Physics of the Solid State, 2024, Vol. 66, No. 2

12,13

Dependence of the sizes of associates in the structure of an amorphous polymer on thermal history

© V.M. Egorov, V.A. Ryzhov, A.K. Borisov

Ioffe Institute,
St. Petersburg, Russia

E-mail: victor_egorov1@inbox.ru

Received December 24, 2023
Revised December 24, 2023
Accepted December 25, 2023

Using the methods of long-wave infrared spectroscopy and differential scanning calorimetry, the influence of thermal history on nano-sized regions of amorphous atactic polystyrene was studied. The spectroscopic method revealed an increase in the concentration of polymer chain segments with stronger intermolecular interactions. The calorimetric method detected endothermic effects, the intensity of which depended on the thermal history of the polymer samples. Thermal effects were analyzed within the framework of the thermodynamic theory of diffuse phase transitions.

Keywords: Molecular dynamics, polystyrene, phase and relaxation transitions, heat capacity.

DOI: 10.61011/PSS.2024.02.57926.276

1. Introduction

The structure of crystallizing polymers at the supermolecular level was studied in sufficient detail, since its study is accessible by conventional structural methods. In particular, a wide range of crystalline supermolecular structures of folded and fibrillar design was studied in detail [1]. Less attention was paid to the study of the structure of amorphous polymers due to the low information of these methods and the supposed lack of structure, i. e., any order in the arrangement of polymer macromolecules in the amorphous state.

More thorough studies showed the presence of nanoscale regions in amorphous polymers that differ in some physical parameters from the bulk of the polymer. Thus, the results of studying amorphous polycarbonate using small-angle X-ray scattering (SAXS) showed the presence of inhomogeneities of size ~ 13 nm with hexagonal packing of individual sections of polymer chains inside these inhomogeneities [2]. A new development method in electron microscopy of amorphous polymers was the application of dark-field microscopy to such objects, which made it possible to observe nodular structures in amorphous polymers, including polystyrene. The size of such structures depended on the heat treatment conditions and ranged from ~ 10 nm to several tens of nanometers with long-term annealing [3]. It also turned out that the density of amorphous polymer decreases when quenched from a highly elastic state, and when annealed at a temperature below the glass transition point (T_g) continuously increases as the annealing temperature increases, which is apparently due to the increase noted above in the size of ordered regions having a higher density [4].

Many experimental data on the heat capacity of amorphous polymers when annealed below the glass transition point showed that during such annealing an endothermic peak appears above the glass transition step in the differential scanning calorimetry (DSC) curves for many amorphous polymers, the intensity of peak depends on the annealing time [5]. The traditional DSC method does not allow us to answer the question whether the nature of this endothermic peak and of the heat capacity step during glass transition is common or separate, corresponding to different processes. The occurrence of temperature-modulated differential scanning calorimetry (TMDSC) made it possible to resolve this issue [6,7]. As a result of numerous studies of various polymers using this method, it was possible to establish that the endothermic peak above the glass transition step relates to such thermodynamic transitions as crystallization and melting [8]. The glass transition step observed in the dependences of heat capacity on temperature is associated with the unfreezing of cooperative segmental mobility and has relaxation nature, not associated with change in latent energy and an irreversible change in the thermodynamic state of the polymer.

Thus, the above experimental data indicate the existence of nanoscale regions in amorphous polymers that differ from the bulk of the polymer. Such regions are also called as associates, which can conditionally be assimilated to imperfect crystal nuclei. When heated, such associates are partially or completely destroyed in the glass transition temperature range up to the temperature of the relaxation transition „liquid–liquid“, or T_{ll}-transition, which appears above T_g. The name of this transition is given by Boyer [9], and it indicates the transformation of liquid with a fixed structure into a true liquid state. The disintegration of associates during T_{ll}-transition can conditionally be considered as a process of local melting, since this process is accompanied by abrupt changes in thermodynamic characteristics — density, endothermic effect associated with latent energy, Experimental data and calculated parameters of heat capacity

