Calorimetric Study of Polystyrenes of Low Molecular Weight

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(Received February 5, 1970)

Heats of mixing ΔH^M at infinite dilution and integral heats of dilution ΔH_d were directly measured for the systems of atactic polystyrenes (PSt: MW$\leqq 10^4$, prepared by Pressure Chemical Co.) with benzene, toluene, and chloroform. The results are summarized as follows: (1) ΔH^M and ΔH_d decrease remarkably with the molecular weight of PSt in all solvents used. (2) The glass energies of the samples treated under the same thermal conditions were investigated and the large difference of heat capacities between liquid and glassy state of PSt was observed in the low molecular weight region. (3) Schulz's theory of osmotic second virial coefficient of athermal polymer solutions was found to agree, to a good approximation, with the differential heat $\overline{\Delta H_1}$ of dilution in toluene in the molecular weight region between 10^3 and 10^4. (4) The NMR and the X-ray diffraction analyses were performed for the PSt oligomer liquid (MW 600). All alkyl end group of molecules and an order formation in the liquid were observed. They are discussed in terms of calorimetric data.

The present study is concerned with the heats of solution and dilution in low molecular weight polystyrene-solvent systems. The heat of solution of a polymeric glass-solvent system arises partly from the glass energy of the polymer solid.[1] For atactic polystyrene (PSt), calorimetric studies[2,3] have confirmed the glass energy content, glass enthalpy which varies with the packing conditions of the polymer molecules under the glassy state. However, when polymeric glass samples of various molecular weights are treated under the same conditions, the heats of solution in the liquid polymer-solvent systems and the glass energy contents of the polymer glasses should change with their molecular weights. The heats of dilution of PSt solutions have been directly measured by several workers. In particular, studies on the low molecular weight PSt or the oligomer solutions have revealed remarkable changes of the solution properties with molecular weights in the oligomer region.[4,5]

In this work, the heats of mixing (ΔH^M) of PSt samples (prepared by Pressure Chemical Co., average molecular weight $\overline{M}\leqq 10^4$), treated under the same thermal conditions in benzene, toluene and chloroform at infinite dilution, and the heats of dilution of the solutions have been measured. Dependence of the values on molecular weight was examined and information on the polymer and the solution was obtained from the results.

Experimental

Materials. PSt polymers of narrow molecular weight distribution, $\overline{M}_w/\overline{M}_n\leqq 1.10$, products of the Pressure Chemical Co., were used. For the measurement of the ΔH^M, the polymers were subjected to the same thermal treatment with the exception of the polymer of $\overline{M}=600$, a viscous liquid. After removing air in a vacuum 10^{-5} mmHg, PSt samples were heat-treated at 130°C for 10 min in N_2 gas current and were annealed at room temperature. The liquid solute ethylbenzene and the solvents benzene, toluene, and chloroform were commercial products of the highest quality. All but chloroform were dried with sodium wire and fractionally distilled over phosphorus pentoxide before use. Chloroform was washed repeatedly with distilled water, dried over calcium sulfate and fractionally distilled before use.

Calorimetry. For the measurement of ΔH^M, a rotational twin conduction calorimeter[6] in which a mixing cell similar to that described by Malcolm and Rowlinson[7] was used. The principle of the detection of heat is similar to that reported previously.[8] Almost all ΔH^M values at infinite dilution were obtained from the measurements for final concentration of 0.7—1.3% using 20—30 mg of the solute and about 3 m*l* of the solvent. Measurements were performed within ±4% of standard deviation. For the determination of the integral heat of dilution (ΔH_d), a revised type of calorimeter[9] with multiple modules[10] was used. The ΔH_d values were obtained by diluting 1—7 m*l* of 5—10% solution to about 2×10^{-3} % concentration, *i.e.*, almost infinite dilution. The values were obtained with a maximum error of ±20%.

