Amorphous structure heat: Molecular structure from solution heats of polymethylmethacrylate in orthodichlorobenzene

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The heats of solution in orthodichlorobenzene were measured as a function of temperature for both as-reprecipitated and quenched atactic polymethylmethacrylate. The as-reprecipitated curve decreases linearly with a slope of 0.096 cal/g °C from room temperature to 90 °C, and above 110 °C has a constant value of +1.5 cal/g. The quenched material data decreases linearly with a slope of 0.12 cal/g °C from room temperature to 55 °C, jumps +2 cal/g at 55 °C, and continues the linear decrease with a slope of 0.096 cal/g °C from 55 to 90 °C. The data suggests that isotactic stereochemical impurities in the atactic material are able to crystallize at 55 °C which is the T_g of i-PMMA, and therefore must be associated as i-PMMA islands in a rigid atactic-syndiotactic PMMA matrix. This also suggests that the β transition in PMMA may be associated with the isotactic impurities

INTRODUCTION

Methods involving solution microcalorimetry are providing new and interesting information concerning the structure in solid polymers. Such measurements are of particular importance in low-crystalline or amorphous polymers because they provide the only method of quantitatively determining very small amounts of order or crystallinity (< 1%). In addition, solution enthalpies measured at various temperatures and on samples of different thermal treatments are providing new and important information on the glassy-structure-related enthalpy[1] and on primary and secondary transitions. The exothermic amorphous enthalpy is a new parameter (which so far can only be obtained by these techniques) which is primarily related to solvent-induced disruption or liberating of constrained molecular degrees of freedom and partly due to excess enthalpies of the glass. In the systems studied thus far, however, indications are that this exoamorphous heat has a very characteristic behavior as a function of temperature and in the vicinity of secondary transitions.

A recent series of papers have appeared in various texts describing experimental techniques,[2,3] single temperature measurements on polyvinylchloride (PVC) and polyethylene oxide,[4,5] measurements on polystyrene cooled under various pressures,[6] and measurements on polystyrene as a function of temperature.[1] This paper presents results on presumably atactic polymethylmethacrylate (PMMA) from 30 to 150 °C in orthodichlorobenzene for both the quenched and annealed polymer. This polymer was chosen because it is considered amorphous, is easily soluble in a large number of solvents, and has two reported secondary transitions within the temperature range of our measurements. The largest transition is the normal T_g at approximately 110 °C, while the other is a so-called β peak which appears around 50 °C. It has been suggested by Heijboer[7] that the β transition results from motion of the ester side group, while Roetling[8] in quoting Havriliak indicates that it is probably due to rotation within the main chain. Andrews,[9] however, suggests it may be due to breakdown of dipole-dipole interactions between ester side groups. Our results indicate, however, that irrespective of what the motion is, this transition is related to the presence of isotactic impurities in the stereochemically impure atactic PMMA.

EXPERIMENTAL

Atactic PMMA (MS 1034) of $\bar{M}_n = 49\,200$ and 19 400 was obtained from Rohm and Haas in the form of pellets. A fine powder was obtained by slowly dripping a dilute benzene solution of the polymer into a rapidly stirred bath of methanol. The powder was subsequently dried in a vacuum oven at 100 °C until no traces of residual solvent could be observed by infrared. The samples used in the measurements were prepared by compacting the powdered PMMA into disks $\frac{3}{8}$ in. in diameter by approximately $\frac{1}{64}$ in. thick. The compaction of the powder was necessary for the high-temperature measurements since trapped air in the sample increases the standard deviation of the measurements. Likewise, the thin disks were used to increase the rate of solution of the polymer

