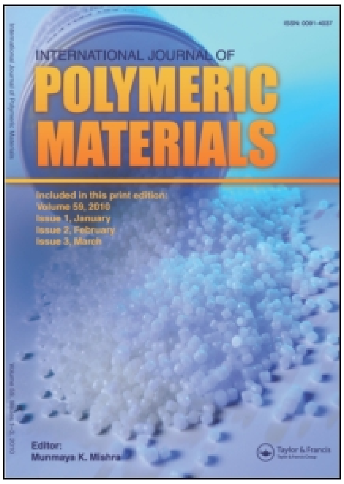

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Structural and Mechanical Behavior of Polymethylmethacrylate Containing Diethyl Siloxane Oligomer

M. S. Arzhakov[a]; S. A. Arzhakov[a]; V. V. Gustov[b]; I. B. Kevdina[b]; V. P. Shantarovich[b]
[a] Polymer Department, Faculty of Chemistry, Lomonosov Moscow State University, Moscow, Russia [b] Semenov Institute of Chemical Physics, Moscow, Russia

To cite this Article Arzhakov, M. S. , Arzhakov, S. A. , Gustov, V. V. , Kevdina, I. B. and Shantarovich, V. P.(1998) 'Structural and Mechanical Behavior of Polymethylmethacrylate Containing Diethyl Siloxane Oligomer', International Journal of Polymeric Materials, 39: 3, 319 — 333

To link to this Article: DOI: 10.1080/00914039808039776

URL: http://dx.doi.org/10.1080/00914039808039776

Intern. J. Polymeric Mater., 1998, Vol. 39, pp. 319–333
Reprints available directly from the publisher
Photocopying permitted by license only

Structural and Mechanical Behavior of Polymethylmethacrylate Containing Diethyl Siloxane Oligomer

M. S. ARZHAKOV[a], S. A. ARZHAKOV[a], V. V. GUSTOV[b],
I. B. KEVDINA[b] and V. P. SHANTAROVICH[b]

[a]*Polymer Department, Faculty of Chemistry, Lomonosov Moscow State University, Vorob'evy Gory, Moscow, 119899 Russia;*
[b]*Semenov Institute of Chemical Physics, Kosygina, 4, Moscow, 117977 Russia*

(Received 2 May 1997)

Using the method of positron annihilation, structural changes induced by introduction of diethyl siloxane oligomers to PMMA were studied. The effect of these structural changes on the mechanical behavior of PMMA was discussed in terms of structural inhomogeneity of PMMA: existence of structural sublevels with different packing density and ordering. Deformation of glassy polymers at low strains as well as such mechanical characteristics as yield stress and contribution of low-temperature component to the temperature-induced relaxation of plastic deformation were shown to be controlled by segmental mobility in structural sublevels with a lower packing density.

Keywords: Polymer glasses; PMMA; low-molecular-mass additives; structure; mechanical properties

INTRODUCTION

Structural pattern of plastic deformation and further temperature-induced relaxation of glassy polymers was discussed in [1,2]. Structure of glassy polymer is presented as a set of structural sublevels with different packing density and ordering. Local segmental mobility within a certain structural sublevel is controlled by local packing density in this region. From this standpoint, mechanical behavior of glassy polymers may be treated in terms of gradual involvement of various structural sublevels to deformation and relaxation. In this case, any changes in initial polymer structure and concomitant changes in packing density and ordering within the above sublevels should have a certain effect on both mechanical and relaxation properties of glassy polymers.

Structural changes in polymer may be accomplished by introduction of incompatible low-molecular-mass compounds, which are unable to produce an uniform distribution in polymer volume. This approach was formalized in terms of structural plasticization of polymers [3, 4]. Structural plasticization may be rationalized as follows: a low-molecular-mass compound with a low thermodynamic affinity to polymer is localized within local structural regions at boundaries between supramolecular or suprasegmental structures of glassy polymer. In this case, within these regions, changes in mobility of macromolecules or their fragments is observed, and this has a certain effect on mechanical behavior of polymer material. For PMMA, diethyl siloxane oligomers (DES) can be used as such low-molecular-mass modifying agents [5].

In this work, structural changes in PMMA induced by introduction of DES were studied, and the effect of these structural changes on polymer mechanical response was examined. The aim of this work was to elucidate the role of different sublevels of structural inhomogeneity of glassy polymer in polymer mechanical behavior.