Density Measurements. Measurement of the change in density Δd between pure solvent and PSt dilute solution was carried out by means of Cahn electromagnetic balance RG using a density cell at 25°C. The measurement is entirely similar to that reported by Elgret *et al.*[11] The apparent specific valumes $v_2{}^*$ of PSt oligomers in dilute solution were found from the equation[12]

$$v_2{}^* = d^{-1}(1+\Delta d/c) \tag{1}$$

where d is the density of pure solvent and c is polymer concentration. The PSt concentrations were about 2% in benzene and in toluene, and about 1% in chloroform. Reproducibility of the values of $v_2{}^*$ derived from the value of Δd was within ±0.1% on an average. The densities measured were 0.87405 for benzene, 0.86273 for toluene,

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[1] G. V. Schulz, K. V. Guenner, and H. Gerrens, *Z. Phys. Chem. (N. F.)*, **4**, 192 (1955).

[2] A. A. Tager, M. V. Tsilipotkina, A. I. Podlensnjak, and E. V. Makovskaya, International Symposium on Macromolecular Chemistry, Tokyo-Kyoto, 1966, preprints VII, p. 89.

[3] U. Bianchi, C. Cuniberti, E. Pedemonte, and C. Rossi, *J. Polym. Sci., Part A-2*, **5**, 743 (1967).

[4] G. V. Schulz and A. Horbach, *Z. Phys. Chem. (N. F.)*, **22**, 377 (1959).

[5] H. Sotobayashi and K. Ueberreiter, *J. Polym. Sci.*, **A**, **2**, 1257 (1964).

[6] K. Amaya, S. Takagi, and S. Hagiwara, 2nd Calorimetry Conference, Japan (1966), p. 16.

[7] G. N. Malcolm and J. S. Rowlinson, *Trans. Faraday Soc.*, **53**, 921 (1967).

[8] S. Morimoto, *J. Polym. Sci., Part A-1*, **6**, 1547 (1968).

[9] K. Amaya and S. Hagiwara, 2nd Calorimetry Conference, Japan (1966) p. 18.

[10] S. Morimoto, 4th Calorimetry Conference, Japan (1968), p. 103.

[11] K. F. Elgert and K. Camman, *Z. Anal. Chem.*, **226**, 193 (1967).

[12] B. Rosen, *J. Polym. Sci.*, **17**, 559 (1955).

0.4753 for chloroform, and 0.86281 g/m*l* for ethylbenzene.

Other Measurements. NMR spectra were taken with a Nihon Denshi C-60 HL spectrometer using about 5% solution of the sample in $CDCl_3$. X-ray diffraction diagrams and photographs were obtained with a Rigaku Denki X-ray diffraction apparatus.

Results and Discussion

Heats of Solution. The results are given in Figs. 1 and 2. In Fig. 1, the values of ΔH^M of the low molecular weight PSt samples, subjected to the same thermal treatment in three solvents at 18 and 45°C are plotted against the molecular weights. The values of ΔH^M of ethylbenzene which can be regarded as the monomeric substance of PSt were endothermic for benzene, athermal for toluene and exothermic for chloroform. The larger exothermic change in ΔH^M suggests the larger exothermic contribution from the glass enthalpies which increase with the molecular weight of PSt. This tendency is made clear by the study of Schulz *et al.*[1] and also by the relation between the heat capacity C_p and the temperature of the glass transition of PSt as shown in Fig. 3. The relation between the glass enthalpy and the heat of mixing ΔH_l^M of liquid polymer at infinite dilution is given by

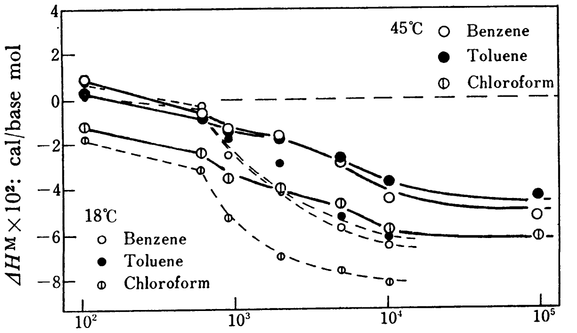

Fig. 1. Heats of mixing ΔH^M at infinite dilution of PSt samples plotted against their avg. molecular weights.

