Dedicated to Prof. Edith A. Turi in recognition of her leadership in education

ANOMALOUS MELTING OF POLY(PHENYLENE OXIDE)

H. E. Bair and T. K. Kwei[*]

Bell Laboratories, Lucent Technologies Inc., Murray Hill, NJ 07974, USA

Abstract

Slow evaporation of toluene from poly(2,6-dimethyl-1,4-phenylene oxide), PPO, at 23°C produced crystals which melt between 185 and 265°C and have a crystallinity of 0.58. About 8 wt% of the crystals appear to melt temperatures below 220°C. The latter temperature marks the end of the glass transition interval for this polymer.

Keywords: crystallinity by DSC, enthalpy relaxation, glass transitional interval, heat capacity, melting below T_g, physical aging, PPO crystals

Introduction

Two unusual thermal properties were noted in an earlier study of poly-2,6-dimethyl phenylene oxide (PPO) [1, 2]. First, the ratio of the glass transition temperature, T_g, (208°C) to the melting temperature, T_m, (262°C) equals 0.90 which is the highest reported value to date (most polymers have a value which falls between 0.5 and 0.7) [3]. Second, the semi-crystalline polymer did not show the customary rise in heat capacity C_p, at T_g. This latter phenomenon was observed as an evolution of heat and a consequent drop in the calculated values of C_p. In this work differential scanning calorimetry (DSC) was used to follow the melting of PPO crystals which started below the glass temperature and to check for signs of physical aging after crystals were dried at temperatures below T_g.

Experimental

Materials

Poly(2,6-dimethyl-1,4-phenylene oxide) was obtained through the courtesy of Katchman of General Electric Company. The material was purified by precipitating a 5% toluene solution into a large volume of methanol. The powdery precipitate was dried under vacuum at 100°C for 16 h. The molecular mass of the purified PPO was determined by gel permeation chromatography, using tetrahydrofuran as solvent.

---

[*]   Present address: Polytechnic University, Brooklyn, NY 11201

When compared to polystyrene standards, the molecular mass of PPO was calculated to be: $M_n = 1.10 \cdot 10^4$, $M_w = 4.35 \cdot 10^4$. The density of PPO was 1.066 at 25°C [4].

Sample preparation

The purified PPO powder had a very low degree of crystallinity. But crystallization took place when a 20 ml aliquot of a 2% toluene solution was allowed to evaporate slowly at room temperature over a period of 3 to 4 days. The resulting material exhibited a measurable heat of fusion. Hence, all specimens were prepared from toluene solution in accordance with the above procedure.

In the course of our calorimetric study, the importance of a suitable drying temperature became apparent. Drying at temperatures too far below T_g was often ineffective in the removal of toluene and resulted in low T_m and T_g values. On the other hand, an excessively high drying temperature caused partial melting of PPO crystals and led to erroneous values of the heat of fusion. For these reasons, all specimens were dried in two steps. They were first placed in a vacuum oven at 100°C for 16 h. DSC scans were then made for each sample. After examination of the DSC curves, samples were redried at a temperature chosen to be about 35°C below the inception of melting. But in no case did the drying temperature exceed 160°C in order to avoid thermal degradation of the polymers. Consistent calorimetric results were obtained using the redried samples.

Although PPO has a high glass transition temperature, the drying conditions were apparently effective in the removal of toluene as the T_g and T_m values agreed well with literature data [2, 5].

Calorimetry

A Perkin Elmer differential scanning calorimeter coupled to a computer was used to collect the specific heat data in a manner which has been described previously [6]. Physical aging experiments were carried out on amorphous PPO samples at the various drying temperatures and times. Aged samples were scanned, then quenched and rescanned in order to calculate the amount of enthalpy decrease associated with the drying procedure [7]. Note these endothermic relaxation peaks could contribute to the endothermic melting response of the semicrystalline PPO.

Results and discussion

Two series of heat capacity measurements were carried out. The first, using the solution crystallized PPO described above, was scanned at 20°C min^{-1} from 100 and 300°C. In the second series, the heat capacity of the sample, cooled from the melt at 160°C min^{-1}, was measured again between 100 and 300°C. Karasz *et al.* have shown that when previously crystalline PPO was cooled from the melt at rates of 12°C min^{-1} or greater no crystallization occurred [2]. We shall describe the C_p behavior for amorphous PPO first since we will make use of the linear portion of the C_p curve below T_g as a reference to detect the onset of melting in the solution crystallized sample.

