Physical and Mechanical Behavior of Polymer Glasses: Polymeric Powders

M. S. Arzhakov[a]; S. A. Arzhakov[a]

[a] Polymer Department, Faculty of Chemistry, Lomonosov Moscow State University, Moscow, Russia

PLEASE SCROLL DOWN FOR ARTICLE

Physical and Mechanical Behavior of Polymer Glasses: Polymeric Powders

M. S. ARZHAKOV and S. A. ARZHAKOV

Polymer Department, Faculty of Chemistry, Lomonosov Moscow State University, Vorob'evy Gory, Moscow, 119899 Russia

Deformation behavior of glassy thermoplastic powders under the parallel action of pressure and temperature was studied. Three "pressure-temperature" regions of preparation of monolithic polymer samples with quite different physical and mechanical properties were found. The existence of these regions was shown to be controlled by the relaxation in powderlike polymer during compression. Speculations concerning segmental mobility within polymer glassy state were proposed to describe specific relaxation behavior in the bulk polymer samples.

Keywords: Polymer glasses; powders; molding; deformation; relaxation

INTRODUCTION

At the present time, a variety of polymer thermoplastics are produced as powders and granules. They are processed into final monolithic articles by pressing, extrusion, injection molding, etc. [1–4]. Physical and mechanical properties of the final bulk materials are primarily controlled by deformation and relaxation in powderlike polymers during processing. Hence, studying deformation behavior of polymer powders under the parallel action of pressure and temperature is of a great importance from the standpoint of the fundamental approaches to polymer processing.

On the other hand, the problems of molding of polymeric powders are closely related to the fundamentals of mechanical behavior of polymers under high pressure. These problems are widely discussed in

literature [5–9]. However, in all cases, physical and mechanical behavior of polymers under high pressure was studied for bulk samples, whose pre-history is controlled by processing conditions.

The aim of this work is a thorough description of deformation of powderlike glassy thermoplastics under the parallel action of temperature and pressure, which results in monolithization, and its governing effect on the physical and mechanical behavior of bulk polymers.

EXPERIMENTAL

In this work, we studied PMMA, crosslinked PMMA, copolymers of methyl methacrylate with methacrylic acid, PVC, PS, poly (methacrylic acid) (PMAA), polyacrylonitrile (PAN), and copolymers of acrylonitrile with vinyl acetate.

PMMA ($M_W = 1,500,000$) as well as copolymers of methyl methacrylate with methacrylic acid were prepared by bulk polymerization. The content of methacrylic acid in copolymers was 15 and 25 wt.%. Copolymers of methyl methacrylate with bifunctional monomer, ethylene glycol dimethacrylate (EGDM), were used as cross-linked PMMA. The development of network took place immediately during bulk copolymerization. The content of EGDM in polymerization system was 1.5 and 8.0 mol.%.

PVC ($M_W = 79,000$) was prepared by bulk polymerization.

Bulk polymers and copolymers were dispersed to powders, the dimensions of particles do not exceed 0.25 mm.

Dibutyl phthalate (DBPh) was used as a plasticizing agent for PMMA and PAN.

Molding of polymer powders was carried out under two regimes. A certain amount of powderlike polymer was placed in cylindrical mold with a diameter of 10 mm and compressed at room temperature T_r with a strain rate of 0.1 mm/min up to a certain stress. Then, the stressed sample was heated up to molding temperature T_{mold}, allowed to stay for 15 min, cooled down to T_r, and released ("P–T" regime). In "T–P" regime, a certain amount of polymer powder was heated in the mold up to T_{mold}, compressed with a strain rate of 0.1 mm/min up to a certain stress, allowed to stay for 15 min, cooled down to T_r, and released.

Monolithization of the molded samples (the absence of visual boundaries between the particles of initial powder) was visual inspected at T_r, as evidenced by their transparency. Accuracy of estimation of temperature and pressure of transition from opaque samples to transparent was 5–7%.

To study deformation behavior of powderlike polymers, a certain amount of polymeric powder was compacted in the mold at 0.03 GPa at T_r for 15 min. Then, the samples were unloaded, and initial height of the test samples h_o was estimated. After that, the samples were compressed at a strain rate of 0.1 mm/min up to a certain stress. At this stress, the height of the deformed sample was h_p. Strain was estimated as $\Delta h = h_o - h_p$. The accuracy of measurements was 3%. Deformation of powderlike polymers was carried out in the temperature range from 293 K to glass transition temperature T_g.

To study the temperature-induced relaxation of deformation, the samples molded at certain temperatures and pressures were cooled in the stressed state to the temperature of liquid nitrogen and were released at this temperature. Then, the free-standing samples were heated with a heating rate of 1 K/min starting with 213 K, and the changes in their height were measured with an accuracy of 0.001 mm. The changes in the height of the test samples during their heating was estimated as $\Delta h = h_T - h_{213}$, where h_{213} is the height of the sample at 213 K, and h_T is the height of the sample at a given temperature.