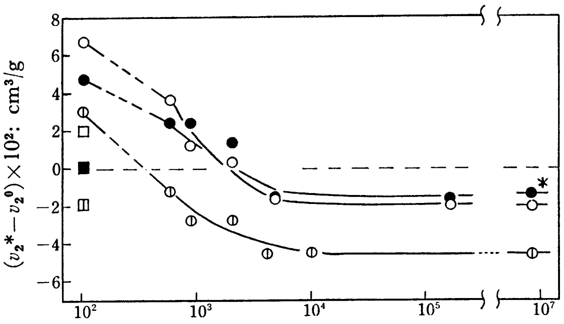

Fig. 2. Excess volume *vs.* avg. molecular weight of PSt. The values v_2^0 are those reported by Fox-Loshaek.[15] Square and asterisked marks are the calculated values from measured v_2^0 and from the reported v_2^* values,[11] respectively.

○ Benzene ● Toluene ◑ Chloroform

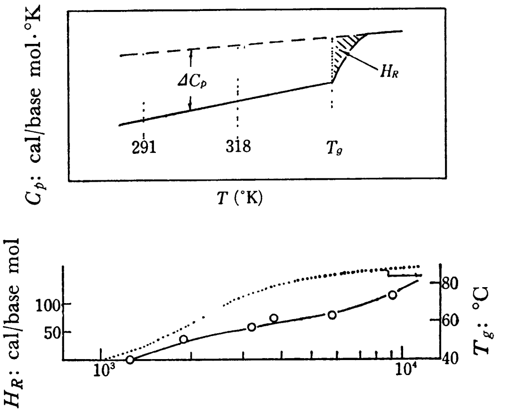

Fig. 3. Correlation of heat capacity with temperature, and the values of H_R[1] and T_g[13] *vs.* the molecular weight of PSt.

$$\Delta H^M = \Delta H_l^M - \Delta H_g^M \tag{2}$$

$$\Delta H_g^M = \int_T^{T_g} \Delta C_p \, dT + H_R , \tag{3}$$

where $-\Delta H_g^M$ is the contribution due to glass enthalpy, T temperature, T_g glass temperature, ΔC_p the difference in C_p between glass polymer and liquid polymer to be assumed at the same temperature as shown in Fig. 3, H_R the rest enthalpy arising from the transition which takes place slowly from the glassy state to liquid phase, and shown as the shaded portion in Fig. 3. This relation can be used to estimate the contributions either of ΔH_l^M or ΔH_g^M to the ΔH^M values. Another approach to the estimation of the value of ΔH^M is from the apparent specific volume of the PSt in dilute solution. Horth *et al.*[14] found that the difference between v_2^* and the specific volume v_2^0 of the pure liquid polymer is approximately proportional to the ΔH_l^M, *viz.*,

$$\begin{aligned} v_2^* - v_2^0 &= \beta \boldsymbol{R} T \kappa_1 v_2^0 \varphi_1 / V_1 (1+\alpha T) \\ &= [\beta/(1+\alpha T)] \Delta H_l^M / M_0 , \end{aligned} \tag{4}$$

where α and β are the coefficients of thermal expansion and the compressibility of the solution, φ_1 and V_1 the volume fraction and the molar volume of the solvent, $\boldsymbol{R}$ gas constant, κ_1 Flory's enthalpy parameter, and M_0 the molecular weight of the repeating unit of the polymer. Using the empirical *v-T-M* equation,[15] we obtained a relative relation between v_2^*-v_2^0 and $\overline{M}$ for the oligomers as shown in Fig. 2. Although not presented here, a similar figure is obtained using the other *v-T-M* relation.[16] The specific volume v_2^0 of ethylbenzene measured was 1.15900 which was used for the calculation. In the high molecular weight

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[13] E. Jenckel and K. Ueberreiter, *Z. Phys. Chem., Abt.* **A182**, 36 (1938).

[14] A. Horth, D. Patterson, and M. Rinfret, *J. Polym. Sci.*, **39**, 189 (1959).

[15] T. G. Fox and S. Loshaek, *ibid.*, **15**, 371 (1955).