N	Temperature of annealing	Time of annealing	$T_{\max}$	B	$\Delta C_{\max}$	q_0	ω	R
	K	min	K		J/gK	J/g	nm^3	nm
1	293	$2.9 \cdot 10^3$	341.0	38	0.025	0.75	240	3.86
2	293	$7.2 \cdot 10^3$	346.0	50	0.030	0.82	280	4.06
3	293	$7.8 \cdot 10^4$	356.0	75	0.045	0.85	430	4.68
4	313	$1.5 \cdot 10^4$	362.5	100	0.080	0.80	630	5.34
5	343	$1.2 \cdot 10^2$	370.0	150	0.080	0.82	950	6.08
6	353	$3.5 \cdot 10^1$	373.0	220	0.160	1.00	1090	6.36
7	353	$2.6 \cdot 10^2$	376.1	360	0.435	1.69	1060	6.30
8	353	$4.3 \cdot 10^2$	377.7	500	0.760	1.96	1280	6.71

order disturbances and amorphization, i. e. with a sharp change in parameters observed during a phase transition. A feature of this process is the blurred temperature, since the glass transition temperature ranges from several to several tens of degrees for different polymers.

In previous paper, using far infrared spectroscopy (FIRS), it was established [10] that conformational mobility in amorphous polystyrene is due to the mobility of individual segments of the polymer chain with a volume of $\sim 1.8\,\mathrm{nm}^3$, comparable to the volume of the statistical segment [5]. In this paper, an attempt was made to detect using this method changes in the concentration of such mobile segments during amorphous polymer annealing. Besides, the endothermic thermal effect observed by DSC was analyzed based on the standpoint of the thermodynamic theory of diffuse phase transitions. The mentioned theory makes it possible to estimate the size of areas whose destruction upon heating leads to a thermal effect.

2. Experiment

The atactic polystyrene with molecular weight $M \approx 3 \cdot 10^5$ was chosen as samples for the study. The samples were pre-quenched in air at temperature of 450 K, and then annealed at different temperatures for different times. Temperature-time annealing modes are indicated in the Table.

IR spectra were recorded on single-beam vacuum spectrometers with diffraction gratings from 10 to $150\,\mathrm{cm}^{-1}$ on device developed at St. Petersburg State University and modernized at the Ioffe Institute using OAP-7 receiver and a new filtration system. The resolution at a signal-to-noise ratio of about 100 was $1-2\,\mathrm{cm}^{-1}$. The accuracy of determining the frequency of the band maximum was $0.5-1\,\mathrm{cm}^{-1}$. The absorption coefficient is $k(\nu) = (t)^{-1} \cdot \ln(J_0/J)$, where J_0 and J — the intensities of radiation incident and transmitted through a sample of thickness t, respectively, was measured with an error of 5 to 10%. The spectra were measured for samples obtained in the form of films with thickness of 200 to $300\,\mu$m; measurements were carried out at room temperature.

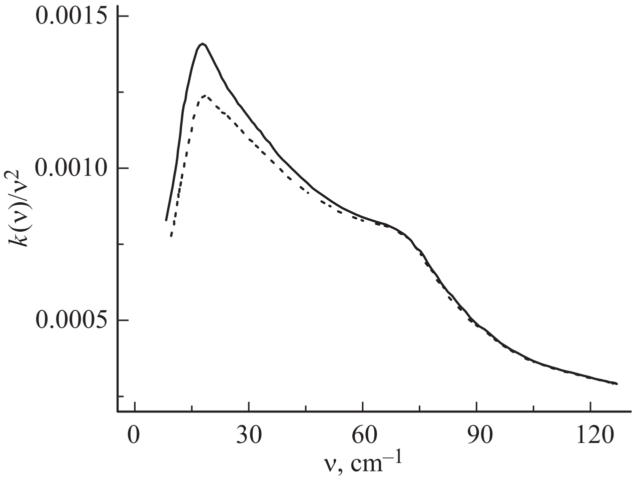

Figure 1. Excess density of vibrational states for samples of quenched (solid line) and annealed polystyrene № 7 (dashed line) in the FIR range.