RESULTS AND DISCUSSION

Molding of PMMA, PVC, and PS powders under "P–T" regime showed that the transparent monolithic samples with no boundaries between particles of initial powder may be prepared in a certain region of temperatures and pressures. For PMMA, this region is bounded by the curve presented in Figure 1.

Compression of powderlike polymer at T_r within the pressure interval AB (Fig .1), which is followed by heating to T_{mold} (in the case presented in Figure 1, $T_{mold} = 400$ K), leads to the formation of opaque samples. Transparent samples may be prepared within interval of pressures BC. Further increase in pressure again results in the formation of opaque samples.

The most interesting feature of this experimental evidence is related to the existence of the upper branch of the curve bounded the region
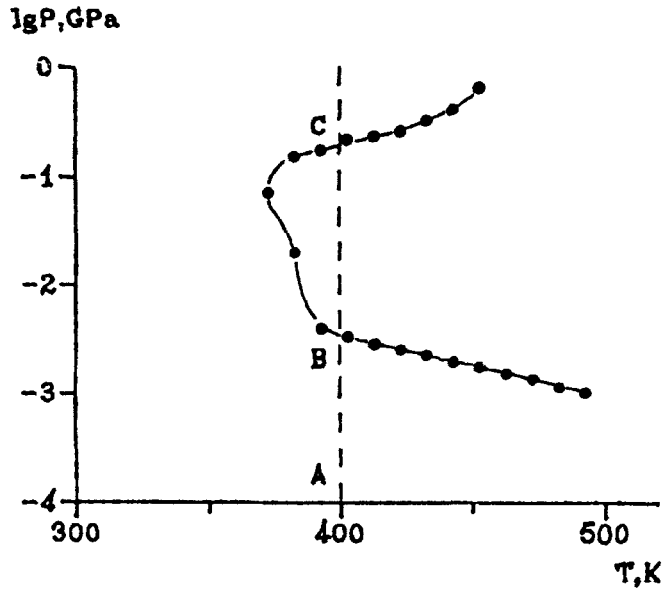
FIGURE 1 "Pressure-temperature" diagram for the preparation of transparent PMMA
samples.

of preparation of transparent samples. This fact was first reported in
[10]. To study this phenomenon, let us consider the deformation of
PMMA powder in the mold at T_r.

Pressure-strain curve may be divided into three regions (Fig. 2).
Within region I ($P \leq P_1$), the dependence of pressure on strain shows a
linear character. This region is characterized by the densification of
powderlike system due to the Hookean elastic deformation of par-
ticles of initial powder. As evidenced by optical microscopy, the shape
of particles remains unchanged after deformation. Within region II
(from P_1 to P_2), densification proceeds via yielding of particles. At
$P \geqslant P_2$, compression of monolithic sample takes place. Let us note
that the compressibility factor of powderlike polymer calculated with-
in this region is equal to that observed for the deformation of bulk
PMMA under the same conditions.

With increasing deformation temperature, a decrease in the pres-
sures associated with the transition from Hookean elastic deformation
to yielding (P_1) and from yielding to the deformation of monolithic
body (P_2) is observed. Figure 3 shows the temperature dependencies of
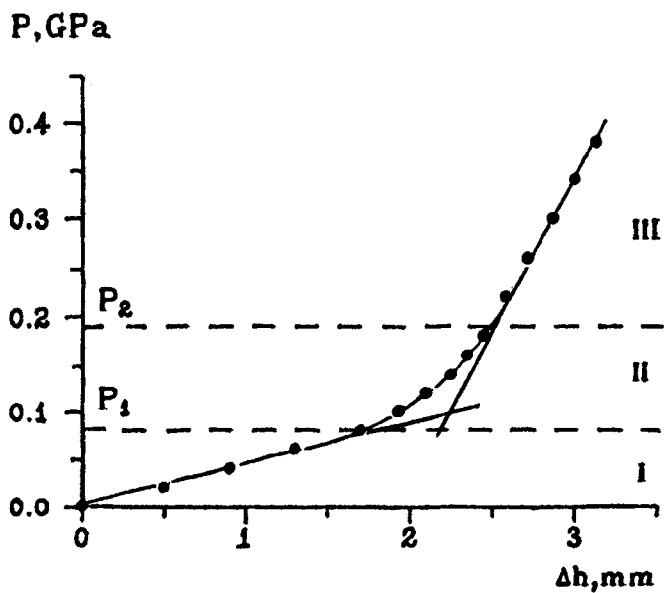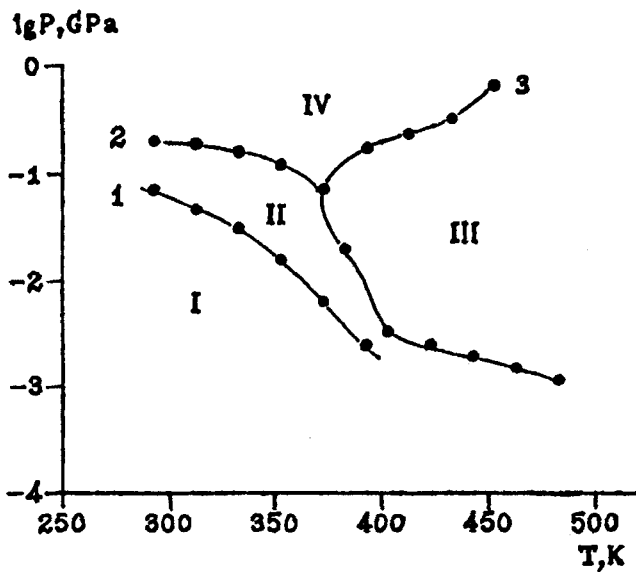
P,GPa