The heat capacity curve as a function of temperature for the quenched sample was smooth showing no sign of any transition from 118 to 208°C (open circles, Fig. 1). Above 208°C a discontinuity in C_p, indicative of a glass transition, T_g, was observed with the change in C_p from the glassy phase to the rubbery state, ΔC_p, equal to 0.054 cal °C^{-1} g^{-1}. T_g was taken as the temperature corresponding to $1/2\Delta C_p$, or 215°C. Above 228°C the C_p rose smoothly again with no sign of any melting. The heat capacity measurements were terminated at 300°C. T_g is 8°C higher in our experiments than found previously using an adiabatic calorimeter [2]; however, one would expect such results considering the large difference in heating rates of 20 by DSC and ~0.08°C min^{-1} by adiabatic calorimeter. The C_p values above and below T_g were in good agreement with earlier measurements made by adiabatic calorimetry [2]. Below T_g the present heat capacity measurements were about 0.8% lower than the earlier values and above the glass temperature values were about 1.5% lower than the older data [2].

The heat capacity of the solution crystallized PPO was found to be identical to that of the amorphous PPO between 118° and 184°C (filled circles, Fig. 1). However, at 185°C the heat capacity began to rise perceptibility above the C_p of the glassy PPO. It is our contention that this is the inception of melting for the thinnest and least perfect PPO crystals. C_p continues to increase with increasing temperature until a maximum is reached at 247°C. Then C_p falls with increasing temperature until it merges at 265°C with the heat capacity for the previously established liquid line of the amorphous PPO.

The fractional crystallinity, X, of the polymer is given by the quantity $\Delta Q_f/\Delta H_f$, where ΔH_f is the heat of fusion for the completely crystalline polymer. In earlier work PPO's heat of fusion was determined by measuring the depression of its melting temperature in mixtures of PPO and chloronapthalene and is equal to 10.0±1.9 cal g^{-1} [1]. In these studies ΔQ_f was found to be equal to 5.8±0.1. Thus, for the solution crystallized sample studied, X=0.58±0.12. This level of crystallinity is about 60% greater than was previously reported [2]. This enhancement in crystallinity in the present sample is probably caused by the slow evaporation of toluene over a four-day period at room temperature.

To calculate the area of the melting peak corresponding to ΔQ_f it is necessary first to establish the baseline which represents the real heat capacity of the quasi-equilibrium mixture of the amorphous and crystalline polymer in the melting region from 185 to 265°C. It was first assumed that the observed C_p curve linearly extrapolated from below T_g to T_m represented C_p of a (hypothetical) completely crystalline PPO sample (dotted line in Fig. 1). Since there is no detectable discontinuity in C_p at T_g for a partially crystalline PPO (≥40%) [2], we assumed the C_p of our semi-crystalline sample is the same as that of the totally crystalline specimen up to 223°C which marks the end of the glass transition interval for the completely amorphous PPO. The dashed line connecting this point to the C_p at T_m (265°C) would then constitute the baseline if C_p increases linearly with temperature from 223 to 265°C as melting progresses. This is probably not the case for as soon as some melting has occurred C_p begins to approximate a more ideal two phase behavior for the amorphous and crystalline components in the sample. One can make a fur-
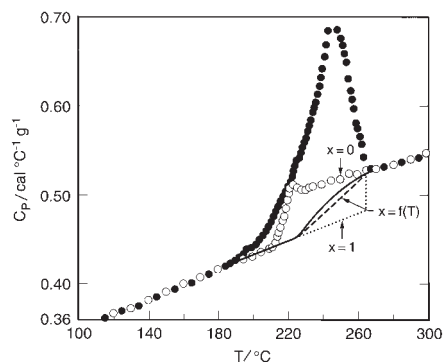
Fig. 1 Heat capacity of poly(2,6-dimethyl-1,4-phenylene ether) and schematic diagram illustrating the method of obtaining the baseline for the apparent heat of fusion calculation. Circles represent experimental results of amorphous (open) and partially crystalline (filled) samples. Solid line indicates final base line used. For other dotted and dashed lines see text

ther minor correction by a series of successive approximations based upon the fact that $X \rightarrow 0$ at the melting temperature. The fractional melt at a series of temperatures between 225 and 260°C was calculated from the area between the C_p curve and the dashed line. The crystal-liquid discontinuity in C_p at T_m was then divided in the same ratio as the calculated fractional melt at a given temperature and extrapolated with the same slope as the hypothetically completely crystalline sample back to that temperature. The solid line in Fig. 1 defines this line.

About 0.6 cal g^{-1} or 10% of the total melt (5.8 cal g^{-1}) occurred below 220°C. This latter temperature marks the end of the glass transition interval. Since amorphous elements within this semi-crystalline specimen can undergo enthalpic relaxation when held below T_g it is necessary to determine if any portion of the melting endotherm is attributable to time the sample has spent drying at temperatures below the glass transition temperature.