Figure 1 shows IR spectra of quenched and annealed (№ 7) PS samples in the coordinates of the overdensity of vibrational states (ODVS) compared to the Debye density of vibrational states. The Figure shows decrease in the peak observed for the annealed sample in comparison with the peak recorded for the quenched one. We interpret the resulting peak reduction effect in accordance with the concepts of the theory of „cohesive" domains [12]. According to this theory, ODVS decreases with decrease in the number of polymer chain segments weakly bound by intermolecular van der Waals forces. With the unchained length and volume of the segment this indicates the increase in the concentration of segments with increased van der Waals interaction between chain segments, i. e. increase in the volume of associates.

Measurements of the temperature dependence of the heat capacity $C_p(T)$ were carried out on DSC „Perkin-Elmer" in dry nitrogen atmosphere in the range 280–450 K. The temperature scale of the device was calibrated by the melting points of indium (430 K) and ice (273.1 K), and the heat capacity scale was calibrated by the heat capacity of sapphire. The temperature reading accuracy was 0.1 K. The sample weight was 5 mg. The rate of temperature change was 5 K/min. To increase the accuracy of thermal effects determination in the glass transition region of polymers, a differential method was used, in which the sample was scanned in parallel with the measurement of reference sample, i. e. sapphire placed in the comparative chamber of the calorimeter. The relative error of the heat capacity measurement with this method was $\sim 0.5\%$.

Figure 2 shows DSC curves obtained by heating the pre-quenched and annealed PS samples. As can be seen from the Figure, in the curves of the annealed samples, along with the glass transition step, which is observed on both quenched and annealed samples, an endothermic effect appears. This effect in the form of spread-out peak can be identified by the difference between the DSC curves for annealed and quenched samples.

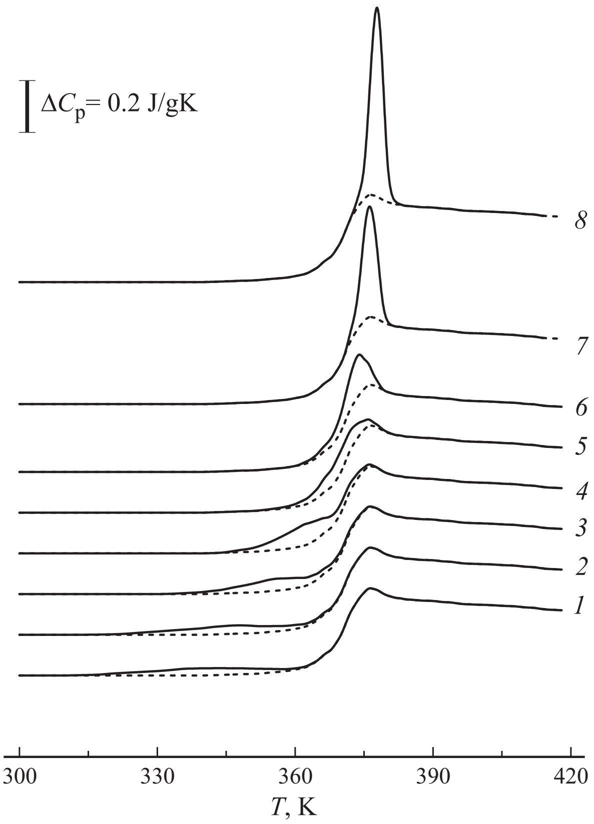

Figure 2. DSC curves obtained by heating annealed (solid lines) and quenched (dashed lines) PS samples. For designations, see the Table.