[16] T. G. Fox and P. J. Flory, *J. Appl. Phys.*, **21**, 581 (1950).

region, the partial specific volume of PSt is almost constant and has been reported[11] to be 0.911 in benzene and 0.917 in toluene solution. These values agree fairly well with our results, 0.911 and 0.914, respectively, obtained as the apparent specific volumes v_2^*. Calculated values $(1+\alpha T)/\beta$ were 316 for benzene, 330 for toluene, and 363 cal/cm^3 for chloroform system by using the values[17] of pure solvents instead of the solutions for α and β. These values are almost the same for the three solvent systems. It is understood that the behavior shown in Fig. 2 is consistent with the one obtained from direct calorimetric measurements.

In Figs. 1 and 2, the values ΔH_t^{M} for all solvent systems show a similar tendency for the change of molecular weight. However, the tendency slightly differed with the characteristics of the solvents. In the case of monomeric solute-ethylbenzene, ΔH^{M} of toluene system showed lower values than those of other systems. However, this relation was reversed when the molecular weight increased. This reversal was observed in the molecular weight region between 10^3 and 10^4, which shifted lower when the temperature was lowered.

The value of ΔH_t^{M} in PSt ($\overline{M}$: 3,980)-toluene system at 25°C has been obtained as 60 cal/base mol from the ΔH_t^{M} and C_p measurements by Schulz.[1] According to this scheme, the ΔH_t^{M} at the higher molecular weight region in benzene and chloroform systems should be constant, *i.e.*, about -100 and -300 cal/base mol for benzene and chloroform systems respectively. This exothermic effect in benzene or chloroform system is attributable to the interactions between the solvent molecules and the phenyl components in PSt molecules, although the slightly exothermic factor can not be ignored when the solute chain length increases.[5,18] The interaction between the solvent and the constituent of polymer molecule is introduced to interpreted ΔH_t^{M} qualitatively.[5,18,19] The values of ΔH^{M} of benzene and *n*-heptane both with chloroform were directly measured and the values -398 and 719 cal/mol were obtained, respectively. A considerably large exothermic value of ΔH^{M} in the chloroform system, as compared with PSt-benzene system, reflects the interactions between the chloroform and the phenyl group in PSt molecule.

A characteristic feature throughout this experiment is that the difference of the glass energies at different temperatures can be estimated from the measurements. In Fig. 4, the difference of the measured ΔH^{M} values at 18°C and 45°C are plotted against the molecular weight of PSt, although the temperature dependence of ΔH_t^{M} values are not completely negligible. The differences in the ΔH^{M} values thus obtained in this molecular weight region were somewhat scattered, but the large difference of glass energies is evident in the range $\overline{M}=10^3$—10^4. The magnitude of the difference in glass energy, when compared for a constant difference in temperature, corresponds to the mean values of ΔC_p between the measured temperatures as shown in Fig. 4. The ΔC_p, or more exactly the ΔC_v at constant volume (generally at T_g), is the contribution of the conformational change of the polymer chains between the rubber and glassy states to the value of C_p, and is called conformational heat capacity.[20] Conversion of ΔC_p to ΔC_v might clarify this behavior, but the constants in the low molecular weight region have not been obtained. In connection with the movement of molecular chains,[21] the larger ΔC_p values may be explained as caused by the increase of the molecular cohesion in the glass of this molecular weight region or by the larger mobility of shorter chains in the liquid state, even though the cohesion might be independent of molecular weight. The sudden increase and the partially higher ΔC_p values were observed in the PSt oligomer region. The ΔC_p value of the higher molecular weight PSt agreed well with the reported value 0.09 cal/g. K[1,3] in this region.