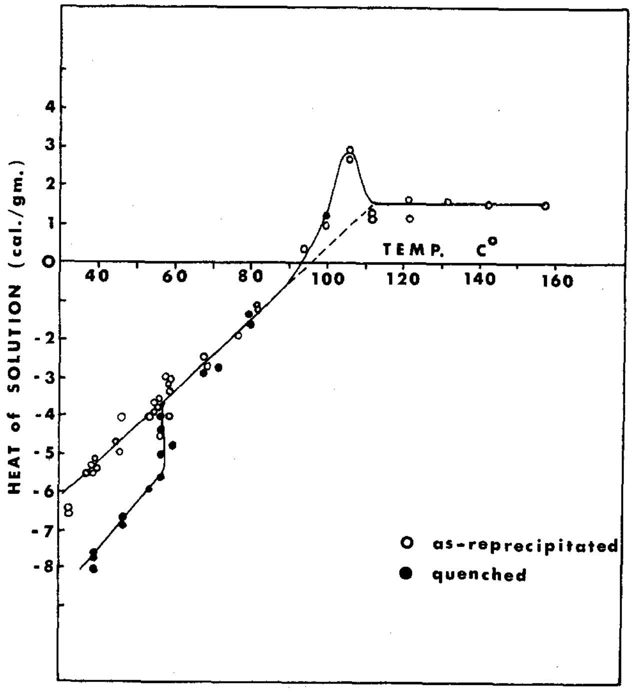

FIG. 1. Heat of solution vs temperature for quenched and as-reprecipitated PMMA in orthodichlorobenzene.

which again gives more reproducible data. Heats of solution of the compacted pellets and the reprecipitated powder were obtained at room temperature to assure that compaction had no effect on the measurements.

The instrument used for the measurements was an isothermal-differential microcalorimeter similar to the Tian-Calvet.[10,11] The sampling arrangement used is detailed in other papers.[1,3-5,11]

Quenched samples were prepared by heating the disks to 200 °C for a short time and quenching them in ice water with subsequent vacuum drying.

The theory and rational behind these types of measurements is covered in detail elsewhere in a number of papers.[1-5]

RESULTS

The heats of solution at various temperatures of the reprecipitated PMMA and the PMMA quenched from 200 °C using orthodichlorobenzene as a solvent are plotted in a single figure (Fig. 1) to allow a direct visual comparison of the results.

AS-REPRECIPITATED PMMA

The data for the as-reprecipitated PMMA are represented by open circles in Fig. 1. There are four regions of this graph which we wish to emphasize: (i) above 110 °C, (ii) between 90 and 110 °C, (iii) between 30 and 90 °C, and (iv) the vicinity of 50 °C where a β transition is reported.[7]

Above 110 °C, the heats of solution are completely endothermic and nearly constant, decreasing only slightly up to 160 °C which is the highest temperature of measurement. Although these measurements are heats of solution which contain a heat of mixing, the nearly constant data as well as the speed at which the heat was generated upon contact of polymer and solvent is a strong indication that this endothermic heat is due to solvent destruction or fusion of ordered or crystalline regions. Further analysis of heats of dilution obtained by Daoust and Hade[12] on the system PMMA-orthodichlorobenzene indicate that the heats of mixing are slightly endothermic (≈ 0.01 cal/g).

Analysis of the same data in a method proposed by Maron[5,13] indicates the heats of mixing may be slightly endothermic or slightly exothermic, depending on how the data is analyzed since it contains a considerable amount of scatter. It is important also that the heats of solution obtained above 110 °C are very reproducible (with $\pm 2\%$), since normally reproducibility decreases at increasing temperatures. This may be an indication that the structure within the polymer in this temperature range is less subject to thermal aging effects than it is below 110 °C.

In the temperature range 90–110 °C, the heats of solution become endothermic, but more importantly, the data deviates from the linearity observed below 90 °C. The data actually reaches a maximum endothermic value at about 105 °C and then drops rapidly to the constant endothermic value above 110 °C. This portion of the curve has also been substantiated in the solvent xylene.[14] Although this is the only system studied thus far which shows the increasing slope on approaching T_g from lower temperatures, the relatively sharp drop at T_g has also been observed in polystyrene.[1]

Between 30 and 90 °C the heats of solution decrease linearly with a slope of 0.096 cal/g °C. If this linear region is extrapolated to higher temperatures, it intersects the high-temperature portion of the curve at approximately 110 °C which is in the vicinity of the normal T_g of atactic PMMA. This linear decrease of the heats of solution with increasing temperature below T_g has been observed in all polymers studied thus far which have a T_g within or above the temperature range studied (30–160 °C). One important exception exists in which a β transition (where T_g is considered the α transition) occurs also in the temperature range studied. In this case an abrupt decrease in slope is observed to occur at the β transition. However, the plots remain linear both below and above the β transition.[11] This linear decrease is associated solely with the solvent-induced freeing of molecular motions which become constrained as the polymer is cooled below a secondary transition. This point will be discussed later.