The semi-crystalline sample in this study was initially held for 16 h at 100°C and then stored at 150°C for 15 h. Annealing an amorphous PPO sample overnight at 100°C in a vacuum oven has no discernible effect on the PPO's enthalpy. However, aging the same sample of PPO at 150°C for 15 h caused a small difference in scans of the aged (broken line) and then quenched (solid line) form of the same sample to occur between 180 and 212°C (Fig. 2). The enthalpy difference between the two curves equals about 0.18 cal g^{-1}. Since the semi-crystalline PPO is about 58% crystalline only about 0.08 cal g^{-1} or 14% of the endothermic activity below T_g is apparently associated with the physical aging of the amorphous portion of the PPO during the drying of the material. Hence, the major fraction (86%) of the endotherm below T_g in the melting of the solution grown crystals of PPO (Fig. 1) is attributable to melting process. In other words, about 8% of the solution grown crystals of PPO melt below T_g.
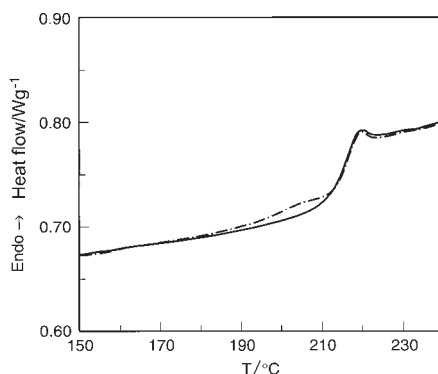
Fig. 2 Comparative DSC scans of amorphous PPO aged for 15 h at 150°C (broken line) and quenched PPO (solid line)

Although the authors are not aware of any other cases of polymers that show signs of melting below T_g it may be that sub-T_g melting does not violate anything other than conventional wisdom. It can be argued that crystallization took place in the presence of a solvent which lowered T_g below the crystallization temperature. Kambour and coworkers found that acetone depressed polycarbonate's glass temperature by 145°C but only lowered the melting temperature by about 60°C and thereby enhanced the crystallization rate in acetone over that in dry, bulk polycarbonate above the normal T_g [8]. It may be that because PPO has a very low entropy of fusion that crystallization is facilitated in amorphous regions, making it possible to produce thin, low melting crystals even below the glass temperature. These thinnest crystals that begin to melt at temperatures between 185 and 190°C and are followed by the melting of thicker, more perfect crystals which stop melting near 265°C yield a broad exotherm measuring about 80°C in width. However, it is not uncommon to see other polymeric crystals with melting exotherms of this breadth [9, 10]. Could it be that the effective T_g for the smallest crystals that melt near 210°C is lower than the 'bulk' T_g. Recently the T_g of materials confined within small pores has been found to decrease to lower temperatures as the size of the pores are diminished [11, 12]. Unfortunately at this time it can be concluded that the basic cause of this unusual melting behavior is not known and warrants further study.

Conclusions

The slow evaporation of toluene from PPO at 23°C produced crystals, which melt between 185 and 265°C and have a fractional crystallinity of about 0.58. Nearly 8% of the crystals melt at temperatures below 220°C. The latter temperature marks the end of the glass transition interval for this polymer at a heating rate of 20°C min^{-1}. In other words, about 10% of PPO's experimental heat of fusion occurs below T_g. Assuming a two-phase model, only 14% of the observed endothermic activity is associated with physical aging of the amorphous portion of the semi-crystalline PPO during the polymer's preparation. Hence, the remaining portion of the endotherm below 220°C is connected with melting of PPO.

References

1 F. E. Karasz, J. M. O'Reilly, H. E. Bair and R. A. Kluge, in Analytical Calorimetry, Vol. 1, R. S. Porter and J. E. Johnson, Plenum Press, NY 1968, p. 59.
2 F. E. Karasz, H. E. Bair and J. M. O'Reilly, J. Polym. Sci., A2 (b) (1968) 1141.
3 R. F. Boyer and R. Chen, Technol., 36 (1963) 1303.
4 J. R. Fried, F. E. Karasz and W. J. MacKnight, Macromolecules, 11 (1978) 150.
5 F. E. Karasz and J. M. O'Reilly, J. Polym. Sci., Part B, 3 (1965).
6 H. E. Bair, G. E. Johnson, E. W. Anderson and S. Matsuoka, Polym. Eng. and Sci., 21 (1981) 930.
7 S. Matsuoka and H. E. Bair, J. Appl. Phys., 48 (1977) 1200.
8 R. P. Kambour, F. E. Karasz and J. A. Daane, J. Polym. Sci., Part A-2, 4 (1966) 327.
9 J. M. O'Reilly, F. E. Karasz and H. E. Bair, J. Polym. Sci., Part C, 6 (1963) 109.
10 J. M. O'Reilly, H. E. Bair and F. E. Karasz, Macromolecules, 15 (1982) 1083.
11 C. L. Jackson and G. B. McKenna, Chem. Mater., 8 (1996) 2128.
12 C. L. Jackson and G. B. McKenna, J. Non-Crystalline Solids, 131 (1991) 221.