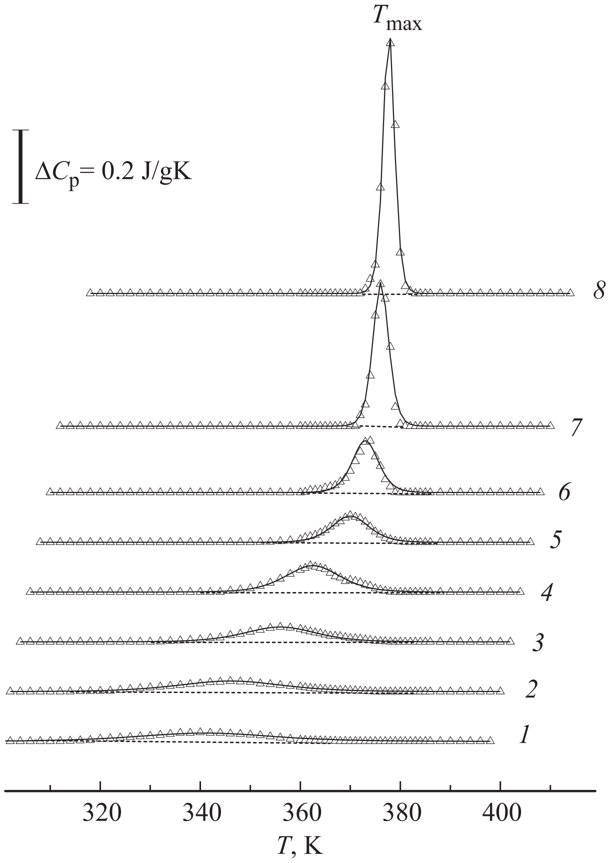

Figure 3. Endothermic peaks obtained from the difference between DSC curves of annealed and quenched samples. Dots — experimental data, lines — calculation results from the dependence {1}, dashed lines — base lines.

Figure 3 shows these selected peaks with the temperatures of the maxima $T_{\max}$indicated in the Table. Note that the shape of the peaks has its own features. It is clear from the Figure that with $T_{\max}$ increasing the amplitudes of the peaks or heat capacity maxima $\Delta C_{\max}$ increase, and Λ —shape of the peaks becomes narrower. The analysis of the peak shapes in the dependence of the heat capacity on temperature was carried out in accordance with the theory of spread out phase transitions according to the following relation [13]:

$$\Delta C_p(T) = 4\Delta C_{\max} \cdot \exp\left[B\left(T - T_{\max}\right)/T_{\max}\right] \times \left[1 + \exp[B(T - T_{\max})/T_{\max}]\right]^{-2}, \quad (1)$$

where $T_{\max}$ — peak maximum temperature, $\Delta C_{\max}$ — maximum heat capacity at $T = T_{\max}$, B — athermal parameter. As can be seen from the Figure, the experimental and calculated dependences practically coincide for all the studied samples.

The parameter B in the above relation (1) is related to the magnitude of the peak of heat capacity $\Delta C_{\max}$ as follows:

$$\Delta C_{\max} = q_0 B/4T_{\max}, \quad (2)$$

where q_0 — heat of transformation, and the elementary volume of transformation ω

$$B = \omega\rho q_0/kT_{\max}, \quad (3)$$

where k — Boltzmann constant, ρ — density. The parameter B is a structure-sensitive parameter, since it determines the volumes of the new phase in materials with diffuse phase transitions. From relation (2) one can find the values of the specific heat (enthalpy) of transformation, from relation (3) — elementary volume of transformation ω (density of atactic PS $\rho \sim 1.05\,\mathrm{g\cdot cm^{-3}}$ [1]).

3. Results and discussion

The results of calculations using these relations, given in the Table, show that the elementary volumes of transformation ω correlate with the above-mentioned linear dimensions of nodular structures in polystyrene [3]. To directly compare volumetric and linear characteristics, it is necessary to have an idea of the geometry of these nodular structures or associates.