As was shown in recent works [6–8], the method of positron annihilation is widely used to study polymer structure. Model experiments showed that positron and positronium occupy ordered and disordered polymer regions, respectively. Maximal dimensions of structural inhomogeneities in polymer detected by this method are equal to tens of nanometers and are controlled by mobility of positron and positronium in ordered regions. Taking into account that structure of most of glassy polymers satisfy this requirement [the dimensions of ordered regions do not exceed several nanometers (for example, [9, 10])], concentration and effective dimensions of free volume microregions in ordered and disordered sublevels in oligo (ester acrylate) as well as the effect of intermolecular interaction and size of oligomer blocks on the content of free volume microregions were examined [8]. This experimental evidence was used to study structural changes in PMMA during plastic deformation and temperature-induced relaxation [7]. The method of positron annihilation was also used for characterization of structural changes in polymers containing low concentration of low-molecular-mass additives [11, 12].

EXPERIMENTAL

We studied PMMA prepared by bulk polymerization ($M_w = 1{,}500{,}000$). Structure modification of PMMA samples involved introduction of diethyl siloxane oligomer (DES) with 5 repeat units during polymerization. The content of DES in PMMA was 0.1, 0.5, and 1.3 wt%.

Glass transition temperature was estimated by differential scanning calorimetry using a DuPont 1090 thermal analyzer. Heating rate was 20 K/min. Glass transition temperature was equal to 393 K for all samples.

Constancy of glass transition temperature at all concentrations of DES in PMMA as well as turbidity of all PMMA samples, containing DES, suggest a thermodynamic incompatibility between this low-molecular-mass compound and polymer matrix.

Thermostimulated luminescence analysis was carried out using TGL-68 [13]. Samples were exposed to radiation using γ-ray source ^{60}Co up to 10 kGy at temperature of liquid N_2. All measurements were carried out at 80 – 375 K, heating rate was 10 K/min. Thermostimulated luminescence data are presented in Figure 1. As follows from Figure 1, in the case of PMMA/DES systems, DES manifests itself as a narrow peak at 135 – 140 K (curves 2 – 4). This peak is likely to be related to glass transition of this additive in polymer matrix. Note that intensity of this peak shows a linear increase with increasing the content of DES in PMMA.

For mechanical tests, the samples were cylinders with a height of 30 mm and a diameter of 15 mm. Prior to testing, all polymer samples were annealed at temperatures above T_g by 10–15° and were slowly cooled down to room temperature.

The samples of initial PMMA and PMMA, containing DES, were uniaxially compressed at 293 K with a strain rate of 0.1 mm/min using an UTS-100 tensile machine (Germany). Then, the samples were cooled with liquid nitrogen in a stressed state. Finally, the free-standing samples were heated from 213 K at a heating rate of 1 K/min. The

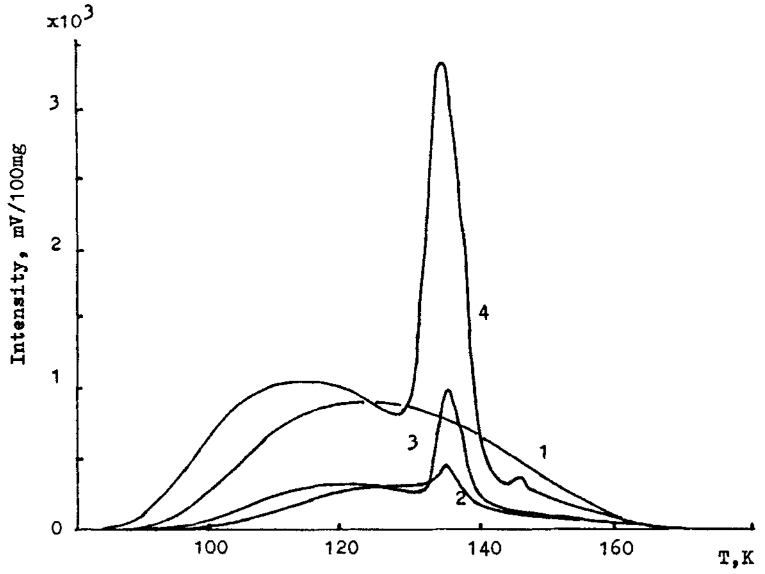

FIGURE 1 Thermostimulated luminiscence curves of PMMA (1) and PMMA with 0.1 (2), 0.5 (3), and 1.3 wt.% of DES (4).

relaxation (recovery) of residual plastic deformation $\varepsilon_{\mathrm{res}}$ was estimated by measuring the height of the test samples with an accuracy of ± 0.001 mm.

Initial structure of PMMA and PMMA with DES was studied by positron annihilation lifetime spectroscopy. Lifetime measurements were carried out using a conventional ORTEC spectrometer with a time-resolution (full width on a half maximum of the prompt coincidence curve) of 230 ps. In our experiments, ^{22}Na sandwiched between two sheets of nickel foil was used as a positron source. Annihilation in the source material, background of random coincidences and resolution function were examined using a well-known POSITRONFIT program [11].