For the temperature region in the vicinity of 50 °C, we would merely like to point out that although a β transition is reported here, nothing significant is observed in the plot for the as-reprecipitated material in this region.

QUENCHED PMMA

Data for the PMMA quenched in ice water from 200 °C is shown in Fig. 1 as solid circles. Data was obtained only up to 100 °C since above 110 °C the material can no longer be considered quenched. Above approximately 55 °C, the quenched PMMA data virtually superimposes with the as-reprecipitated PMMA data. However, below 55 °C, the quenched PMMA data has a steeper slope and is more exothermic than the as-reprecipitated material data. The relatively sharp jump in the data at 55 °C is due to the fact that at or near this temperature the data varied between the quenched data curve and the as-reprecipitated curve; the variable being the length of time a quenched sample was held at the temperature before being run. The minimum amount of time a sample must be held at this temperature before running is about 2 h. Thus, samples run after 2 h would give a value nearer to the lower line, while samples run after 10 h would give a value almost identical with the upper line. This, of course, suggests that some annealing was probably taking place.

The slope of the data below ≈ 55 °C is 0.12 cal/g °C, which is significantly steeper than the slope for the as-reprecipitated material. Thus, for the quenched material a slope change is observed at ≈ 50 °C as well as a jump in the plot of heats of solution versus temperature.

One final point concerns the magnitude of the jump at 55 °C which is about + 2 cal/g. Because this jump is a difference between measurements on the same polymer and at the same temperature, it must be totally a difference in internal enthalpy between the quenched and as-precipitated samples.

DISCUSSION

Because these measurements represent a new method of characterizing structure within polymers and most of the initial results are still in press, the data has not yet been subjected to a thorough analysis by the polymer scientific community. We can therefore only state our empirical analysis of the data thus far which will be substantiated when the data is published.

The first point is that a jump in the data at any temperature to a less *exo*thermic or more *endo*thermic value is indicative of a first-order transition or crystallization occurring.

The second point is that below the T_g of a low-crystalline polymer, an exothermic contribution to the heat of solution appears which decreases linearly, presumably going to zero at and above T_g,[1] except in the case where a β transition exists in the temperature range of the measurements. In this case the heats will decrease linearly until the β temperature, will decrease the slope at the β temperature, and will continue the linear decrease with the reduced slope above the β temperature; an example is polyphenylene oxide.[11]

Therefore, structure-related enthalpies below T_g or any secondary transition are a sum of endothermic fusion heats, exothermic amorphous heats, and heats of mixing. It has been shown, however, that the structure-related portions (called residual enthalpies) are truly independent of the heats of mixing.[2-5] Although the values represented here contain the heat of mixing, they cannot account for the behavior with temperature of the data. Furthermore, they are probably only a small portion of the total heats of solution measured.

The rise of the curve or increasing slope in the data above 90 °C, as suggested by Petrie,[15] is probably related to the relaxation of the excess enthalpy of the glass.[16,17] Since this relaxation can take a considerable length of time, it is not surprising that the data for the as-reprecipitated and quenched material are the same in this region. The rise near T_g has only been observed thus far in PMMA as opposed to PVC and polystyrene. However, the rapid drop in the data has also been observed in polystyrene. We further have observed that even though excess enthalpy of the glass may, in fact, be present in these measurements, they only serve to shift the linear portion of the curve by a constant value, i.e., the slope of the linear portion of the curve is unchanged by the excess enthalpy of the glass. We feel that the exothermic heat observed upon solvent-induced disruption of the glass may contain at least two components: (i) a nonequilibrium part associated with the excess enthalpy in the sample which depends on how the sample was cooled below T_g [16,17] and (ii) an equilibrium part which is due to solvent-induced freeing of molecular motions which became constrained on going below T_g. The slope of the curve of 0.096 cal/g °C could then be considered as the specific heat capacity of this motion.

