DENSITY MEASUREMENTS OF ANNEALED AMORPHOUS POLYMERS

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Dedicated to Dr Blahoslav Sedlacek on the occasion of his 70th birthday.

The flotation method of the density measurement was adapted to reach sufficient accuracy with which the differences due to annealing amorphous polymers above their glass transition temperature can be traced. The densities of amorphous poly(methyl methacrylate) and polystyrene increase logarithmically in the course of the annealing, which suggests that some arrangement or ordering takes place. However, the changes are not stable.

It is a generally known fact that below the glass transition temperature, T_g, specific volume of an amorphous polymer (which is inversely proportional to its density), depends on the kinetics with which the state was reached (cooling rate from the annealing temperature T_a above T_g to the reference temperature T_r below T_g (Fig. 1; cf. refs[1,2]). On the other hand, it appears to be assumed in all theoretical studies that the liquid above T_g is in a state of equilibrium[3], i.e., that the specific volume (or density) of an amorphous polymer is a material constant at a given temperature above T_g. As several experimental findings suggest, this assumption is questionable[3,4].

In our previous transmission electron microscopical study of amorphous polymers deformed above the glass transition temperature[5], we found textures suggesting the development of regions with higher Young modulus than in amorphous matrix. Discussions on the ordering and “structures” in the amorphous state still continue[6] testifying that the problem is not completely solved.

The objective of this study is to contribute to tackling the above-mentioned problem and accumulating further experimental data, the main goal being to find whether it is likely that some arrangement of macromolecular chains in amorphous non-crystallizable polymers can occur.

EXPERIMENTAL

Polymer Samples

Poly(methyl methacrylate) (PMMA), and polystyrene (PS) were obtained by polymerization of the respective monomers in the presence of 0.5% dibenzoyl peroxide at 70 °C. From 2 mm-thick plates, samples of the size up to 10 mm were cut. The samples were annealed at 130 °C for about 24 h and then kept at room temperature for several days. Prior to the density measurement, the samples were annealed for the specified time at 114 °C (PS) or 130 °C (PMMA) and then quenched in water (PS) or heptane (PMMA). The density measurement followed immediately after the quenching.

Polymer Density Measurement

The measurements were performed in the set-up utilizing the flotation technique.

Flotation device. The flotation vessel was placed in a water bath, the temperature of which was carefully controlled and kept at the same value as the second part of the measuring device, the liquid densimeter, viz., 25 °C. The stability of the temperature bath was checked by a Beckmann thermometer and was better than 0.1 °C. The flotation bath was titrated; after each addition of the liquid from a reservoir, the flotation bath was stirred with a magnetic stirrer, then the sample was left moving without stirring until it reached an equilibrium position. The accuracy of the density measurement of the polymers was better than $1 . 10^{-4}$ g cm^{-3}. Flotation liquids were introduced into the flotation bath through tiny plastic tubes from two burettes. The tubes passed through the opened stopcock of the measuring vessel and were slowly taken out after each completed measurement before closing the stopcock. The flotation procedure was repeated until the density of the flotation liquid was equal to that of the measured sample.

Glass flotation vessel. In order not to cause experimental errors and to make it possible to continue measurements without unnecessary delays, two equal flotation vessels were combined in a pair connected with two glass tubes with the possibility of closing each of them (Fig. 2). The measurement was carried out in one of the vessels (with the measured sample and a magnetic stirrer inside), with plastic tubes for introduction of flotation liquids passing through the upper open stopcock. The other vessel had the upper stopcock closed and the tubes connecting both vessels were open during the measurement. After finishing the measurement, the plastic tubes were removed, the upper stopcock closed, and a portion of the flotation bath (the density of which was equal to that of the sample) was poured via the connecting glass tube into the other, so far empty vessel. After that, the connecting tubes could be closed, the upper part of the measuring vessel was opened and the sample removed and subjected to the following heat treatment. Then the liquid closed in the adjoining vessel could be transferred into the liquid densimeter. A simpler, single flotation vessel was also tested; its only drawback was less convenience if serial measurements were performed.

Measurement of the density of the flotation liquid. The density of the flotation liquid (equal to that of the measured sample) was measured with a DMA 02-C densimeter (Anton Paar, Graz, Austria). The densimeter used is based on the measurement of the resonance frequency of its measuring cell and is calibrated. All the measurements were performed at the same temperature, equal to the temperature at which the flotation was carried out. For the reasons discussed later, the only admittable way of opening the vessel with the measured liquid was turning the stopcock. The necessary amount of the liquid was then sucked with a syringe through the opened stopcock and introduced into the densimeter. The measured value was read after equilibration, and the density of the liquid was then calculated using the calibration equation. The accuracy of the density measurement of the polymers was better than $1 . 10^{-4}$ g cm^{-3}.

Flotation liquids. Only such media can be used as flotation liquids in which no measurable swelling occurs. For the polymers measured in this study, mixtures of heptane and carbon tetrachloride were used. The densities of the liquids were adjusted to the polymer measured, the difference between them being not higher than about 0.003 g cm^{-3}. Carbon tetrachloride containing traces of chloroform, in which the measured polymers swell, cannot be used. Therefore, we always used freshly distilled carbon tetrachloride kept in dark brown glass burettes.