Three-component analysis of lifetime distribution of annihilation radiation involved calculations of positron annihilation lifetimes $\tau_i (i = 1-3)$ and intensities of the corresponding components $I_i (i = 1-3)$ in measured distributions. Reliability of this examination was verified by parameter χ^2/ν with a standard deviation of 0.072. Integral statistics for the curve of delayed coincidences was $(0.5 - 1.0) \times 10^6$ counts.

RESULTS AND DISCUSSION

Figure 2 shows the dependence of yield stress σ_y on DES content in PMMA for uniaxial compression of polymer samples. As follows from Figure 2, at 0.1 wt % of DES in PMMA, an increase in σ_y is observed. With increasing concentration of DES in polymer, σ_y decreases.

This behavior (maximum in concentration dependencies of σ_y) is quite characteristic of polymers plasticized with thermodynamically compatible low-molecular-mas compounds. Introduction of minor amounts of plasticizing agents into polymer matrix is accompanied by a concomitant increase in elastic modulus and yield stress σ_y. This phenomenon is referred to as antiplasticization. With further increase in the content of plasticizing agent, mechanical properties of plasticized polymers are much lower as compared with initial polymer. According to [14, 15], antiplasticization is rationalized by a decrease in polymer free volume and increase in polymer packing density giving rise to a dramatic inhibition of mobility of polymer chains.

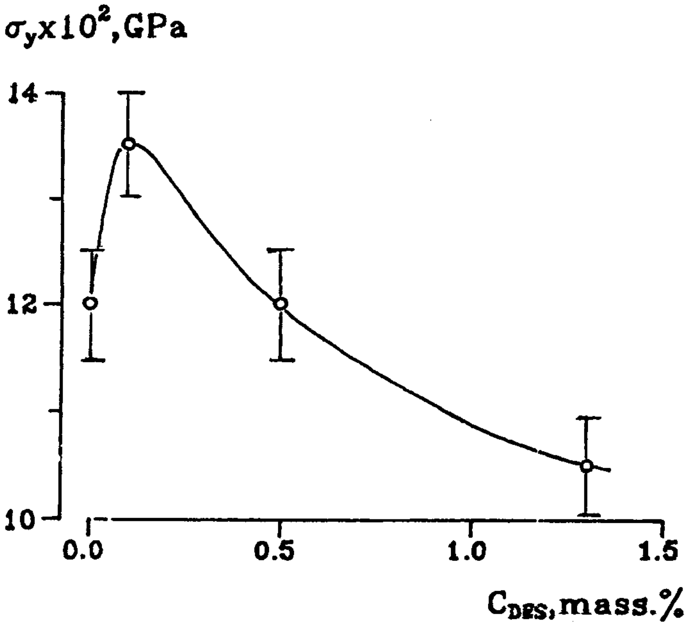

FIGURE 2 Dependence of yield stress σ_y of PMMA on DES content.

Mechanical behavior of polymer containing incompatible low-molecular-mass additives is treated in terms of structural phenomena [3–5]. According to this approach, incompatible low-molecular-mass additive occupies structural regions with lowered packing density and increased free volume. Hence, an increase in σ_y with introduction of 0.1 wt % of DES may be related to an increase in density of these structural regions and inhibition of molecular mobility in them. As concentration of DES increases to 1.3 wt %, a decrease in σ_y is associated with loosening of these microregions and enhancement of mobility of macromolecules in them.

Experimental evidence concerning temperature-induced relaxation of plastic deformation in PMMA is presented in Figure 3. Relaxation is seen to take place in two well-defined temperature regions: at temperatures below glass transition temperature (low-temperature component ε_1) and in the temperature region of glass transition (high-temperature component ε_2). Figure 3a shows both components for PMMA samples containing 1.3 wt % of DES.