FIGURE 2   Pressure-strain curve of powderlike PMMA.

lgP,GPa

FIGURE 3   Temperature dependence of pressure P_1 (1) and P_2 (2). 3 —curve bounding the region of preparation of transparent PMMA samples.

P_1 and P_2 (curves 1 and 2, respectively) as well as the curve, which bounds the region providing preparation of transparent samples (curve 3).

At temperatures and pressures corresponding to region I (Fig. 3), Hookean elastic deformation of powderlike polymer takes place. At pressures above P_1 (Fig. 3, curve 1), within region II, the densification of polymer powder is provided by yielding. At pressures above P_2 (Fig. 3, curve 2), mechanical behavior of polymer powder is similar to that of bulk PMMA. Hence, one may conclude that, under these conditions, the boundaries between powder particles disappear. To verify this assumption, polymer samples compressed in region IV were cooled down in mold in the stressed state with liquid nitrogen and released at this temperature. At the temperature of liquid nitrogen, the samples are transparent but they become oipaque on heating to T_r. Hence, at temperatures and pressures corresponding to region IV, powderlike polymer is monolithic under compression.

To summarize, monolithization of polymer powder (disappearance of boundaries between powder particles) takes place within regions III and IV. Generally, monolithization is provided by the diffusion of macromolecules or their fragments through the boundaries between particles. Let us note that the samples prepared in region IV are monolithic at rather low temperatures below T_r. In contrast, the samples prepared in region III remain monolithic at T_r.

For the samples molded within region IV on heating to T_r the loss in transparency is explained by polymer relaxation associated with the recovery of the boundaries between powder particles. These processes are not related to the relaxation of Hookean deformation, because, at low temperatures, the samples remain monolithic for a long period of time. From ths standpoint, at a given pressure, the temperature corresponding to the relaxation of the component of relaxation spectrum that is observed in molded samples below T_r is described by an upper branch of the curve 3 (Fig. 3). Increase in macromolecular mobility provided by plasticization enhances relaxation and, finally, leads to shifting region III toward lower temperatures (Fig. 4).

When molding is carried out in "T–P" regime, the upper branch of the curve, which bounds the area of formation of transparent samples, is shifted toward lower temperatures (Fig. 5). This behavior may be rationalized by the fact that in this regime powderlike polymer is
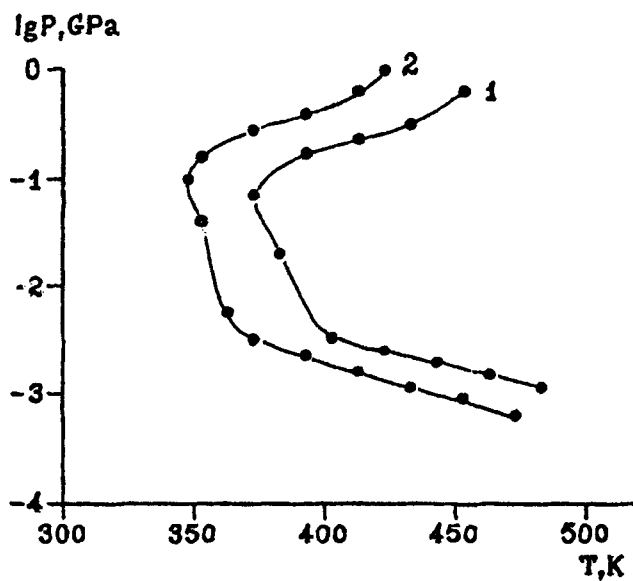
FIGURE 4 "Pressure-temperature" diagram for the preparation of transparent samples from PMMA (1) and PMMA plasticized with DBPh (2). (content of DBPh: 5 wt.%).
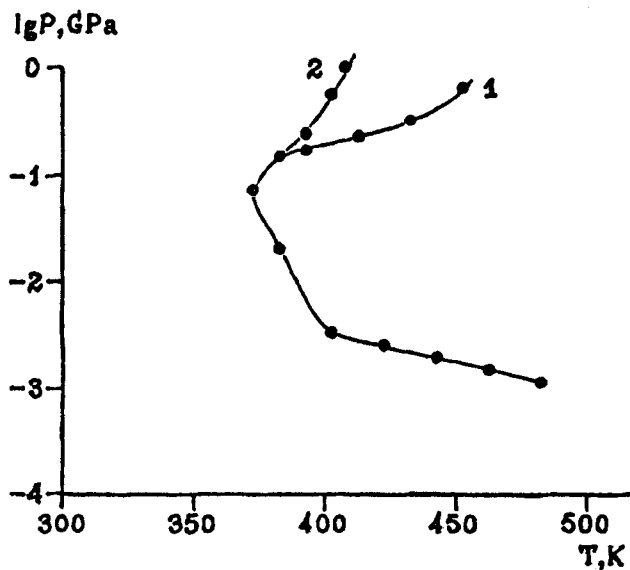