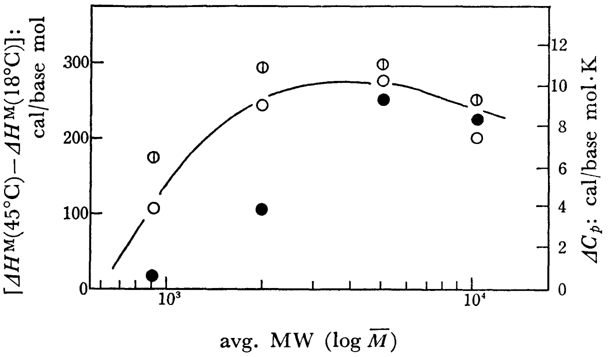

Fig. 4. The difference of glass energies between two measured temperatures and concluded ΔC_p value plotted against the avg. molecular weight of PSt.
○ Benzene ● Toluene ⦶ Chloroform

Heats of Dilution. Measurement of the heats of dilution in the three solvent systems was performed at 25°C by diluting about 5 m*l* solution of the concentration 5—10% to infinite dilution for the toluene and the benzene systems and by diluting about 1 m*l* solution of the concentration 10% to infinite for the chloroform system. In order to obtain the differential heat $\overline{\Delta H_1}$ of dilution per mol solvent and the enthalpy term $B_{\mathrm{H}}(=\boldsymbol{R}TA_{2,\mathrm{H}})$ of the second virial coefficient $B(=\boldsymbol{R}T\text{-}A_2)$ from the heats of dilution ΔH_d measured, the following equations were used.[4,22]

$$B_{\mathrm{H}} = (\Delta H_d/w_2)/(c_e-c_a) \qquad (5)$$

$$B_{\mathrm{H}} = \boldsymbol{R}TA_{2,\mathrm{H}} = -\overline{\Delta H_1}/\overline{V}_1c^2 \qquad (6)$$

where A_2 and $A_{2,\mathrm{H}}$ are the second virial coefficient and the enthalpy term of A_2, w_2 the weight of the solute to be diluted, c_a and c_e the initial and the final concentration of the solution. The value of B_{H} was found to depend on the concentration[4,23] and molecular weight,[24] but the dependence was neglected here for the sake of simplicity. The results are given in Fig. 5.

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17) "International Critical Tables," McGraw-Hill, New York (1933), **3**, pp. 27, 35.

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24) A. Kagemoto, S. Murakami, and R. Fujishiro, *ibid.*, **40**, 11 (1967).

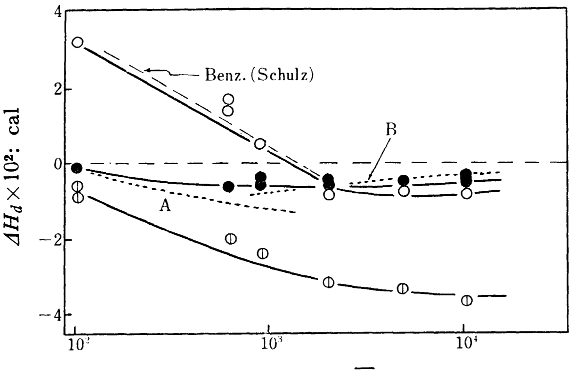

Fig. 5. Heat of dilution *vs.* molecular weight of PSt. Dotted lines A and B are shown for the values from Eqs. (7) and (8), respectively.
○ Benzene ● Toluene ⦶ Chloroform.

The values of ΔH_d were calculated from the B values according to the above equations, assuming that the c_a and $(c_a - c_e)$ are both 7.0×10^{-2} g/cm³. The ΔH_d value corresponds to the heat arising from the dilution of 5 m*l* solution from 7% to infinite dilution. In Fig. 5, the molecular weight dependence is similar to that of ΔH_l^{M} at infinite dilution obtained from the heat of solution.

A characteristic feature of this experiment is the behavior of the toluene system which can be considered as an athermal solution. Theories of the second virial coefficient A_2^{ath} for athermal solutions have been given by several authors. From the equation derived by Schulz for A_2^{ath}[25] and by Schulz, Inagaki, and Kirste[26] for the relation between A_2 and $A_{2,\mathrm{H}}$, the following equations are derived approximately for the value of $B_{\mathrm{H}}^{\mathrm{ath}}$.

