Notes

The Glass Transition of Nylon 6

R. GRECO,* L. NICODEMO, *and* L. NICOLAIS

Istituto di Principi di Ingegneria Chimica, Università di Napoli, and Laboratorio di Ricerche su Tecnologia dei Polimeri e Reologia del CNR, Naples, Italy.

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It is well known that the glass transition temperature (T_g) of polymers can be measured in different ways. The most common procedures are based on dilatometric[1] or dynamic mechanical[2,3] measurements. Recently, a method, proposed by Tobolsky,[4] in which the isochronal curve of the shear modulus G vs. the temperature is used to calculate T_g, has been applied by several workers. With Tobolsky's method, the temperature T_i (K) at which the modulus assumes the value given by

$$\log G(K) = (\log G_1 + \log G_2)/2 \tag{1}$$

can be determined, and it can be related for amorphous polymers[5,6] to the glass transition temperature (T_g), obtained with dilatometric measurements.

In eq 1, G_1 and G_2 are the shear moduli in the glassy and rubbery state, respectively, and K is the fixed time after which the moduli are measured. In particular Tobolsky[4] suggested use of $K = 10$ s.

Other methods are based on the dependence of thermal properties upon temperature as in differential scanning calometry (DSC) or differential thermal analysis (DTA). The results obtained from noncrystalline polymers generally show more than qualitative agreement with the T_g determined with the previously discussed systems, in spite of the difficulties connected with the heating rate and the sensibility of the analyzer.

In this note measurements of the glass transition temperature of Nylon 6 (Renyl, Montecatini-Edison) obtained using some of the methods indicated above are presented and discussed.

The results obtained with the Differential Scanning Calorimeter are very similar to those obtained by Gordon.[7] Using differential thermal analysis on different Nylons, Gordon found that the endothermic peak observed in the heating cycle disappeared in the subsequent cooling curve. This phenomenon, "related to the alternation of nonpolar chain segments with strongly hydrogen bonding groups along the polymeric chain", seems to be detectable only by thermal analysis. In fact a different behavior is observed using the method proposed by Tobolsky[4] for the determination of T_g.

In Figure 1 data of shear moduli after 10 s, $G(10)$, obtained using a Clash-Berg stiffness torsional tester, are reported vs. temperature. It can be noticed that there is no dependence of the modulus on the thermal history. In particular, data obtained at temperatures steadily increasing up to 140 °C (triangles) show no sensible difference with data obtained in the subsequent cooling to room temperature (open circles). Furthermore the residence time at a given temperature does not seem to have any influence on the elastic properties of the material. It must be recognized, however, that the heating and cooling rates are necessarily lower than those used in DTA or DSC measurements. Then, to test the effect of the rate of heating we have measured the modulus on samples subjected to different thermal histories. For example, data were taken at steadily increasing temperature up to 70 °C, the maximum temperature reached with the DTA,[7] and then the sample was rapidly cooled down to 4 °C and the modulus was measured at increasing temperature (full circles). In this test the cooling rate was strongly increased without noticeable effect on the mechanical behavior of the material (Figure 1). Finally in the last experiment the heating rate was increased, by suddenly putting the sample into a thermostatic bath at $T = 85$ °C and the modulus was measured (black triangle). Then it was quenched to 7 °C and the modulus is reported in Figure 1 (X).

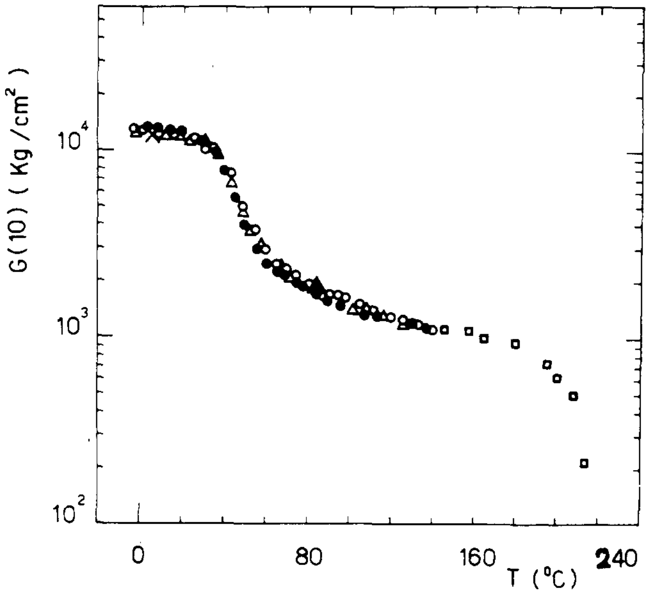

Figure 1. Shear modulus $G(10)$ as a function of temperature at different thermal histories: (△) with steadily increasing temperature up to 140 °C; (○) subsequent cooling down to 0 °C; (●) with increasing temperature after quenching from 140 to 4 °C; (▲) with sudden heating up to 85 °C; (X) subsequent quenching to 7 °C; (□) with increasing temperature from 140 to 220 °C.

The curve plotted in Figure 1 shows a behavior analogus to that of other polymers; namely, the modulus with increasing temperature decreases very steeply at first from the initial plateau at low temperatures and then forms a second plateau, followed at last by the liquid behavior of the material (open squares). It is to be noted that whereas the low temperature plateau value is that characteristic of the glassy state of the polymers (10^4 kg/cm^2), the second plateau value situated in the range of temperature between 140 and 160 °C is two or three orders of magnitude larger with respect to the rubbery plateau of completely amorphous polymers like polyisobutylene or polystyrene.[5] This feature is due to the unavoidable presence in the Nylon 6 of a larger percentage of crystallized polymer.