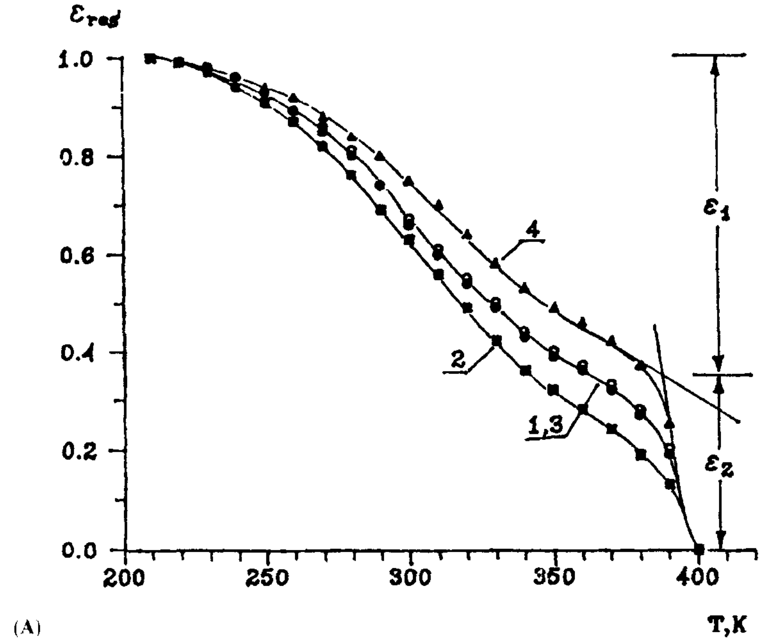

FIGURE 3 Recovery of residual deformation ε_{rec} of PMMA (1) and PMMA with 0.1 (2), 0.5 (3), and 1.3 wt.% of DES (4). Strain: 20 (A), 30 (B) and 50 % (C).

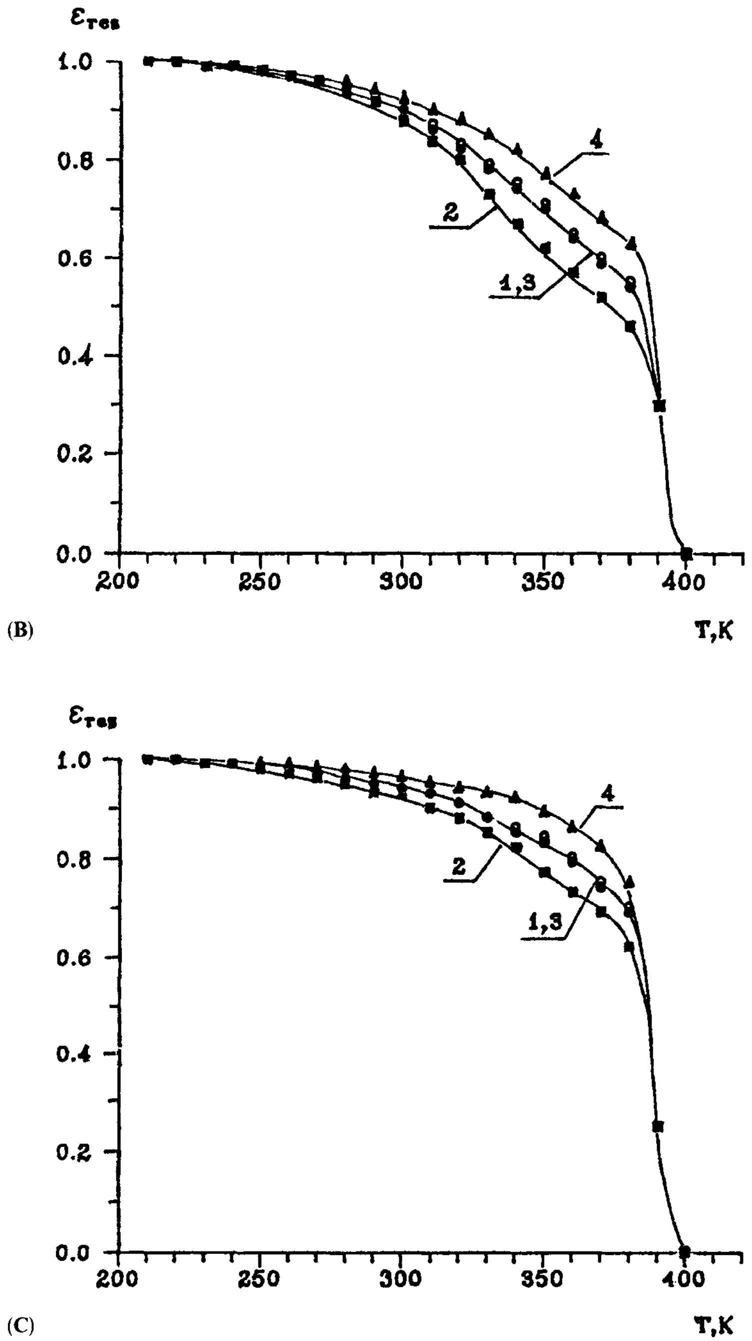

FIGURE 3 (Continued).

At the present time, two alternative approaches allow explanation of this two-step character of temperature-induced relaxation of plastic deformation: gradual recovery of short-scale plastic shear transformations and excited chain conformations [16, 17] (i) and structural heterogeneity of glassy polymers [1, 2, 5] (ii).

According to the approach concerning structural heterogeneity of glassy polymers, structure of a glassy polymer is presented as a set of structural sublevels with different packing density and ordering. Each of these sublevels is associated with its own relaxation time and activation energy of segmental mobility. Hence, at each temperature below glass transition temperature T_g, within a given sublevel, a local segmental mobility is allowed. With increasing temperature, structural sublevels with higher packing density show their segmental mobility; and, finally, at glass transition point, the whole sample is involved in segmental mobility.