FIGURE 5 "Pressure-temperature" diagram for the preparation of transparent PMMA samples under "P–T" (1) and "T–P" regimes (2).

compressed at temperatures above T_r. It leads to the development of relaxation during compression. It is worth noting that increase in rate of compression leads to shift of upper branch toward that obtained in "P–T" regime.

Studies in molding of PAN and PMAA powders using "P–T" regime showed the absence of upper pressure limit of preparation of transparent samples (Fig. 6). It evidences that these polymers are characterized by the absence of relaxation at $T < T_r$. This fact is likely to be connected to high energy of intermolecular interaction specific for PAN and PMAA.

Decrease in energy of intermolecular interaction of PAN due to plasticization or copolymerization with vinyl acetate results in appearance of upper branch of P–T curve (Fig. 7). The same behavior is characteristic for copolymers of methyl methacrylate with methacrylic acid (Fig. 8). On contrary, introduction in polymer intermolecular covalent bonds in the case of copolymers of methyl methacrylate with EGDM is accompanied by the restriction of relaxation and shift of the region where transparent samples can be formed toward higher temperatures (Fig. 9).
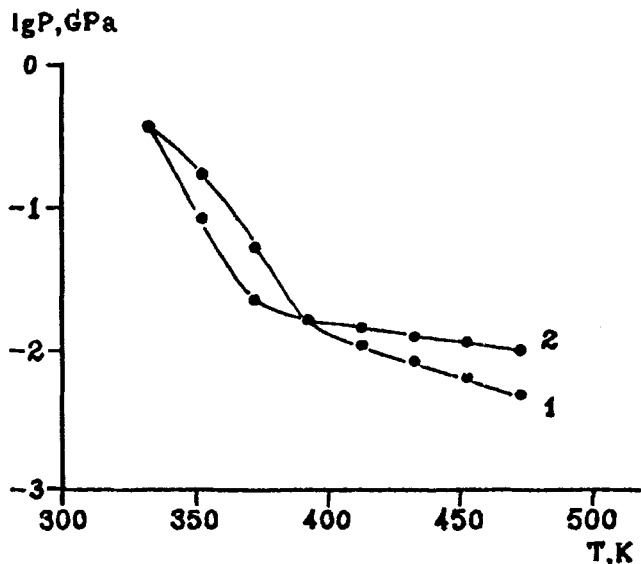