The jump in the quenched data at 55 °C is indicative of a first-order transition as a crystallization taking place. Clearly, this crystallization cannot be in atactic or syndiotactic PMMA. However, since the T_g of isotactic PMMA is reported to be between 45 and 55 °C,[18,19] it is not unrealistic to speculate that isotactic PMMA may be crystallizing at this temperature. The fact that isotactic stereochemical impurities exist in the seemingly atactic PMMA has been reported in many papers.[20-23] However, if this is a crystallization of isotactic material, then clearly it must occur without diffusion of the isotactic segments throughout the rigid atactic and syndiotactic matrix. In other words, the isotactic material must already be associated or exist as isotactic islands within the atactic-syndiotactic matrix. This is also possible since it has been reported that isotactic PMMA is incompatible with atactic PMMA.[24]

It has also been reported recently by Klement and Geil[25] that thermal crystallization of *i*-PMMA proceeds very slowly even at 125 °C, that is in order to produce a well-developed lamellar structure. Our measurements, however, are confirming that some crystallization or ordering is, in fact, taking place at the T_g of the isotactic material. These results are in no way contradictory, however, since ordering can presumably occur on a local level before the growth of lamellae proceeds. Furthermore, we have no evidence as to the size of the isotactic material within these blocks or whether they consist of isotactic segments of chains or purely isotactic chains.

It has been mentioned previously that the slope of the data for the quenched material is 0.12 cal/g °C below 55 °C. Although enough data to establish a slope for the quenched material above 55 °C has not been obtained, if the slope from 55 to 90 °C is the same as for the as-reprecipitated material, i.e., 0.096 cal/g °C, then a decrease in slope occurs also at 55 °C. This decrease in slope as explained earlier is indicative of a second-order transition existing at this temperature. The slope change is not as obvious as it is in polyphenylene oxide[11] because the amount of material contributing to it which is the *i*-PMMA is probably 5% or less of the total material.

Finally, the jump at 55 °C of approximately + 2 cal/g should be a true heat of fusion as mentioned previously. However, above 110 °C the constant endothermic value if consisting solely of a heat of fusion should be identical to this jump. It, however, has a value of + 1.5 cal/g. This discrepancy we feel is possibly due to the fact that the data obtained above 110 °C contains the heat of mixing, which, if slightly exothermic would account for the difference in the values.

By this analysis of the data, we do not necessarily mean to extrapolate our results to cover all atactic PMMA. Measurements of this type on samples of PMMA seeded with various amounts of isotactic material are needed before our explanation can definitely be confirmed. This, however, would require a considerable amount of time considering the very tedious and time-consuming heat-of-solution measurements.

We feel, however, that the evidence is quite strong from these results to warrant our analysis of the data.

CONCLUSIONS

We believe the current results serve to strengthen the supposition that the exothermic amorphous heat observed upon solvent-induced disruption of amorphous regions at a temperature below T_g decreases linearly with increasing temperature and presumably goes to zero at and above T_g. Furthermore, the data suggests that the β transition at 55 °C in atactic PMMA is associated with isotactic stereochemical impurities which are observed to crystallize at approximately 55 °C from a quenched sample. In order for the observed crystallization to occur, however, the isotactic material must have been associated within the rigid atactic-syndiotactic PMMA matrix. Clearly, the fact that the isotactic PMMA in our reprecipitated sample appeared to be associated does not imply that the isotactic material will also be associated in material processed under high shear. In fact, it would be interesting to observe the effect on mechanical properties of having the *i*-PMMA segments associated and isolated. The isotactic blocks if associated, if crystalline, and if consisting of isotactic segments from a number of molecules could act as intermolecular cross-links and possibly be used to explain the relatively low creep rate of annealed PMMA as opposed to the quenched material.

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