In the case of the plastically deformed polymer samples, with increasing temperature, a gradual appearance of segmental mobility in structural sublevels with higher packing density is accompanied by a gradual recovery of plastic deformation via transition of excited chain conformations to initial equilibrium state within above structural sublevels. A complete recovery of plastic deformation is accomplished at T_g, when all sublevels are involved in segmental mobility.

Contribution of low-temperature component ε_1 to total recovery of plastic deformation was estimated from Figure 3. The dependencies of contribution of ε_1 to total recovery $\varepsilon_1/(\varepsilon_1 + \varepsilon_2)$ on the content of DES in PMMA are presented in Figure 4. Comparison between Figures 2 and 4 suggests similar changes in σ_y and $\varepsilon_1/(\varepsilon_1 + \varepsilon_2)$ with increasing DES content in PMMA.

Note that examination of the effect of deformation temperature on E_o, σ_y, and $\varepsilon_1/(\varepsilon_1 + \varepsilon_2)$ [1] suggests that these parameters are closely related to local segmental mobility within structural sublevels with lower packing density. Hence, the effect of concentration of DES in PMMA on σ_y and $\varepsilon_1/(\varepsilon_1 + \varepsilon_2)$ is likely to be related to changes in segmental mobility in the above structural sublevels because of changes in packing density and fractional content of free volume.

To verify this assumption, the positron annihilation lifetime technique was used to follow changes on elementary free volume in polymer induced by introduction of DES into PMMA samples. Annihilation characteristics for pure PMMA and PMMA, containing DES, are summarized in Table I. The component with lifetime τ_2 and intensity I_2 stands for preferential localization of positrons in free volume microregions within structural sublevels with an increased packing

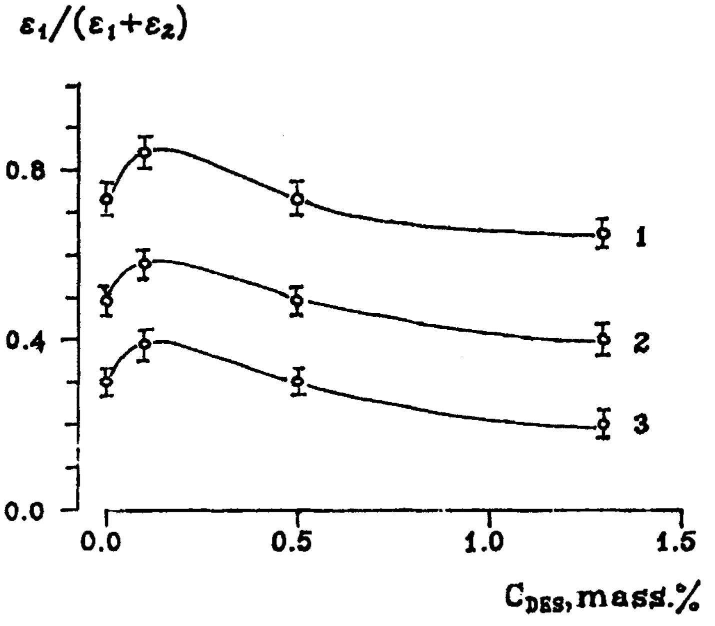

FIGURE 4 Contribution of low-temperature component ε_1 to total recovery of residual deformation $\varepsilon_1/(\varepsilon_1+\varepsilon_2)$ on the content of DES in PMMA. Strain: 20 (1), 30 (2), and 50 % (3).

TABLE I Annihilation characteristics of PMMA containing DES for three-component analysis of positron lifetime spectra

DES Content	*Annihilation characteristics*					
in PMMA wt %	τ_1	I_1	τ_2	I_2	τ_3	I_3
0	0.262 ±0.008	58.11 ±3.20	0.610 ±0.036	30.31 ±2.67	2.025 ±0.058	11.58 ±0.69
0.1	0.266 ±0.009	58.97 ±3.27	0.651 ±0.042	29.67 ±2.67	2.213 ±0.075	11.36 ±0.79
0.5	0.246 ±0.013	47.06 ±5.25	0.527 ±0.037	35.60 ±4.70	1.915 ±0.040	17.36 ±0.72
1.3	0.243 ±0.012	44.21 ±4.59	0.513 ±0.029	37.91 ±4.14	1.905 ±0.032	17.88 ±0.59

density, whereas the component with lifetime τ_3 and intensity I_3 is associated with a preferential localization of positronium in microregions involved in structural sublevels with a reduced packing density. Parameters I_2 and τ_2 are associated with concentration N_+ and effective radius R_+ of free volume microregions for the regions with increased packing density, and I_3 and τ_3 – with corresponding values for the structural sublevels with reduced packing density [6, 8].