In fact, the value of the elastic modulus of a crystalline polymer is of the same order of magnitude as that of a glassy polymer since the crystallinity has no appreciable influence on the low-temperature plateau level; but it contributes, instead, to an increase in the stiffness of the amorphous polymer in its rubbery plateau. The influence of crystallinity on the rubbery plateau level is a well-known effect.[8,9a]

Since the change in crystallinity is negligible, the transition zone in the mechanical properties vs. temperature results obtained by means of a Clash-Berg tester reflects mainly the increase of the chain mobility of the amorphous phase of the polymer. Thus, from a phenomenological point of view, the temperature obtained by the Tobolsky method is essentially equivalent to that obtained by the dilatometric method. In fact by the latter procedure[10] the T_g was found to be 50 °C, whereas in Figure 1 $T_1(10) = 54$ °C is in good agreement with the above result. Moreover the measurements given by the dilatometric method are not influenced by the previous thermal history of the samples as well.

In conclusion, it seems that dilatometric or mechanical measurements on Nylon 6 give the glass transition temperature in its classical meaning, without any of the troubles that seem to arise from measurements based on variations in thermal properties.

On the other hand, as discussed by Gordon[7] the peak observed on heating in DTA or DSC measurements can be due to the breaking of some of the hydrogen bonds present in the amorphous phase that cannot reform in time during the subsequent cooling. The results shown in this work are in agreement with the Gordon interpretation. In fact it is possible that the presence of a high percentage of crystallinity makes the variation in the thermal dependence of the mechanical properties of the amorphous fraction so small that it cannot be detected because of the low sensitivity of the apparatus.

Also the effect of crystallinity is detectable in dilatometric measurements,[10] where the ratio between the slopes above and below T_g is only about 1.5. That is a lower value with respect to those obtained for completely amorphous polymers.[9b]

In the DTA or DSC experiments, according to our interpretation, one would detect therefore only the phenomenon suggested by Gordon in his paper. But this mechanism does not seem to be the main cause of the increase in the chain mobility usually invoked to describe the transition zone between the glassy and rubbery states, since there is an absence of anomalous behavior in dilatometric and mechanical experiments.

Furthermore, as reported by Gordon, the peak of the DTA or DSC measurements does not appear at the same temperature because of its dependence on the thermal history of the samples and this again is reasonably explained through the delay in reforming of hydrogen bonds in the amorphous phase.

A final remark concerns the eventual presence of multiple glass transition temperatures as reported by Boyer[11] for other semicrystalline polymers. This is related to the nature of what we have called the "amorphous phase", which may not be considered perfectly distinguishable from the crystalline phase. That is, between the two phases an intermediate structure can be present, the relative amount of which increases with increasing degree of crystallinity. It seems to us that the Tobolsky method cannot resolve the different glass transitions connected with the motions of the various types of macromolecules interacting with the crystalline phase. But this situation can affect the measured $T_i(10)$ at increasing crystallinity, and on this point more experimental study is planned.

However, the isochronal curve representing modulus-temperature results also gives for a semicrystalline polymer an easy way of determining the phenomenological glass transition temperature besides the levels of the glassy and rubbery plateaus which could be very useful from the technical point of view.

References and Notes

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The Dimensions of Polystyrene Near and Below the Theta Temperature

E. SLAGOWSKI, B. TSAI, and D. McINTYRE*

Institute of Polymer Science, The University of Akron, Akron, Ohio 44325.

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In the course of examining the behavior of extremely high molecular weight polystyrenes[1,2] it seemed worthwhile to examine the behavior of the highest molecular weight sample near the theta temperature. Stockmayer[3] had earlier suggested that the collapse of a coil might occur near the theta temperature. However, viscosity measurements near the theta temperature with the commonly available polystyrene samples had shown no particularly dramatic effect. It is the purpose of this note to show that the radius of gyration of an extremely high molecular weight polystyrene fraction measured by light scattering does show a rapid decrease just below the theta temperature. An analysis of the asymptotic behavior of the scattering curves for this same system in the same temperature range has recently been published[4] and the theoretical implications are extensively discussed there.

A sample of polystyrene anionically polymerized as discussed in ref 1 and 2 was examined by light scattering and equilibrium centrifugation in cyclohexane solutions. The light scattering photometer was designed to measure down to 12° (angle) and the cell was thermostated to ±0.05 °C.

The weight-average molecular weight determined by the light-scattering method at the theta temperature based on calibration with standard NBS sample 705 was 44.4×10^6 g/mol. The weight-average molecular weight determined by equilibrium sedimentation using a Spinco Model E at 800 rpm was 43.5×10^6 g/mol. The *z*-average molecular weight was also measured by sedimentation analysis and found to be 48.8 so that the polydispersity (M_z/M_w) of the sample is known to be low (ca. 1:1). Furthermore the molecular weight is known to

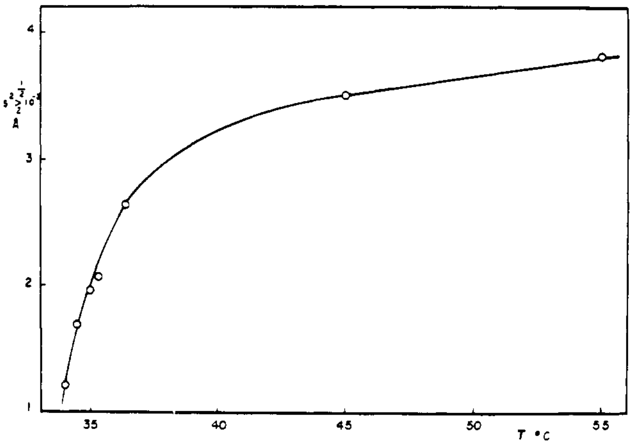

Figure 1. Phase diagram of polystyrene (4.4×10^7 mol wt).