Model ideas about the possible structure of ordered regions in amorphous polymers appeared much earlier than experimental data confirming the existence of such regions. The general question of the existence of micro- and nanoscale ordered formations in liquids for polymers, in contrast to low molecular weight substances, has a significant feature, namely, the chain structure of the polymer molecule, numbering hundreds and thousands of monomer links in the chain.

The first model — model of „stacked“ structure of amorphous polymer was proposed by Kargin and employees in 1957 [14]. The main idea of this model was that the polymer structure in the amorphous state shall be similar to its structure in the crystalline state. This idea is based on the principle of dense packing, which is satisfied by parallel stacking of chain molecules with varying degrees of this parallelism keeping. According to the authors, „stack“ is a separate set of parallel-laid polymer chains with alternating regions with increased intermolecular interaction between chains and regions with a high degree of disorder, and relatively low intermolecular interaction. Fibrils have such structure in amorphous-crystalline polymers have a similar structure, in which regions with increased intermolecular interaction are crystalline.

Electron microscopic data on the observation of nodular structures in amorphous polymers allowed us to put forward a model of the structure of amorphous polymers, described in detail by Yeh [15]. This model is based on the same idea of the similarity of the polymer structure in the amorphous and crystalline states. The difference between this model and the model described above is that the structure of nodules in the amorphous polymer is similar not to the fibrillar, but to the folded lamellar structure of the crystalline polymer.

Finally, note that Hoseman proposed a paracrystalline model of the structure of polymers as a whole [16]. The term „paracrystal“ in this model refers to a three-dimensional lattice, all three parameters of the latice cell of which are not constant, but obey some coordination statistics, the type of which determines the degree of molecular ordering from liquid to single crystal.

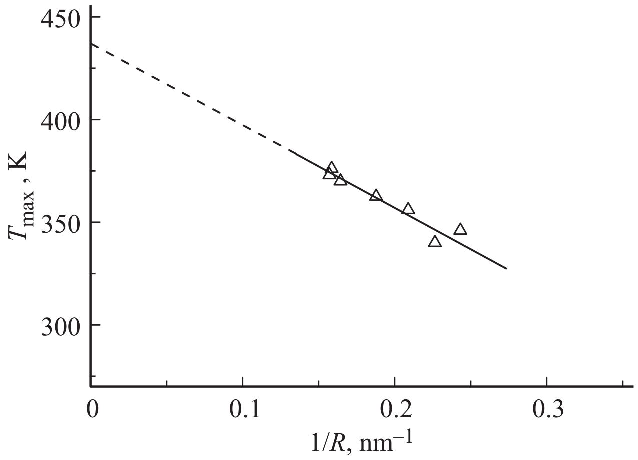

Figure 4. Temperature of the peak maximum of heat capacity vs. radius of the associate.

The data presented in the Table indicates a correlation between T_{max} and ω: the higher T_{max}, the greater the value ω. This correlation is typical for nanoobjects with linear dimensions less than 100 nm and represents the dependence of the phase transition temperature in such objects on size (the so-called scale dependence). In the general case, this dependence is described by the well-known Thomson–Gibbs relation [17]:

$$T_{max} = T_0(1 - A/R), \tag{4}$$

where T_0 — the limit temperature of phase transition in material of unlimited dimensions; T_{max} — temperature of phase transition in small particle; parameter A depends on the ratio of the surface and internal energy of this particle; R — the linear size of particle, such as the diameter or radius of droplet-shaped particle. In the coordinates $T_{max} = F(1/R)$, this dependence, at constant ratio of the surface and internal energy of the particle, is a linear function with pole T_0 at $R \to \infty$. The slope of this dependence is determined by the parameter A. Since the habit of associates in amorphous polystyrene is not yet established, the form of associates in the form of droplet-shaped particles is adopted in this paper, for them the particle radius was chosen as the parameter R. Its values, based on volumes ω are given in the Table.