As follows from Table I, introduction of 0.1 wt % of DES into PMMA has no effect on annihilation characteristics. As concentration of DES in PMMA increases, a slight increase in I_2 and a sharp increase in I_3 are observed. The increased values of intensities I_2 and I_3 suggest that free volume increases, i. e., introduction of low-molecular-mass additive is accompanied by structural loosening. As evidenced by more pronounced changes in I_3 as compared with I_2, this loosening is primarily associated with structural sublevels with lower packing density.

Correlation between annihilation characteristics and dimensions and concentration of free volume microregions was studied by many authors and, for example, was described in [6]. In this case, the rate of positron trapping in defects v_+ is related to intensity I_2 of intermediate component $\tau_2 = 1/\lambda_2$ of lifetime distribution of annihilation radiation by the following relationship:

$$v_+ = (\lambda_f^+ - \lambda_2)I_2/[(1-Q)-I_2] \tag{1}$$

$$v_+ = 4\pi D_+ R_+ N_+ \tag{2}$$

where R_+ and N_+ stand for dimensions and concentration of free volume regions occupied by positrons, and λ_f^+ is the rate of free positron annihilation.

For positronium,

$$v_{Ps} = (\lambda_f^+ - \lambda_3)(4I_3/3)/(Q - 4I_3/3) \tag{3}$$

$$v_{Ps} = 4\pi D_{Ps} R_{Ps} N_{Ps} \tag{4}$$

$$\lambda_f^+ = (I'/\tau' + I_2/\tau_2 + I_3/\tau_3)/(I' + I_2 + I_3), \tag{5}$$

$$I' = 1 - I_3/3,\ \tau' = \tau_1 + [\tau_1 + \tau_3/(\lambda_S^O \tau_3 + 1)I_3/3I',$$

where λ_f^+ is annihilation rate of free (nonlocalized) positrons, and λ_S^O is annihilation rate of singlet positronium. Parameter Q defines the fractional content of positrons involved in positronium formation; D_+ and D_{Ps} are diffusion coefficients for positron and positronium, respectively.

Correct estimation of parameter Q is not available, and this does not allow a nonambiguous characterization. Actually, positronium atoms, which are not localized in microregions, do not manifest themselves in long-lived component with intensity I_3, and their direct identification is not possible. In connection with this, parameter Q is obtained from additional experiments or is estimated from two limiting cases. In the case of fast entrapment of all positrons by free volume microregions and existence of a certain fraction of nonlocalized positronium,

$$Q - 4I_3/3 = I_1 - I_3/3 = I' \tag{6}$$

and equation (3) takes the following form:

$$\nu_{Ps} = (\lambda_f^+ - \lambda_3)(4I_3/3)/I' \tag{7}$$

where I' is associated with the fraction of nonlocalized positronium. In contrary, in the case of complete entrapment of positronium and existence of certain number of nonlocalized positrons,

$$I_1 - I_3/3 = (1 - Q) - I_2 = I'$$

and equation (1) takes the following form:

$$\nu_+ = (\lambda_f^+ - \lambda_2)I_2/I' \tag{8}$$

Here, I' stands for the fraction of nonlocalized positrons. According to [18,19], in the case of polymer systems, $D_+ = 0.1$ cm^2/s and $D_{Ps} = 10^{-4}$ cm^2/s.

Application of these approaches allows one to estimate the effective radius R_+ and concentration of free volume regions N_+ in structural sublevels with increased packing density as well as the corresponding values of R_{Ps} and N_{Ps} for structural sublevels with decreased packing density. For all samples studied, $R_+ \simeq 0.34$ nm and $R_{ps} \simeq 0.42$ nm. For initial PMMA and PMMA containing 0.1 wt % of DES, $N_+ \simeq 0.9 \times 10^{16}$ cm^{-3} and $N_{Ps} \simeq 1.0 \times 10^{19}$ cm^{-3}. As content of DES in PMMA increases, N_+ and N_{Ps} increase. For PMMA samples containing 0.5 and 1.3 wt % of DES, $N_+ \simeq 1.15 \times 10^{16}$ cm^{-3} and $N_{Ps} \simeq 2.2 \times 10^{19}$ cm^{-3}.