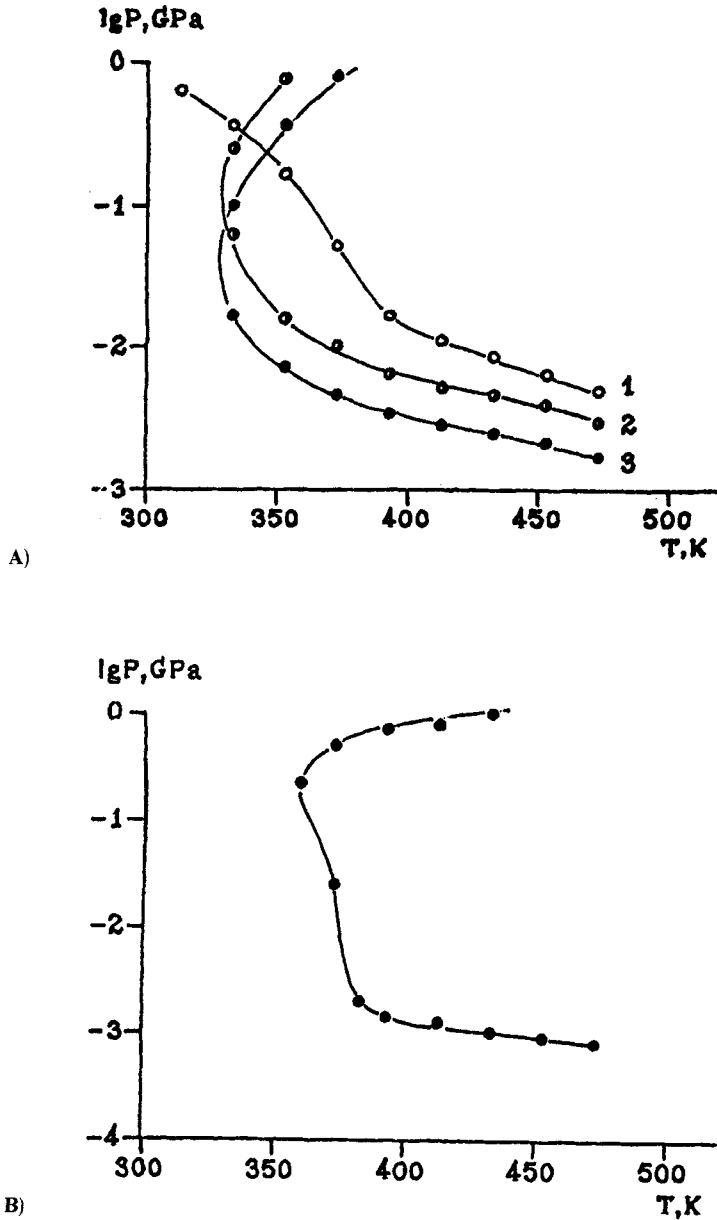FIGURE 6 "Pressure-temperature" diagram for the preparation of transparent samples of PAN (1) and PMAA (2).

FIGURE 7 "Pressure-temperature" diagram for the preparation of transparent samples from PAN (1) and PAN plasticized with 9 (2) and 14 wt.% DBPh (3) (A), and from copolymer of acrylonitrile with 15% of vinyl acetate (B).
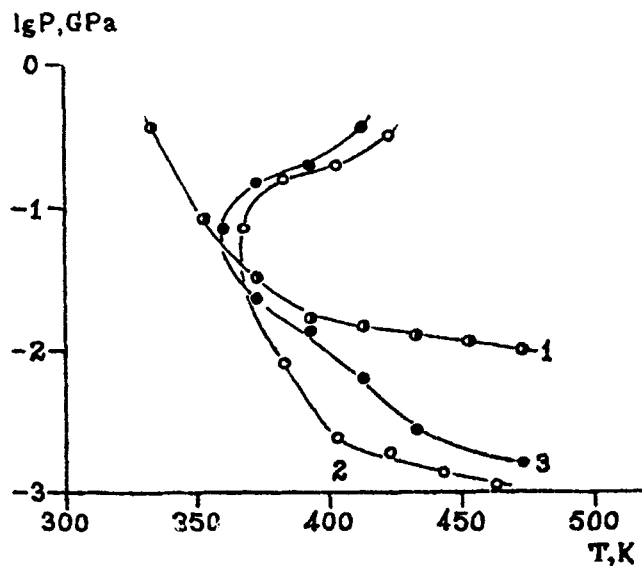
lgP,GPa

FIGURE 8 "Pressure-temperature" diagram for the preparation of transparent samples from PMAA (1) and copolymers of methacrylic acid with 15 (2) and 25 wt.% of methyl methacrylate (3).
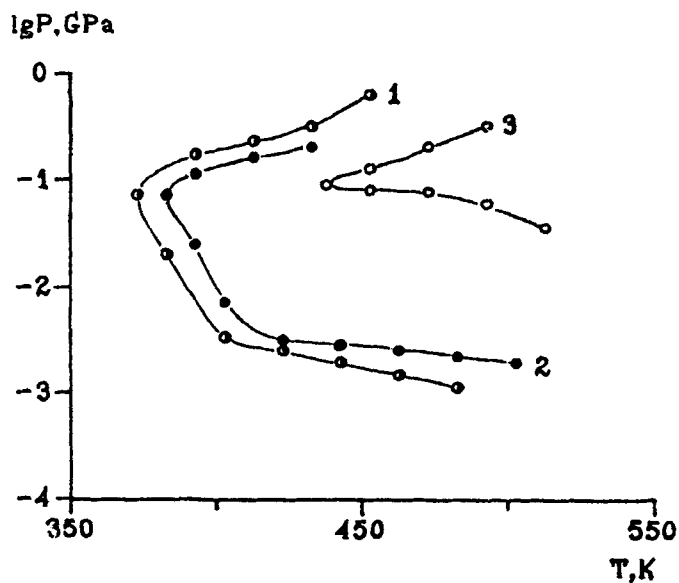
lgP,GPa

FIGURE 9 "Pressure-temperature" diagram for the preparation of transparent samples from PMMA (1) and copolymers of methyl methacrylate with 1.5 (2) and 8 mol.% of EGDM (3).

