

## The Heats of Dilution of Isotactic Polystyrene Solution in Toluene and in Anisole

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In the previous papers, we measured the heat of dilution of the atactic polystyrene solution and found that the interaction heat parameter between the polymer and the solvent depended on the concentration and molecular weight of the polymer.

In this paper, we measured the heats of dilution of the isotactic polystyrene-toluene and -anisole systems in order to see the effect of tacticity on the solution property. The results indicate that the isotactic-anisole system behaves similarly, but the isotactic-toluene system dissimilarly to the atactic polystyrene solutions.

It is well known that the solutions of atactic polystyrene in various solvents show unusual dependences of the interaction heat parameter on the concentration and on the molecular weight of polymer.

The calorimetric studies on the atactic polystyrene-toluene system have been reported by other authors.<sup>1,2)</sup> The interaction heat parameter of this system is small and has a negative sign (almost zero). This system may be considered as one of an athermal solution. Schulz<sup>1)</sup> has reported that the interaction heat parameter of the atactic polystyrene-benzene system changes its sign from positive to negative as the molecular weight of polymer increases. A similar behavior was also found in atactic polystyrene-ethylacetate,<sup>3)</sup> and -methyl-ethylketone<sup>4)</sup> systems.

Recently, we measured the heat of dilution of atactic polystyrene-anisole<sup>5)</sup> system using an isothermal microcalorimeter at 303 K. We found an interesting fact that the interaction heat parameter in dilute solution was negative and its absolute value increased at first, reached a maximum and then decreased as the molecular weight of polymer increased. Such a drastic behavior of the system can not be explained from a consideration of polarity of the solvent molecule. Another factor such as specific conformation of the polymer in the solvent may help to induce this behavior.

In the present paper, we measured the heats of dilution of isotactic polystyrene solutions with toluene and anisole using a twin-type of microcalorimeter at 298 K, in order to confirm the similar effect for this system. The twin microcalorimeter is the same as that described in previous papers.<sup>6,7)</sup> The isotactic poly-

styrene sample with degree of polymerization of about 200 was supplied kindly by Dr. T. Matsuo of the Chemical Institute of Kyoto University (Present address: Fukui University). Toluene and anisole used as the solvents were purified by ordinary methods described in the literature.<sup>8)</sup>

The heats of dilution of the isotactic polystyrene solution were measured over the concentration range from 0.10 to 0.02 in the volume fraction, by adding successively 10 or 50 cm<sup>3</sup> of the solvent to the polymer solution of a known concentration.

Both of the isotactic polystyrene-toluene and -anisole systems are exothermic. As shown in the previous paper,<sup>6)</sup> the heat of dilution,  $\Delta\bar{H}_d$ , is related to the initial volume fraction of polymer,  $\phi_2$ , and the final one,  $\phi_2'$ , as follows;

$$\Delta\bar{H}_d = RT \phi_2 \phi_2' \Delta n_1 \chi_H, \quad (1)$$

where  $\Delta n_1$  is the number of moles of the solvent added. We plotted the values of  $\Delta\bar{H}_d$  against  $RT \phi_2 \phi_2' \Delta n_1$  in Fig. 1, together with the atactic polystyrene data. As is seen in Fig. 1, these plots are not linear, indicating that the interaction heat parameter depends on the concentration of polymer. Assuming that the interaction heat parameter,  $\chi_H$ , is expressed as  $\chi_H = \chi_1 + \chi_2 \phi_2$ ,

$$\Delta\bar{H}_d = RT \phi_2 \phi_2' \Delta n_1 \left[ \chi_1 + \frac{\phi_2 + \phi_2'}{2} \chi_2 \right]. \quad (2)$$

In order to obtain the dependence of the interaction heat parameter on the concentration of polymer, a least square analysis of the data was carried out according to Eq. (2), giving the values of  $\chi_1$  and  $\chi_2$  as summarized in Table 1. By using these values, the  $\Delta\bar{H}_d$  versus  $RT \phi_2 \phi_2' \Delta n_1$  curves for each system are shown by the solid lines in Fig. 1, and are in good agreement with the experimental data.

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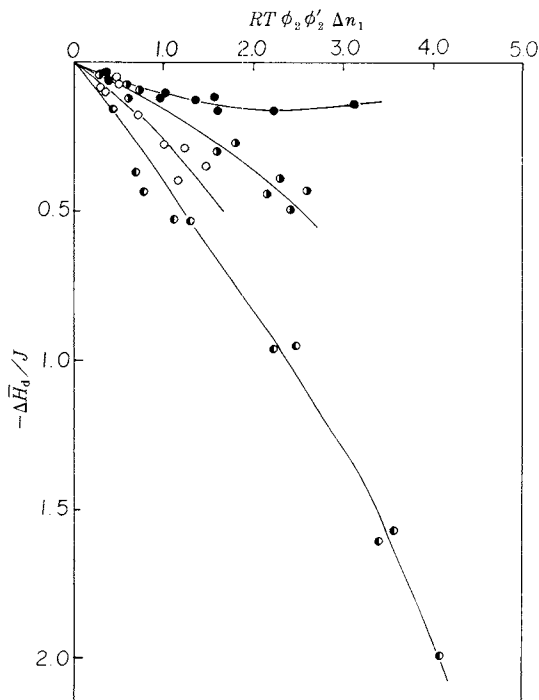


Fig. 1 Plots of heat of dilution against the concentration of polymer

- isotactic polystyrene — toluene
- atactic polystyrene — toluene
- isotactic polystyrene — anisole
- atactic polystyrene — anisole

Table 1 Interaction heat parameter of isotactic and atactic polystyrene at 298 K

	isotactic polystyrene		atactic polystyrene	
	$\chi_1$	$\chi_2$	$\chi_1$	$\chi_2$
Toluene	-0.12	0.72	-0.09	-0.94
Anisole	-0.30	-0.36	-0.60	-1.18

The curve for the isotactic polystyrene-anisole system indicates the same tendency as those for the atactic polystyrene systems. The interaction heat parameter,  $\chi_2$ , in the concentrated region of the isotactic polystyrene-toluene system has opposite sign as compared with those of the atactic polystyrene systems. It

can be considered that the isotactic polystyrene-toluene system may contain an insoluble polymer fraction. Therefore, the heat of dilution of this system may change from a negative value to a positive one as the concentration of polymer increases.

Equation (2) proved to be unsatisfactory to represent the concentration dependence of the integral heat of dilution for this system. A power-series expansion for the concentration dependence of the apparent interaction heat parameter,

$$\chi_H = \chi_1 + \chi_2 \phi_2 + \chi_3 \phi_2^2 + \dots$$

may improve the situation. The interaction heat parameter in dilute region in this system may be small as compared with those of atactic polystyrene systems.

Anisole is a good solvent for isotactic as well as atactic polystyrene. Toluene and anisole are good solvents for isotactic polystyrene in dilute solution region, and therefore it may be concluded that the solution properties in this region do not differ greatly from the results obtained by the measurement of osmotic pressure.<sup>9)</sup>

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