Figure 4 shows the obtained dependence of T_{max} on R in the coordinates described above. When extrapolating $R \to \infty$, the value T_0 is within 436 ± 5 K, which, based on the literature data [5], practically coincides with the temperature interval 440–450 K of relaxation transition „liquid–liquid“ in polystyrene, i.e. $T_0 \approx T_{ll}$. Thus, the possibility of the existence of associates not only in the nanoscale range, but also in the micro- and macro-scale, up to the size of the tested samples or polymer products, is theoretically admitted. The difficulty in obtaining such samples is that here the annealing times become practically impossible.

4. Conclusion

The results of this paper allow us to make the following conclusions, useful for the practical use of the polymer. Firstly, it is necessary to expand the temperature range of the so-called „physical aging“, during which structural changes occur in the polymer without the participation of chemical processes (oxidation, destruction as a result of various effects), since the possibility of the existence of associates above the glass transition temperature is admitted T_g. This range should be supplemented by the temperature range T_g-T_{ll}. Secondly, when processing polymer materials by extrusion, pressing, mixing microphases in multicomponent polymer systems, and diffusion of plasticizers, it is necessary to know the low-temperature processing limit. Such limit is the temperature $T_0 \approx T_{ll}$, above which the polymer is in the true liquid state necessary for processing.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] B.Wunderlich. Macromolecular Physics, Volume 3: Academic Press. (1980). 363 p.
[2] Wen Lin, Ed. J. Kramer. J. Appl. Phys. **44**, 4288 (1973). DOI: 10.1063/1.1661953
[3] G.S.Y. Yeh. J. Macromol. Sci. B **6**, 451 (1972). DOI: 10.1080/00222347208219127
[4] M.F. Milagin, N.I. Shishkin. Polymer Science U.S.S.R. **14**, *2*, 400 (1972).
[5] V.A. Bershtein, V.M. Egorov. Differential Scanning Calorimetry of Polymers: Physics, Chemistry, Analysis, Technology. Ellis Horwood, N.Y. (1994). 253 p.
[6] C. Schick. In: Handbook of Thermal Analysis and Calorimetry / Ed. P.K. Gallagher. Applications to Polymers and Plastics. Elsevier Science, N.Y. (2002). V. 3. P. 713–808.
[7] B. Wunderlich. Prog. Polym. Sci. **28**, 383 (2003). DOI: 10.1016/s0079-6700(02)00085-0
[8] M.U.H. Joardder, Md.H. Bosunia, Md.M. Hasan, A.A. Ananno, A. Karim. Food Rev. Int. **39**, *1*, 1–22 (2023). DOI: 10.1080/87559129.2023.2204131
[9] R. Boyer (ed.). Transitions and Relaxation in Polymers. Wiley-Interscience, N.Y. (1966). 340 p.
[10] V.A. Ryzhov. Optics and Spectroscopy. **131**, *1*, 28 (2023). DOI: 10.61011/FTT.2024.02.57254.276
[11] G.A. Malygin. Phys. Usp. **44**, 173 (2001). DOI: 10.3367/UFNr.0171.200102c.0187
[12] E. Duval, T. Achibat, A. Boukenter, B. Varrel, R. Calemczuk, B. Salce. J. Non-Cryst. Solids. **190**, *3*, 258 (1995). DOI: 10.1016/0022-3093(95)00274-X
[13] G.A. Malygin. FTT **43**, *10*, 1911 (2001). (in Russian).
[14] V.A. Kargin, A.I. Kitaigorodsky, G.L. Slonimsky. Kolloid. zhurn. **19**, *2*, 131 (1957). (in Russian).
[15] G.S.Y. Yeh. J. Macromol. Sci. B **6**, 465 (1972). DOI: 10.1080/00222347208219128
[16] R. Hosemann. Polymer **3**, 349 (1962). DOI: 10.1016/0032-3861(62)90093-9
[17] Weihong Qi. Acc. Chem. Res. **49**, *9*, 1587 (2016). DOI: 10.1021/acs.accounts.6b00205

Translated by I.Mazurov