It is worth to emphasize that the preparation of the samples which are transparent and monolithic at T_r does not unambiguously evidence the temperature stability of polymer material obtained. To understand in detail deformation and relaxation behavior of powderlike polymer under molding, let us consider temperature-induced relaxation of deformation of molded samples.

Temperature dependences of the height of PMMA molded samples are presented in Figure 10. A noticeable portion of deformation of PMMA samples molded in region IV (Fig. 3) relaxes at temperatures below T_g (Fig. 10A, curve 1). Increase in height of molded sample during heating is controlled by the relaxation of deformation of powder particles. It leads to the recovery of the boundaries between powder particles and, as a result, loss in monolithization.

As was mentioned earlier, monolithization within region IV is controlled by yielding of powder particles, that is, the diffusion of segments of macromolecules through the boundaries between powder particles. Hence, temperature-induced relaxation of samples prepared
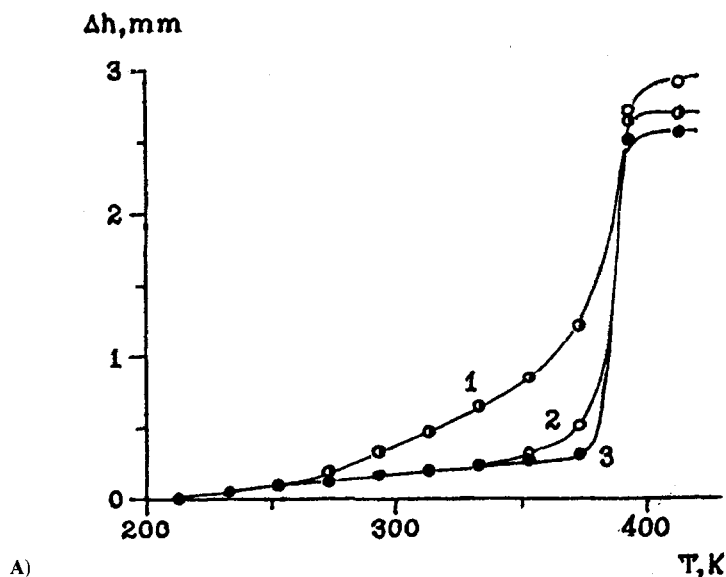

FIGURE 10 Temperature dependences of the height of PMMA samples molded at 0.15 GPa and temperatures 353 (1), 393 (2), and 433K (3) (A); at pressure 0.04 GPa and temperatures 393 (1), 433 (2), and 473K (3) (B); at pressure 0.02 GPa and temperatures 393 (1), 433 (2), and 453K (3) (C).
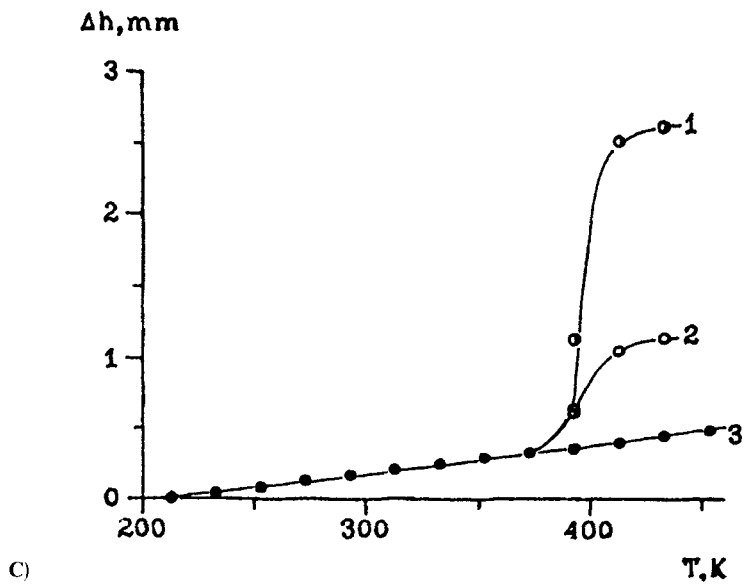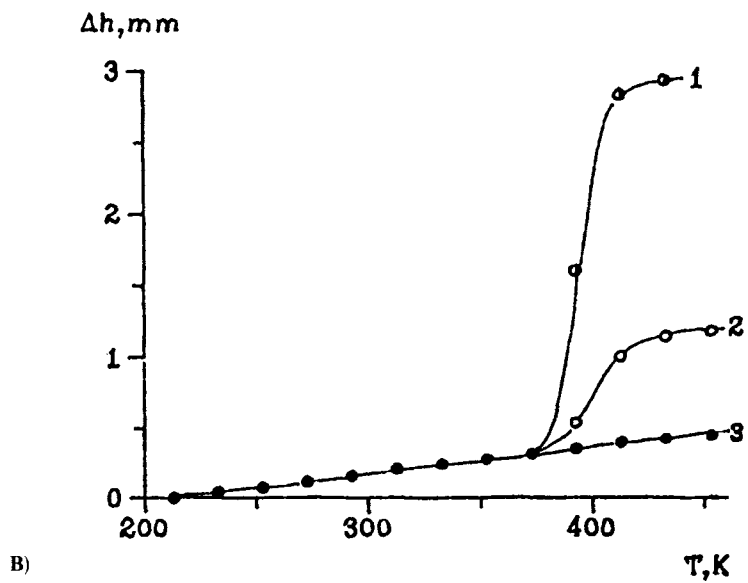
B)

