Thermal Conductivity of Polystyrene in Toluene Solutions—Effect of Structure

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The thermal conductivity of polystyrene in toluene solutions increases linearly with polymer concentration. Measurements are made by the nonsteady state hot wire method. The thermal conductivity is measured at 30°C for polystyrene concentrations up to 10 g/l. The data obtained in this work are compared qualitatively with published values for the thermal conductivity of polystyrene and polystyrene in a toluene solution.

In an attempt to measure the effect of structure on the thermal conductivity of liquids, Horrocks and McLaughlin (*4*) studied a series of liquid polyphenyls. They were able to correlate the temperature dependence of the thermal conductivity but did not show any correlation of the absolute value of thermal conductivity with structure for the series benzene, toluene, diphenyl, *o*-, *m*-, and *p*-terphenyl.

A more pronounced structural effect might be exhibited by polymer solutions. Bridgman (*1*) observed that solutions of varying strengths of gelatine in water exhibited increased values of thermal conductivity. However, the variation in thermal conductivity was much less than the variation in viscosity. Tautz and Lippmann (*7*) measured the thermal conductivity of solutions of polystyrene in bromobenzene and toluene. They found the thermal conductivity of bromobenzene solutions to increase with polystyrene concentration, but the value which they measured for the thermal conductivity of toluene decreased when a 5% polystyrene solution was tested.

Experiment and Results

Polystyrene in toluene solutions was chosen to study because polystyrene has the structure of toluene joined by methelene groups. Polystyrene can thus be considered a structured arrangement of toluene. The toluene used was reagent grade. The polystyrene was commercial grade with a viscosity averaged molecular weight of 269,000 (*2*).

Thermal conductivity measurements were made by the time-dependent hot wire method. The measuring device was interfaced with a computer as described elsewhere (*9*). The one modification in the equipment for the present study was the use of a bare, rather than insulated, platinum wire as a heat source. All measurements were made at 30°C. The thermal conductivities of the solutions were measured relative to the thermal conductivity of the solvent. Mallan et al. (*5*) have reviewed experimental measurements of the thermal conductivity of toluene.

The results of the present work are shown in Table I. For polystyrene concentrations above 10 g/l., the solutions were so viscous that small air bubbles would not rise, which made accurate measurements of the thermal conductivity very difficult. The relative thermal conductivity increased linearly with polystyrene concentration. The relative thermal conductivity can be described by the following mathematical relationship:

$$\lambda/\lambda_t = 1 + 0.00856\,c \qquad (1)$$

The correlation coefficient for the above relationship is 0.994.

Discussion

The above results contradict the previous observations by Tautz and Lippmann (*7*). There are at least two mechanisms whereby Tautz and Lippmann would observe a reduction of the value they measured for the thermal conductivity even though the true value increases upon addition of polystyrene. First, trapped air bubbles are easily excluded from pure toluene but rise very slowly or not at all in a 5% polystyrene in toluene solution, such as studied by Tautz and Lippmann. Trapped air bubbles, if present, would act as a barrier to heat transfer and cause the observed thermal conductivity to go down. Second, Tautz and Lippmann used a steady state concentric cylinder apparatus to measure thermal conductivity. Their method is more susceptible to errors owing to convection than is the present nonsteady state method. If a small amount of convection were present when Tautz and Lippmann measured the thermal conductivity of toluene and this convection was damped out by the greater viscosity of the polystyrene solution, this would also explain the inverse dependence on concentration which Tautz and Lippmann observed.

The effect of polystyrene on thermal conductivity as measured in this work is much less than the effect on viscosity. A 1 g/l. concentration doubles the viscosity of toluene solution but causes less than a 1% rise in the thermal conductivity. Also, the thermal conductivity is linear with concentration over the entire range of concentration studied, but the viscosity is linear for only very dilute solutions. Horrocks and McLaughlin state that the strong dependence of viscosity on structure is because molecules must move with respect to each other. They did not allude to the mechanism by which structure affects thermal conductivity. Some insight into the mechanism of heat transfer in the present system comes from research on solid polymers.

Müeller (*6*) stretched solid polymer sheets to orient the polymer molecules. He found that the thermal conductivity of polystyrene parallel to the polymer chains was 50% larger than values perpendicular to the chains. In a polymer solution the molecules are randomly oriented, but the fraction of molecules aligned parallel to the direction of heat flow is proportional to the concentration.

