

# Amorphous structure heat: Molecular mechanisms from solution heats of poly(2,6-dimethyl-*p*-phenylene oxide) in orthodichlorobenzene

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The heats of solution in orthodichlorobenzene were measured as a function of temperature for both quenched and as-received polyphenylene oxide. The curves are linear below 110°C with slopes of 0.098 cal/g°C and linear above 110°C with slopes of 0.032 cal/g°C. The inflection at 110°C is attributed to a  $\beta$  transition. The plot for the as-received material is displaced vertically from that of the quenched material by 2.75 cal/g which is attributed to the fact that the as-received material contains about 27.5% crystallinity. The major component of the heats of solution is the exothermic contribution from the solvent-induced freeing or relaxation of the constrained molecular motions.

## INTRODUCTION

The three powerful methods of mechanical spectroscopy, dielectric loss, and nuclear magnetic resonance are commonly used to study internal molecular motions in polymers over a wide range of temperatures and frequencies. Several investigations<sup>1-4</sup> involving such experimental methods have been made to study the relaxation mechanisms of poly(2,6-dimethyl-*p*-phenylene oxide), subsequently to be referred to as PPO.

Heijboer<sup>1</sup> measured the shear modulus and damping of many polymers at a frequency of 1 Hz using a torsion pendulum in attempts to relate secondary transitions to dynamic mechanical properties and impact strengths. For PPO, he reports maxima in damping above 190 and near 0°C, the lower-temperature transition being very small. The transition in impact strength is near -80°C, and he reports no dynamic mechanical relaxation in this region.

In mechanical relaxation studies of Chung and Sauer<sup>2</sup> on PPO, two secondary transitions are reported: one very broad loss peak at 4°C (1.32 Hz) which they designate as  $\beta$  and another broad relaxation in the temperature range from -150 to -130°C.

Baccaredda *et al.*<sup>2</sup> investigated several other poly(*p*-phenylene oxides) including poly(2,6-dimethyl-*p*-phenylene oxide). They observe a rapid increase in the damping factor in the temperature region -200 to -130°C which then remains constant up to about -30°C. In the range -30 to -180°C, a broad relaxation is observed with a loss maximum occurring at 97°C. They attribute this  $\beta$  transition to oscillating paraphenylene rings around C-O-C bonds.

Karasz and co-workers<sup>4,5</sup> studied the dielectric properties of PPO as a function of temperature in the frequency range from 0.1 to 10 kHz. The temperature range used was -160 to 260°C. They report relaxation maxima at -100 and 220°C. The transition at 97°C reported by Baccaredda was not observed.

Heijboer<sup>1</sup> recently measured the unnotched impact strength of PPO, and DiBenedetto and Trachte<sup>6</sup> calculated fracture surface energy in plane strain for this polymer. Heijboer<sup>1</sup> concluded that no relationship exists between impact strength and secondary transitions.

DiBenedetto and Trachte,<sup>6</sup> however, seemingly unaware of the 97°C transition reported by Baccaredda,<sup>1</sup> reported a maximum in fracture energy at 102°C when analyzing their results in light of free-volume concepts.

More recently, techniques involving solution microcalorimetry are giving a new and interesting insight into the nature of the glassy state.<sup>7,8</sup> This method stems from observations by many researchers<sup>9-12</sup> that upon solution of a glassy polymer a quantity of heat is released that is solely a function of the state of the solid polymer and independent of any polymer-solvent interactions.<sup>8</sup> Recent work by Allen<sup>13</sup> as well as by the present authors<sup>14</sup> on polystyrene indicates that this heat is characteristic of the glassy state, independent of the specific volume of the polymer, and decreases linearly with increasing temperature to zero in the vicinity of  $T_g$  for polystyrene.

In this paper we will show that for PPO this heat not only decreases linearly with increasing temperature, but changes slope at 110°C which is in the vicinity of a reported  $\beta$  transition. Above this temperature, the residual heat versus temperature again decreases linearly but with a smaller slope.

## THEORETICAL CONSIDERATIONS

The integral heat of solution  $\Delta h_m$  is the total heat measured calorimetrically when a polymer is dissolved. The heat of solution can be separated into a solvent-dependent term, referred to as the heat of mixing  $\Delta H_m$  resulting from interactions between polymer and solvent molecules, and a solvent-independent term, which we call the residual heat  $\Delta H_r$ , i. e.,

$$\Delta h'_m = \Delta H_m + \Delta H_r \quad (1)$$

$\Delta H_r$  depends on any structure in the polymer over and above that of a perfectly "amorphous liquid state." It may consist partly of an endothermic heat of fusion due to solvent-induced disruption of crystallinity or order and/or an "exothermic amorphous heat" due to solvent-induced disruption of noncrystalline regions if the measurement is below the  $T_g$  of the polymer. Written in the form

$$\Delta h'_m - \Delta H_m = \Delta H_r \quad (2)$$

this equation can and has been used to show that the residual heat is independent of the solvent, provided a consistent theory for calculating  $\Delta H_m$  is used.<sup>15</sup>  $\Delta H_m$  values can also be obtained directly from heat-of-dilution measurements.<sup>7,8</sup>

The above equations [Eqs. (1) and (2)] and analysis apply only if the polymer dissolves completely to a random coil conformation in solution. The existence of structure, i. e. order, association, or molecular conformations other than random coil in solution can modify the above, but then the difference in residual heats for the same polymer in different solvents is a measure of the extent of this structure. Such is the case with poly(ethylene oxide) in water<sup>16</sup> where the PEO molecule is helical in aqueous solution.