C)

FIGURE 10   (Continued).

in region IV appears to be also controlled by segmental mobility. Let us note, that, in this case, the appearance of segmental mobility takes place at temperatures below T_g.

To explain this phenomenon, let us consider the mechanism of yielding [4, 11–13]. Yielding is controlled by the mechanical activation of segmental mobility in polymer within glassy state. This process takes place when relaxation time of segments $\tau = \tau_0\, e^{(U - \gamma\sigma)/kT}$, where U is the energy of activation of segmental mobility, becomes equal to the time of strain development due to a decrease in U under the applied stress σ. The mechanism of low-temperature segmental mobility in the molded samples is supposed to be similar to that. However, in this case, mechanical activation of segmental mobility is observed not under applied stress but under inner stress stored in the deformed polymer sample.

Increase in T_{mold} leads to degeneration of low-temperature relaxation and preparation of the samples, which show relaxation only in the vicinity of T_g (Fig. 10 A, curves 2, 3). Let us note that degeneration of low-temperature relaxation takes place under the transition from region IV to region III (Fig. 3).

Hence, in general case, temperature-induced recovery of the dimensions of the molded polymer samples is controlled by the relaxation of deformation of particles of initial polymer powder and involves low-temperature component within polymer glassy state and high-temperature component in the vicinity of T_g. Both components are related to the appearance of segmental mobility in the deformed polymer samples. At temperatures below T_g, segmental mobility is induced under inner stresses stored in polymer during molding. With increasing T_{mold} degeneration of low-temperature component of relaxation controls the critical temperature and pressure of transition from region IV to region III (Fig. 3, upper branch of the curve 3). These critical values determine the temperature of relaxation of the low-temperature component of segmental mobility spectrum at a given pressure during compression. Increase in T_{mold} above this temperature leads to the preparation of polymer samples, which show relaxation only at T_g. This reasoning allows one to conclude that the upper branch of curve 3 (Fig. 3) is the pressure dependence of T_g.

Relaxation of deformation of the samples molded in region III (Fig. 10 B, C) suggests, that increase in T_{mold} is accompanied by degeneration of high-temperature relaxation in the vicinity of T_g. When the critical T_{mold} is achieved, the changes in the height of the molded

samples is controlled only by thermal expansion (Fig. 10 B, C, curves 3). This evidence implies, that, under these conditions, true monolithization takes place.

The results obtained show the existence of several "pressure-temperature" regions providing the preparation of monolithic samples with quite different properties. The general "pressure-temperature" diagram for PMMA is presented in Figure 11.

Preparation of the samples, which remain monolithic at temperatures above T_g, is allowed in region I. In this case, the monolithization of powderlike polymer is controlled by the diffusion of centers of masses of macromolecules through the boundaries between the powder particles. The lower branch of the curve bounded region I is associated with both temperatures and pressures, at which diffusion of centers of masses of macromolecules through the boundaries between the powder particles is allowed. The existence of the upper branch of the above curve is related to the fact that diffusion of the macromolecules requires the existence of the sufficiently large free volume microregions in polymer. With increasing pressure, these free volume
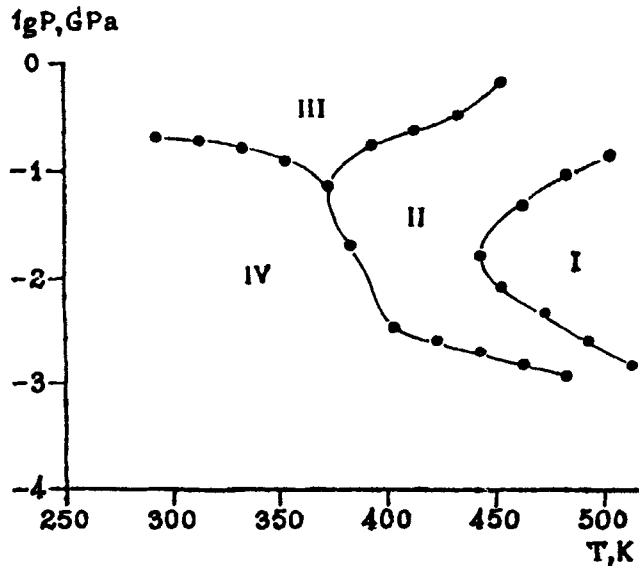