$$B_{\mathrm{H}}^{\mathrm{ath}} = \boldsymbol{R}T^2\alpha\bar{v}_2(\boldsymbol{\pi}^3 a^3 \boldsymbol{N}_{\mathrm{A}})^{1/2}/M_0(4^3 M_0 \bar{v}_2)^{1/2} \tag{7}$$

$$B_{\mathrm{H}}^{\mathrm{ath}} = \boldsymbol{R}T^2\alpha\bar{v}_2(\boldsymbol{\pi}^3 a^3 \boldsymbol{N}_{\mathrm{A}})^{1/2}/M_0(4^3 M_0 \bar{v}_2)^{1/2} h(z)\ , \tag{8}$$

where α is the thermal expansion coefficient of the solution, $\bar{v}_2$ the partial specific volume of PSt, a the length of monomer unit, $\boldsymbol{N}_{\mathrm{A}}$ the Avogadro number. With regard to the flexibility of polymer molecules, Schulz, Baumann, and Darskus[27] tried to combine the effect of coiling of long chain molecules. Miltiplying $A_{2,\mathrm{H}}^{\mathrm{ath}}$ by function $h(z)$ derived by Casassa,[28] they obtained good agreement with the experimental A_2 of athermal high polymer solutions. Equation (8) was thus derived and its applicability was examined. As seen in Fig. 5, our results show good agreement with the calculated values and the theory expresses the molecular weight dependence of the heat of dilution fairly well. Definite changes in the solution properties of the oligomers ($\overline{M}$: 10^3—10^4) have been observed by the measurements of the second virial coefficient,[5] the intrinsic viscosity,[29] and the partial specific compressibility.[30] The behavior can be explained as due to the flexibility of molecular chains in the solution (*i.e.*, rigid nature of the short chain molecule). This effect was observed in the direct measurement at the molecular weights between 10^3 and 10^4.

The enthalpy parameters χ_{H} and the $z\Delta w/\boldsymbol{k}T$ values[31] both involved in the Van Laar equation were calculated as a function of the molecular weight as shown in Fig. 6.

$$\chi_{\mathrm{H}} = \overline{\Delta H_1}/\boldsymbol{R}T\varphi_2^2 \tag{9}$$

$$\chi_{\mathrm{H}} = (\overline{V}_1/\overline{V}_2)z\Delta w/\boldsymbol{k}T\ , \tag{10}$$

Where φ_2 is the volume fraction of the solute PSt, z the coordination number, Δw the interchange energy, $\boldsymbol{k}$ the Bolzmann constant, $\overline{V}_2$ the partial molar volume of PSt. The $z\Delta w/\boldsymbol{k}T$ values of the benzene system for the higher molecular weight PSt ($\overline{M} \geqq 3000$) coincide with those for the toluene system. The comparatively higher χ_{H} values were observed in the low oligomer region as shown in Figs. 5 and 6. The concentration dependence of the enthalpy parameter was calculated on the basis of the quasi-chemical approximation for polymer solutions,[32,33]

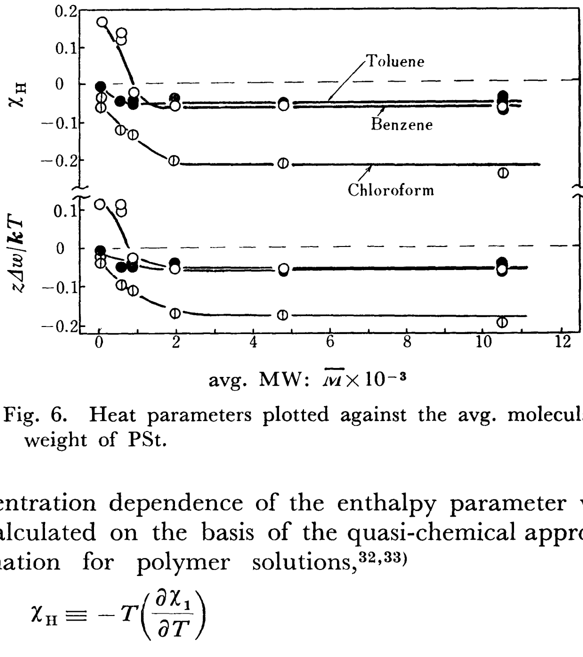

Fig. 6. Heat parameters plotted against the avg. molecular weight of PSt.