RESULTS AND DISCUSSION

Analysis of the Method

If we question the accuracy of the density measurement method, it is necessary to state that the error in the absolute value of density depends on the calibration of the liquid densimeter and on how the equivalence of the temperature in the liquid densimeter and in the bath during flotation is observed. We believe that our absolute error (which remains constant during the measurement) was no higher than $1 \,.\, 10^{-3}$ g cm^{-3}. Systematic errors which can occur during the measurement and which can be caused by various factors like partial swelling or unequal times of flotation, were checked by measuring not in a sequence but in the way that the annealing times were applied

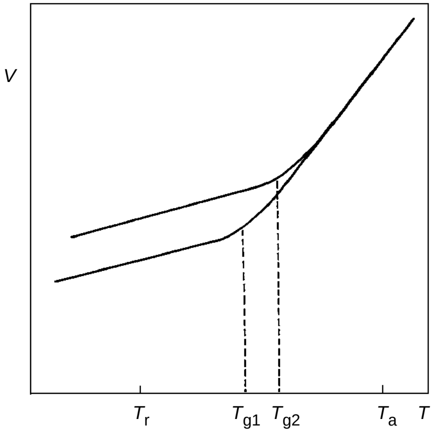

FIG. 1
Outline of the temperature dependence of the specific volume v of amorphous polymers at different rates of cooling: the higher values below the glass transition temperature, T_g, correspond to higher cooling rates. (For T_a, annealing temperature and T_r, reference temperature, see the text.)

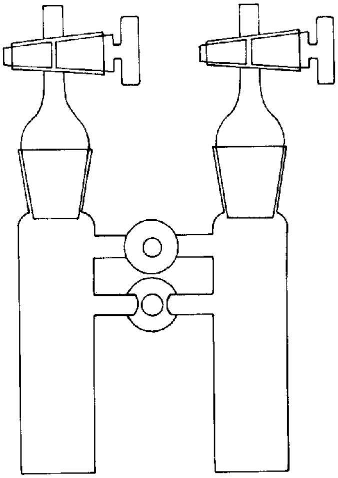

FIG. 2
Flotation vessel (25 mm in diameter, height ca 130 mm)

individually without an order. Thus we believe that the relative error of the method is $1 . 10^{-4}$ or even less. From the repeated measurements we have found that the differences in the measured densities were about $1 . 10^{-5}$ g cm^{-3}. Swelling of the sample can be easily detected, as it is then impossible to titrate the flotation bath into equilibrium. Precautions have to be observed very carefully during the measurement, particularly concerning the changes in composition of the flotation baths as a result of different volatility of the constituent liquids. The usual way of opening a stopper of the flotation bath containing vessel is not permitted; the same holds for pouring the mixture. Opening the space above the liquid via turning the stopcock proved to be acceptable unless it takes long time. To observe all the precautions, the flotation vessel in Fig. 2, as well as a single flotation vessel, proved to be satisfactory if properly handled.

The values of densities we obtained are in a good agreement with those measured by other authors[7,8].

Densities of PMMA and PS

Densities of the two amorphous polymers were measured depending on annealing time, each polymer at one annealing temperature above the glass transition temperature, T_g (Fig. 3). The annealing temperatures for each polymer are almost equidistant from the T_g of the particular polymer. Several new facts can be derived from the observed behaviour.

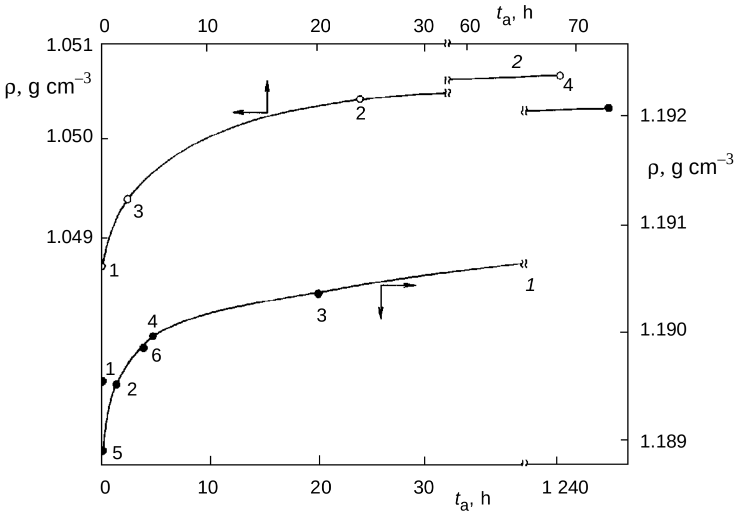

FIG. 3
Dependences of densities of PMMA (*1*) and PS (*2*) on the annealing time. Annealing temperature 130 °C (PMMA) and 114 °C (PS); measuring temperature 25 °C. (The numbers at each measured value indicate the sequence in which the dependence was obtained.)