Table I. Relative Thermal Conductivity of Polystyrene in Toluene at 30°C

Concn, g/l.	Rel thermal conductivity, λ/λ_t
2	1.0164
4	1.0320
5	1.0435
6	1.0493
7	1.0597
8	1.0741
10	1.0829

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Hansen et al. (*3*) summarized data for the thermal conductivity of plasticized polymers. The thermal conductivity was proportional to the weight fraction of polymer. This conclusion for a solid solution is in agreement with the present work.

Hansen et al. (*3*) also found the thermal conductivity of low-molecular-weight polystyrene to increase as much as twofold with increasing molecular weight. In the present work a change in concentration of polystyrene in toluene can be thought of as increasing the average molecular weight of the solution.

Ueberreiter and Nens (*8*) studied the thermal conductivity of distyrene and polystyrene melts. They postulated that the influence of structure was not as important in a melt as in a solid because the polymer chains were free to experience a twisting type of vibration. The same postulate would explain why polystyrene has no more effect on the thermal conductivity when in solution in toluene than has been observed in this work.

Conclusions

Although the effect of structure on thermal conductivity can be important in solids (e.g., the method of production of polymers and the allotropic forms of carbon), the effect of structure in liquids can only be detected by precise methods. However, the thermal conductivity of polystyrene in toluene solutions does increase with polystyrene concentration. The dependence of thermal conductivity on concentration at 30°C can be expressed as a linear function.

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Nomenclature

c = concentration, grams of polystyrene per liter of solution
λ = thermal conductivity of solution, W/m/°C
λ_t = thermal conductivity of toluene, W/m/°C

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Solubility in System NH_3–H_3PO_4–$H_4P_2O_7$–$H_5P_3O_{10}$–H_2O at 25°C

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Measurements were made of the composition of solution in the system NH_3–H_3PO_4–$H_4P_2O_7$–$H_5P_3O_{10}$–H_2O at 25°C in which solid phases of all three phosphate species are in equilibrium over the pH range 4.6–7.1. Solubility expressesd as percent (N + P_2O_5) ranged from 1.5 to 4.7% higher at 25° than at 0°C where the isotherms overlap. The most concentrated solution contained 12.1% N and 46.6% P_2O_5 and had a pH of 5.0.

Previous studies of the properties of ammonium polyphosphates (*1–6*) have been concerned mainly with their saturated solutions at 0°C. In this study the phase relationships in the system ammonia–orthophosphoric acid–pyrophosphoric acid–tripolyphosphoric acid–water at 25°C were determined in regions where solid phases of all three phosphate species are in equilibrium over the pH range 4.6–7.1.

Experimental

The equilibration mixtures were prepared from reagent grade mono- and diammonium orthophosphates and from di-, tri-, and tetraammonium pyrophosphates, and tetra- and pentaammonium tripolyphosphates that were crystallized from liquid fertilizers produced by ammoniation of 80% P_2O_5 electric-furnace polyphosphoric acid (*11*). Stock solutions of the ammonium orthophosphates were prepared by saturating distilled water at 40°C with the respective salts and cooling to room temperature. A portion of the ammonium orthophosphate solution at the desired pH was saturated with the ammonium pyrophosphate salt that is stable at that pH. These orthophosphate–pyrophosphate solutions were readjusted to the desired pH with reagent grade 85% orthophosphoric acid or with gaseous ammonia. The solutions then were saturated with the ammonium tripolyphosphate salt that is stable at the pH of the respective solutions. The different ammoniated salts of ortho-, pyro-, and tripolyphosphoric acid were selected from the ternary systems at 25°C (*1, 2, 9*).

The solutions in plastic bottles were rotated four times per minute in a water bath at 25° ± 0.05°C. The approach to equilibrium was followed by periodic petrographic examinations of the solid phases (*8*) and by determinations of the composition and pH of the liquid phases. When examination of the wet solids indicated the absence of any of the three phosphate species, a few grams of the missing species were added, and equilibration was continued.

Phosphorus was determined gravimetrically as quinolinium molybdophosphate (*10*), and nitrogen was determined by distillation of ammonia with sodium hydroxide; pH measurements on the supernatant liquid phases were made with a commercial meter and a glass electrode. The phosphate distribution was determined by one-dimensional paper chromatography (*7*).

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