$$\begin{aligned} \chi_{\mathrm{H}} &\equiv -T\left(\frac{\partial \chi_1}{\partial T}\right) \\ &= [4\theta^2\Delta w(1-\theta)/\beta\varphi_2^2\boldsymbol{k}T(\beta+1-2\theta)(\beta+1)] \\ &\quad \times \exp(2\Delta w/z\boldsymbol{k}T) \qquad (11) \\ \theta &= \varphi_2(z-2)/(z-2\varphi_2) \\ \beta^2 &= 1 + 4\theta(1-\theta)[\exp(2\Delta w/z\boldsymbol{k}T)-1]\ . \end{aligned}$$

The concentration dependence of the enthalpy parameter in the three solvent systems is shown in Fig. 7. The parameters χ_{H} were calculated on the basis of the $z\Delta w/\boldsymbol{k}T$ values, Eq. (11), and the ΔH_l^{M} values were obtained from Eq. (9) at $\varphi_2 = 1$ and the following

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[27] G. V. Schulz, H. Baumann, and R. Darskus, *ibid.*, **70**, 3647 (1966).

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[30] Y. Nomura and Y. Miyahara, *Nippon Kagaku Zasshi*, **89**, 142 (1968).

[31] H. Tompa, "Polymer Solutions," Butterworths, London (1956), Chapt. III.

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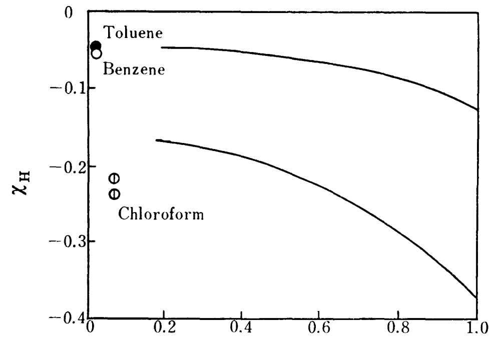

Fig. 7. Concentration dependences of the values of χ_H calculated on the basis of the quasi-chemical approximation. The avg. MW of PSt in toluene and in benzene are both 10500 and those in chloroform are 4800 and 10500.

equation which is expressed by the Van Laar equation.[31]

$$\Delta H_l^M \simeq (\bar{V}_2/\bar{V}_1)RT\chi_H \tag{12}$$

The ΔH_l^M values were −60, −80, and −300 cal/base mol for toluene, benzene, and chloroform solvent systems, respectively, and agreed well with the ΔH_l^M obtained from the direct measurements of the ΔH^M in the glassy PSt-solvent systems. From the results, the glass enthalpies of the higher molecular weight PSt can be calculated to be about 300 cal at 45°C and about 600 cal/base mol at 18°C.

An Order formation in the Oligomer Liquid. In examining the molecular weight dependence of ΔH^M and $\overline{\Delta H_1}$, we came across some problems concerning the behavior of low oligomers, in particular, the oligomer liquid ($\bar{M}$: 600, T_g: −18—−20°C). First, the integral heat of dilution ΔH_d of the benzene solution at 25°C has a larger positive value than that reported.[4] Secondly, the heat of mixing ΔH^M at infinite dilution in the system, on the contrary, is exothermic, *i.e.*, of negative value. This suggested some questions on the chemical composition and ordering structures of the PSt oligomer sample.

The NMR spectrum of the oligomer showed the existence of long alkyl group, possibly *n*-butyl group, to the end as expected from the method of polymerization.[34] The NMR spectra of PSt and the oligomer are shown in Fig. 8. From the integral curves given by the dotted lines, the ratios of the number of protons from the phenyl groups of PSt molecule at the lower magnetic field to that from the methylene and methyne group at the higher field were compared. The ratio of 5 to 3 which is equal to the theoretical value was obtained for the high molecular weight PSt sample of the $\bar{M}$: 10500. For the oligomer sample, the ratio was 1 to 1. This shows that the oligomer molecule has an additional alkyl group, *i.e.* the *n*-butyl end group. Taking this fact into account, we can explain the larger heat of dilution by the endothermic interactions with solvent benzene.