The density data (Fig. 3) were obtained immediately after quenching, thus keeping practically equal cooling rate throughout the glass transition. Therefore, we believe that they can be regarded as representing the material state after the preceding annealing above T_g. We have tested also the dependence of density on the time period of keeping the sample at room temperature after the quenching. The density falls almost exponentially during the period. It seems to be obvious that the density measured at room temperature cannot be identical with that at the annealing temperature. However, the dependences in Fig. 3 show that the densities of amorphous polymers annealed at a temperature above T_g and quenched depend on the annealing time. Looking at Fig. 1 from this point of view, it is obvious that one single value of specific volume at a temperature above T_g is questionable (cf. ref.[3]).

The density of amorphous polymers increasing with annealing time t_a (Fig. 3) means that annealing above T_g (at least in a certain temperature region) must be accompanied by some degree of ordering or a closer packing of macromolecular chains. The dependence can be linearized showing that original curves are logarithmic (Fig. 4). The increase in density, $\Delta\rho(t_a)$ can be expressed as $\Delta\rho(t_a) = K \log t_a$ and the constant K (which may depend on annealing temperature) was found the same for both PMMA and PS.

There appeared several surprising findings for which we have neither satisfactory explanation nor a model of the behaviour. Each particular measured point in Fig. 3 was practically independent of the preceding history of the sample, which means that during a single measuring cycle, the previously reached ordering is completely destroyed. Repeated evaluations proved that the reason can be attributed to the material itself rather than to the measuring method. It seems that if some ordering takes place, it is very closely confined to the particular temperature and may be easily destroyed by the thermal motion at another temperature, at which another arrangement or ordering may

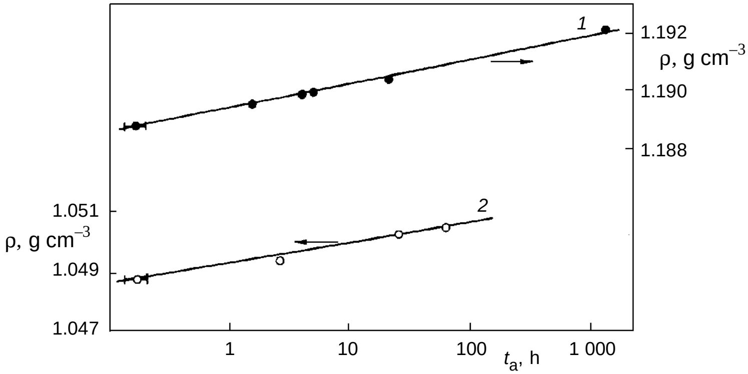

FIG. 4
Linearization of the dependences from Fig. 3. *1* PMMA, *2* PS

occur. A departure from equilibrium was deduced on the basis of measurements of polystyrene below 170 °C which is far above its T_g; at that, a slow contraction was detected upon heating the sample for 24 h (cf. ref.[9]).

Our findings and those reported are obviously in agreement with our previous results obtained with the same polymers slowly deformed at temperatures above T_g. We had no explanation for the fact that the observed heterogeneities became imperceptible after the deformation had been suddenly released at this temperature. Of the same origin is obviously the decrease in time of birefringence found after quenching the deformed amorphous PMMA with the fixed deformation[10]. It cannot be excluded that in PMMA the macromolecular chain motion associated with both the decrease of the sample density, when kept at room temperature after annealing, and the above-mentioned time decrease in birefringence is due to its β relaxation which is relatively strong.

REFERENCES

1. Kovacs A. J.: J. Polym. Sci. *30*, 131 (1958).
2. McKenna G. B. in: *Comprehensive Polymer Science* (C. Booth and C. Price, Eds), Vol. 2, p. 311. Pergamon Press, Oxford 1989.
3. Boyer R. F. in: *Encyclopedia of Polymer Science and Technology* (H. F. Mark and N. M. Bikales, Eds), Suppl. Vol. 2, p. 745. Wiley-Interscience, New York 1977.
4. Fatou J. G. in: *Encyclopedia of Polymer Science and Engineering* (H. F. Mark, N. M. Bikales, C. G. Overberger, G. Menges and J. I. Kroschwitz, Eds), Suppl. Vol., p. 256. Wiley-Interscience, New York 1989.
5. Lednicky F., Pelzbauer Z.: J. Macromol. Sci.-Phys., B *21*, 19 (1982).
6. Killian H.-G.: *28th Europhysics Conf. on Macromol. Phys. “Transitions in Oligomer and Polymer Systems”, Ulm 27.9.–1.10.1993.*
7. *Polymer Handbook* (J. Brandrup and E. H. Immergut, Eds), p. V-77, V-82. Wiley-Interscience, New York 1989.
8. Ito E., Kawashima T., Nishi Y., Kobayashi Y.: Rep. Prog. Polym. Phys. Jpn. *19*, 265 (1976).
9. Hocker H., Blake G. J., Flory P. J.: Trans. Faraday Soc. *67*, 2251 (1971).
10. Lednicky F.: Unpublished results.