Hence, introduction of DES into PMMA is not accompanied with the changes in the dimensions of free volume microregions both in structural regions with increased and decreased packing density in polymer. The content of free volume microregions in more densely packed structural regions N_+ changes with increasing DES content in PMMA but still lies within expected error (20%). Concentration of free volume microregions in loosely packed structural regions N_{Ps} increases by two times, and this evidence suggests that introduction of DES into polymer is associated with loosening of these structural regions. Constancy of annihilation characteristics for PMMA samples containing 0.1 wt % of DES as compared with virgin PMMA may be rationalized by the fact that low-molecular-mass additive occupies rather large free volume microregions. These regions are located far away from each other, and distances between them are much higher than diffusion paths of positron and positronium. As a result, they appear to be beyond the detection limit of this method.

This structural interpretation of experimental evidence obtained by the method of positron annihilation correlates well with earlier structural studies in polymer glasses (for example, [20–22]). Structure of glassy polymer was shown to be characterized by a set of densely packed regions (domains) separated by structural regions with lower packing density. (Let us note that the term "domains" is used only to specify structural elements with increased packing density and carries no information concerning the structure of these regions.) Domains are able to aggregate with each other and produce more complicated supradomain structures. The boundary regions between supradomain structures are more loosely packed as compared with interdomain regions. Hence, experimental evidence obtained allowed identification of three structural sublevels in glassy polymers listed in order of increase in free volume: domains, interdomain regions, and boundary regions between supradomain structures. Three-component treatment of lifetime distributions of annihilation radiation allows one to obtain information concerning free volume fraction for domains and interdomain regions.

According to this approach, the effect of introduction of DES on mechanical properties of PMMA containing DES may be presented as follows. At low content of DES (0.1 wt %), DES molecules occupy rather large free volume microregions located at boundaries between supradomain structures. As a result, segmental mobility in the vicinity of these microregions is hindered, and mechanical properties of polymer material increase (Figs. 2 and 4). With increasing the content of DES in PMMA to 0.5 and 1.3 wt %, low-molecular-mass additive is able to enter interdomain structural regions. This penetration is accompanied by loosening of these regions and additional free volume microregions appear. As a result, within these structural regions, segmental mobility of macromolecules is enhanced, and σ_y and $\varepsilon_1/(\varepsilon_1+\varepsilon_2)$ decrease (Figs. 2 and 4). During introduction of DES into PMMA, densely packed domains remain intact and do not contribute to changes in mechanical properties of the system.

The effect of DES on segmental mobility of PMMA is supported by DSC data (Fig. 5). At 0.1 of DES in PMMA, endothermic jump in glass transition region increases as compared with initial PMMA (transition from curve 1 to curve 2). This evidence suggests a suppressed segmental mobility of polymer chains for polymer samples containing low-molecular-mass additive. As concentration of DES in PMMA increases (curve 3), endothermic jump decreases, and this behavior is related to an enhanced segmental mobility of polymer chains. Let us note that as evidenced by thermostimulated luminescence (Fig. 1) characterizing mobility of polymer chains and chain fragments [23], introduction of DES has a certain effect not only on large-scale (segmental) mobility of polymer chains but also on small-scale mobility of chain fragments. Introduction of 0.1 wt % of DES into PMMA is accompanied by a marked decrease in intensity of a broad peak of PMMA at temperatures from 100 to 120K (curve 2). This behavior is related to inhibition of mobility of small kinetic elements responsible for this relaxation transitions. As concentration of DES in polymer increases (transition to curve 4), mobility of these kinetic elements is enhanced, and intensity of the peak associated with PMMA increases.

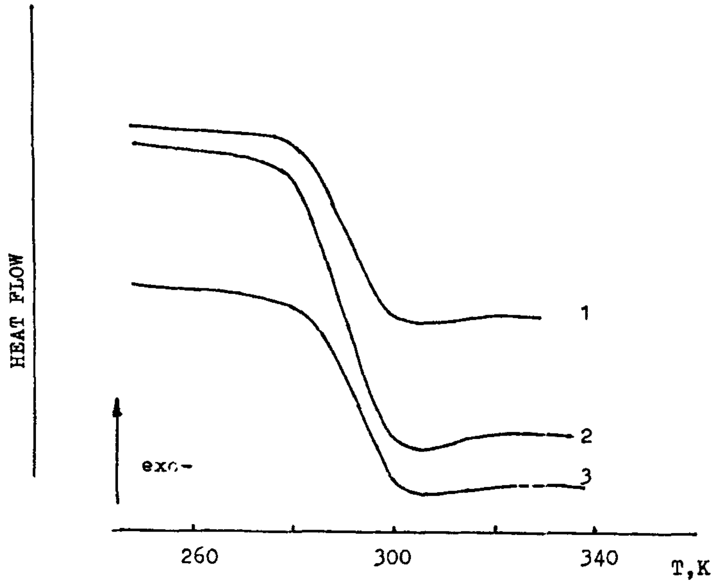

FIGURE 5 DSC curves of PMMA (1) and PMMA with 0.1 (2) and 1.3 wt.% of DES (3).

