mol^{-1} (Fig. 5), and causes the disappearance of glass transition in the FSPS4 sample with the shortest arms. Nevertheless, the indirect influence of chain grafting, which leads to enhanced non-covalent PS-C_{60} interactions, is also to be taken into account. Presumably, both some loosening of molecular packing and sharp reduction of such interactions provided the cardinal changes in glass transition characteristics for quenched S15AM sample, at the second scanning (Fig. 2b).

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