FIGURE 11 General "pressure-temperature" diagram for molding of powderlike PMMA. Comments are given in text.

microregions are likely to be dispersed, and their sizes decrease. As a result, diffusion of macromolecules is prohibited. From this standpoint, the upper branch of the curve bounding region I represents the pressure dependence of flow temperature. Let us note that for PMMA cross-linked with EGDM, when diffusion of macromolecules is not allowed, region I is not observed.

Within regions II and III, monolithization of polymer powder during molding also takes place. In these regions, monolithization is controlled by the diffusion of segments through the boundaries between the powder particles. This process is accompanied by the development of noticeable inner stresses, which are likely to be stored in polymer sample after release. On heating the samples molded in region III, segmental mobility is observed even at temperatures below T_g. This process leads to the recovery of the boundaries between powder particles and loss of monolithization. Molding in region II is accompanied by relaxation of low-temperature component of segmental spectrum during compression. Hence, in this case, segmental mobility in the molded sample takes place only at T_g. The loss in monolithization is observed only in this temperature interval.

At temperatures and pressures corresponding to region IV, opaque samples are produced.

CONCLUSION

Examination of molding of powders of glassy thermoplastics under the parallel action of temperature and pressure showed the existence of three "pressure-temperature" regions providing the preparation of monolithic polymer samples.

Preparation of true monolithic samples is observed in the "pressure-temperature" region, where diffusion of macromolecules through the boundaries between the particles of initial powder takes place. When monolithization is provided by the diffusion of segments through the boundaries between the powder particles, the resultant physical and mechanical behavior of bulk polymer samples is controlled by the segmental relaxation both during molding and after release of molded polymer.

In general case, relaxation of yield deformation of powderlike polymer involves low-temperature component within polymer glassy

state and high-temperature component in the vicinity of T_g. Both components are related to the appearance of segmental mobility in the deformed glassy polymers on heating. At temperatures below T_g, segmental mobility is provided by inner stresses stored in polymer samples during their molding.

Evidently, these features or relaxation of yield deformation in glassy polymers are beyond the scope of molding of polymer powders. Consideration of low-temperature relaxation of plastically deformed glassy polymers seems to be of primarily importance because it is not practical to prepare polymer articles without inner stresses. Relaxation behavior of the plastically deformed bulk polymers will be discussed in the forthcoming papers.

References

[1] Tadmor, Z. and Gogos, K. (1984). Teoreticheskie Osnovy Pererabotki Polimerov (Theoretical Foundations of polymer processing), Moscow: Khimiya, (in Russian).
[2] Gul', V. E. and Akutin, M. S. (1985). Osnovy Tekhnologii Pererabotki Plastmass (Foundations of Technology of Plastics Processing), Moscow: Khimiya, (in Russian).
[3] Gowariker, V. R., Viswanathan, N. V. and Sreedhar, J. (1986). *Polymer Science*, New Delhi: Wiley.
[4] Entsiklopediya Polimerov (Encyclopedia of Polymers), Moscow: Sovetskaya Entsiklopedia, 1977 (in Russian).
[5] Skorodumov, V. F. and Godovskii, Yu. K. (1993). *Vysokomol. Soedin.*, **35**. 214 (in Russian).
[6] Havlicek, J., Ylalsty, M. and Hrouz, J. (1982). *J. Macromol. Sci., Phys.*, **21**, 425.
[7] Sauer, J. A. (1977). *Polym. Eng. Sci.*, **17**, 150.
[8] Sanditov, D. S. and Bartenev, G. M. (1990). *Vysokomol. Soedin.*, Ser. **A 32**, 848 (in Russian).
[9] Ainbinder, S. B., Alkne, K. I., Tyunina, E. P. and Laka, M. G. (1973). Svoistva Polimerov pri Vysokikh Davleniyakh (Properties of Polymers at High Pressures), Moscow: Khimiya, (in Russian).
[10] Arzhakov, S. A. (1975). Doctorate (Chem.) DIssertation, Moscow: Karpov Institute of Physical Chemistry, (in Russian).
[11] The Physics of Glassy polymers, Haward, R. N., Ed., New York, Toronto: Wiley (1973).
[12] Nielsen, L. E. (1974). Mechanical Properties of Polymers and Composites, New York: Dekker.
[13] Kargin, V. A. (1979). Struktura i Mekhanicheskie Svoistva Polimerov (Structure and Mechanical Properties of Polymers), Moscow: Nauka.