It should be emphasized that the data presented here is that of the integral heat of solution. To determine the residual heat,  $\Delta H_r$ , would require knowledge of the PPO-orthodichlorobenzene interaction parameters as could be obtained osmometrically or from heats of dilution. Neither values of the interaction parameters for this system nor heats of dilution appear in the literature, and performing such measurements would be extremely time consuming and do little but to shift the total curve vertically or change the slopes slightly. The temperature dependence of the heats of solution, which is the primary point of interest of this data, are caused primarily by solvent-induced disruption of structure in the solid polymer.

## EXPERIMENTAL

PPO (PR5255) with an intrinsic viscosity of 0.49 was obtained from the General Electric Co. in the form of white powder.

The instrument used for the measurements was a microcalorimeter of the isothermal Tian-Calvet differential type. The instrument was constructed with 64 copper-constantan junctions per measuring element. Copper-constantan junctions were used because although they do not have the largest thermoelectric coefficient of possible junctions, they do have a significantly lower over-all resistance, thus minimizing the Johnson noise that determines the upper limit of sensitivity of the instrument. Furthermore, the greater thermal conductivity of the copper allows a more rapid dissipation of heat from the cell.

A major problem was in achieving suitable temperature stability of the instrument at high temperatures so that variations were slow enough and small enough so as not to be picked up by the detecting elements. Proportional controllers were completely inadequate. The solution was in isolating the main block and main-block heating coils in a high-thermal-mass insulated enclosure. An aluminum cylinder  $\frac{1}{4}$  in. thick, 15 in. in diameter, and 20 in. high was used. The enclosure containing the main block and main-block heaters was then placed in a large forced-air oven; the temperature of the oven was controlled by a proportional controller. The main-block heating was then done by a constant Variac-controlled ac current. The arrangement gave a baseline as stable at 200 °C as at room temperature.

The sampling arrangement used was essentially the same as that reported earlier<sup>8</sup> with the exception that no cuvettes were used. Rather, the sample was introduced in the form of a pressed disk that was held directly below the mercury by a glass rod. This was necessary at higher temperatures due to the drastic effects of having trapped air bubbles in the system. The solvents used were boiled prior to usage to eliminate possible low boiling contaminants.

The samples used consisted of thin disks  $\frac{3}{8}$  in. in diameter by approximately  $\frac{1}{64}$  in. thick which were formed by compacting the powdered polymer on a pellet press. Heats of solution obtained at room temperature were identical for the powder and the pressed disks. Quenched samples were obtained by heating the pellets to 270 °C and quenching in ice water with subsequent drying under vacuum for 24 h.

## RESULTS

The heats of solution versus temperature for both the as-received and quenched PPO are plotted in Fig. 1. Many points are immediately apparent. First, the data for both samples are parallel over the complete temperature range studied, the quenched material having the more exothermic values. The difference between the two plots of about 2.75 cal/g is due primarily to the heat of fusion per gram of polymer, but must also contain a contribution from the differences in excess enthalpy in the glassy amorphous regions of the quenched and annealed specimens.<sup>17,18</sup>

Second, the total heats of solution are always exothermic. Although the data is presented as the heats of solution which contain the heat of mixing, the bulk of the heats of solution are due to solvent-induced disruption of amorphous structure, i. e., that portion of the material that is noncrystalline. As observed previously in polystyrene<sup>8</sup> and poly(vinyl chloride)<sup>9</sup> as well as all other polymers tested below their  $T_g$ ,<sup>19</sup> an exothermic structure related heat is evolved upon solution. Allen observed that for polystyrene such an amorphous struc-

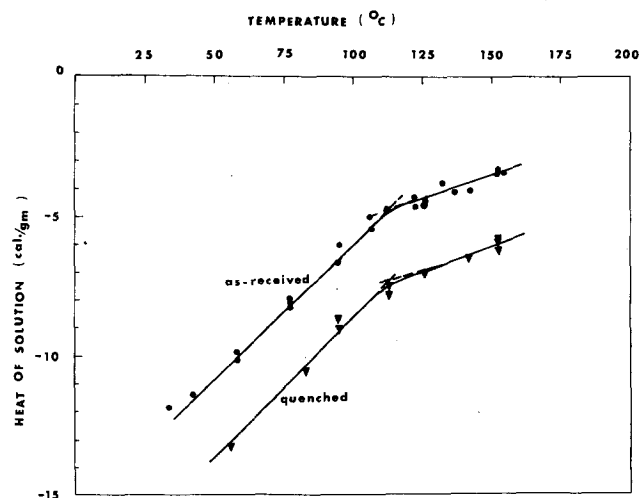


FIG. 1. Heats of solution vs temperature in orthodichlorobenzene for quenched and as-received polyphenylene oxide.