CONCLUSION

Mechanical and structural studies of PMMA containing thermodynamically incompatible low-molecular-mass additive DES allow one to explain the effect of DES on polymer mechanical behavior. At low concentration of DES in PMMA, rather large free volume microregions (presumably, at boundaries between supradomain structures) are occupied by DES molecules. As a result, segmental mobility in these regions is inhibited. This process manifests itself in increase in σ_y and contribution of low-temperature component $\varepsilon_1/(\varepsilon_1+\varepsilon_2)$ to total recovery of plastic deformation. With increasing the content of DES in PMMA to 0.5 and 1.3 wt %, low-molecular-mass agent is able to penetrate interdomain structural regions, and their structure becomes more loosened. As a result, within these structural levels, segmental mobility of polymer chains is enhanced, and σ_y and $\varepsilon_1/(\varepsilon_1+\varepsilon_2)$ decrease. During introduction of DES into PMMA, densely packed domains remain intact.

According to this approach, deformation at low strains as well as such mechanical parameters as E_O, σ_y, and $\varepsilon_1/(\varepsilon_1+\varepsilon_2)$ are controlled by segmental mobility of polymer chains in structural regions with lower packing density.

Acknowledgment

This work was supported by the Russian Foundation for Fundamental Researches, project no. 95-03-08325a.

References

[1] Arzhakov, M. S. and Arzhakov, S. A. (1995). *Intern. J. Polymeric. Mater.*, **28** (in press).

[2] Arzhakov, M. S., Arzhakov, S. A. and Chernavin, V. A. *New Polymeric Mater.*, (in press).

[3] Entsiklopediya Polimerov (Encyclopedia of Polymers), Moscow: Sovetskaya Entsiklopediya, 1974 (in Russian).

[4] Kozlov, P. V. and Papkov, S. P. (1982). Fizikokhimicheskie Osnovy Plastifikatsii Polimerov (Physical and Chemical Foundations of Plasticization of Polymers), Moscow: Khimiya, (in Russian).

[5] Arzhakov, S. A. (1975). Doctorate (Chem.) Dissertation, Moscow: (in Russian).

[6] Shantarovich, V. P., Yampol'skii, Yu. P. and Kevdina, I. B. (1994). *Khim. Vys. Energ.*, **28**, 53 (in Russian).

[7] Kevdina, I. B., Arzhakov, M. S. and Shantarovich, V. P. (1995). *Polymer Science* **B37**, 171.

[8] Shantarovich, V. P., Sivergin, Yu. M. and Kevdina, I. B. (1995). *Khim. Vys. Energ.*, (in Russian) (in press).

[9] Lebedev, V. P. (1978). *Usp. Khim.*, **47**, 127 (in Russian).

[10] Geil, P. H. (1987). *Proc. 17th Int. Symp.*, **83**.

[11] Sanchez, V., Lopez, R., Fucugauchi, L. A. and Ito, Y. (1995). *J. Appl. Polym. Sci.*, **56**, 779.

[12] Macquenn, R. C. and Granata, R. D. (1993). *J. Polym. Sci.* **B31**, 971.

[13] Nikol'skii, V. G. and Mironov, N. A. (1973). Zavodskaya Laboratoriya, 1272 (in Russian).

[14] Vrentas, J. S., Duda, J. L. and Ling, H. -C. (1988). *Macromolecules*, **21**, 1470.

[15] Liu, Y., Roy, A. K., Jones, A. A., Inglefield, P. T. and Ogden, P. (1990). *Macromolecules*, **23**, 968.

[16] Oleinik, E. F., Salamatina, O. B., Rudnev, S. N. and Shenogin, S. V. (1993). *Polymer Science*, **35**, 1532.

[17] Oleinik, E. F., Salamatina, O. B., Rudnev, S. N. and Shenogin, S. V. (1995). *Polymers for Advanced Technologies*, **6**, 1.

[18] Maurino, M. and Brandt, W. (1979). *Bull. Am. Phys. Soc.*, **24**, 72.

[19] Eldrup, M., Vehanen, A., Schulz, P. J. and Lynn, K. G. (1983). *Lynn, Phys. Rev. Lett.*, **51**, 2007.

[20] Neki, K. and Geil, P. H. (1973). *J. Macromol. Sci.* **B8**, 295.

[21] Bair, H. E., Matsuo, M., Salmon, W. A. and Kwei, T. K. (1972). *Macromolecules*, **5**, 114.

[22] Racich, J. L. and Koutsky, J. A. (1976). *J. Appl. Polym. Sci.*, **20**, 2111.

[23] Nikol'skii, V. G. (1982). *Pure Appl. Chem.*, **54**, 493.