ture heat was independent of the pressure under which the polymer was glassified.<sup>13</sup> This was confirmed by the present authors.<sup>14</sup>

Third, the heats of solution versus temperature for both samples decrease linearly with a slope of 0.098 cal/g°C below 110°C, change slope at 110°C, and continue a linear decrease above this temperature with a reduced slope of 0.036 cal/g°C. Such a linear decrease of the exoamorphous heat has been observed as well for other systems studied below their  $T_g$ . However, this is the first system that an abrupt change in slope has been observed below  $T_g$ , although other systems presently under investigation have also produced this effect.<sup>19</sup>

## DISCUSSION

This difference in enthalpies of mixing between the as-received and quenched samples is attributed primarily to the heat of fusion associated with crystallinity in the as-received material. In DSC studies on PPO (General Electric), Karasz *et al.*<sup>20-22</sup> report that the as-received material is semicrystalline as indicated by a melting endotherm on the initial heating. However, after cooling, the melting endotherm disappears and subsequent heating shows no evidence of crystallinity but only a  $T_g$  at approximately 220°C. This indicates crystallization is extremely slow.

Using a value of 10 cal/g for the heat of fusion of 100% crystalline PPO as determined by Karasz *et al.*,<sup>21</sup> the difference between the two curves in Fig. 1 of 2.75 cal/g would predict a value of 27.5% crystallinity, which should be slightly high due to the excess enthalpy difference between the quenched and annealed glasses. However, this value agrees well with the 25% crystallinity deduced by Karasz *et al.* from x-ray diffraction measurements, but is lower than the 40% value deduced by them from DSC measurements.<sup>21</sup> Because different samples of PPO were used, we cannot speculate as to why our value agrees better with the x-ray-determined value. This does, however, indicate the extreme sensitivity of this method in determining relative amounts of crystallinity in polymer samples.

The second point to be discussed concerns the exothermic enthalpy released upon solution of a glassy polymer and the linear decrease of this value with increasing temperature. We feel the source of this heat is due to solvent-induced freeing of a molecular motion which had become frozen-out or constrained as the temperature of the polymer was lowered below the transition temperature of this motion. Thus a molecular motion gains energy upon temperature increase by increasing its amplitude of oscillation and loses energy upon decrease of temperature by decreasing its amplitude of oscillation. When the temperature of the material is dropped below the temperature where this motion becomes frozen-out by the constraints imposed on it by neighboring molecules, the amplitude of the motion can no longer decrease or the motion can no longer lose energy. However, if the constraints are removed at a temperature below the transition temperature, the motion will again begin operating but with an amplitude

corresponding to the lower temperature. This sudden decrease in energy of the motion in question we feel is responsible for the exothermic amorphous enthalpy. Clearly then the magnitude of the exoamorphous heat will depend on the temperature difference below the transition temperature at which the motion was released.

Now we can analyze Fig. 1 as follows. Below 110°C two distinct molecular motions are constrained, one whose transition temperature is 110°C and another whose transition temperature is probably the normal  $T_g$  of PPO (220°C). Below 110°C both motions are frozen-out and will contribute to the exoamorphous heat; while above 110°C one motion is now operating while the other (associated with  $T_g$ ) is still constrained. As a point of interest, if we assume the heat of mixing is temperature independent, the slope above 110°C of 0.036 cal/g°C and below 110°C of 0.098 cal/g°C could be used to obtain specific heats of the corresponding motions. Thus, the motion associated with  $T_g$  would have a specific heat of 0.036 cal/g°C and the motion associated with the 110°C transition would have a specific heat of 0.062 cal/g°C. The linear decrease of the exoamorphous heat implies that these molecular motions must be behaving classically.

A  $\beta$  transition in the vicinity of 110°C has been observed by many others. Baccaredda<sup>2</sup> observes a secondary transition at 97°C which he attributes to oscillations of paraffin rings around C-O-C bonds. DiBenedetto and Trachte<sup>6</sup> report a maximum in fracture energy at 121°C for PPO (General Electric Grade 631-111). Heijboer,<sup>1</sup> however, did not observe such a transition in his impact studies. A possible reason for this is that the high strain rates involved in his tests may have shifted this transition to higher temperatures.

Data of the type presented here raise a number of interesting questions concerning present ideas of the glassy state. Before a complete analysis can be made, however, data of this type must be obtained on a number of other polymers.<sup>23</sup> Other systems presently being studied include polycarbonate, polysulfone, polymethylmethacrylate, and polyvinyl chloride.

## CONCLUSIONS

Heat-of-solution measurements are a unique and sensitive method of determining low amounts of crystallinity in polymers as well as of obtaining information on molecular mechanisms constrained in the glassy state. For polyphenylene oxide a difference of 27.5% crystallinity exists between the quenched and as-received materials based on a heat of fusion of 10 cal/g. Furthermore, the exothermic amorphous heat (which is released upon solvent-induced disruption of the glass) decreases linearly with temperature (slope = 0.098 cal/g°C) to 110°C, above which it decreases its slope to 0.036 cal/g°C.

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