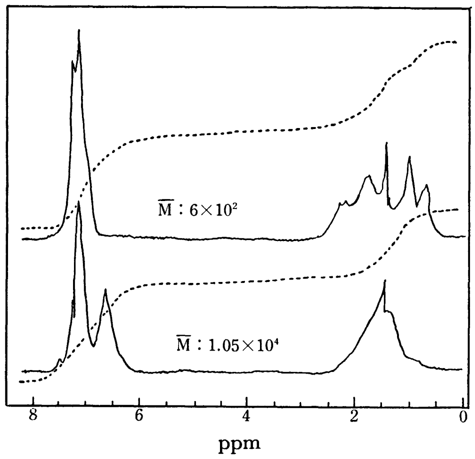

Fig. 8. NMR spectra of PSt and it's oligomer: dotted lines are the integral curves.

In order to check the possible existence of some ordered structure in the oligomer liquid, X-ray diffraction analysis was carried out at room temperature. The results are shown in Figs. 9 and 10. The diffracted amorphous halo of which 2θ is about 5° was found from both the X-ray diffraction intensity curve and photograph. On the other hand, the amorphous haloes ($2\theta \approx 10°$ and 20°) have been observed for the atactic PSt glass. The period calculated according to the Bragg equation was 17 Å, almost equal to the extended molecular chain length.

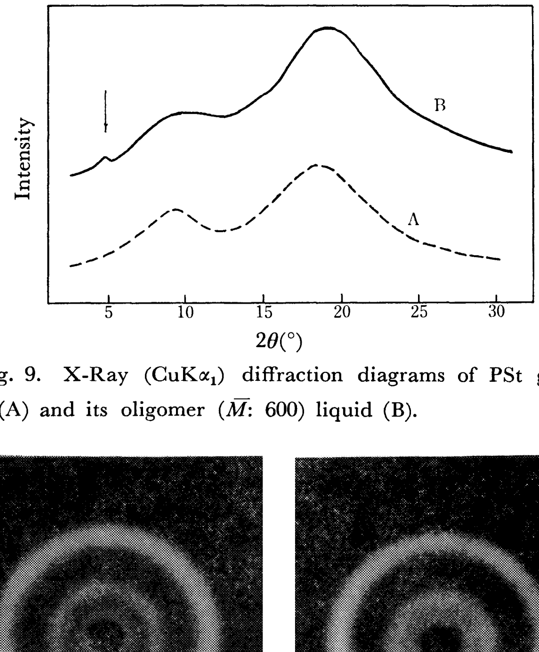

Fig. 9. X-Ray (CuKα_1) diffraction diagrams of PSt glass (A) and its oligomer ($\bar{M}$: 600) liquid (B).

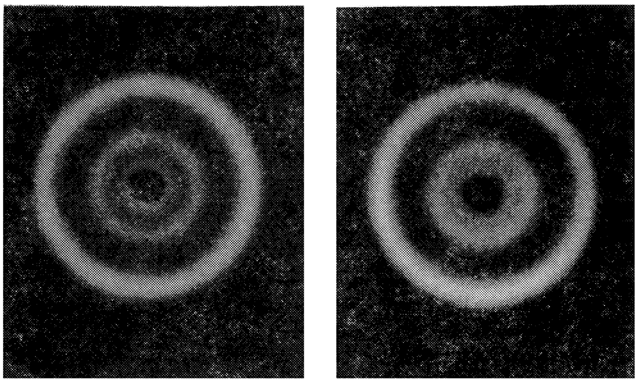
(A) (B)

Fig. 10. X-Ray (CuKα_1) diffraction photographs of PSt glass (A) and its oligomer ($\bar{M}$: 600) liquid (B).

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Such extended chain molecules which have a lower intramolecular energy than the coiled one, should bring an endothermic contribution to ΔH^{M}. This contribution is contrary to our result. Thus some exothermic contributions corresponding to the state of higher energy such as glass should be considered even in liquid state. If not, some strong rotational restriction of the side phenyl group in the ordered molecules is attributable to the endothermic effect. It has not been made clear, however, how such arrangements of chain molecules in general contribute thermally to the ΔH^{M} when dissolved. However, results suggest the existence of a smectic phase of short and rigid PSt oligomer molecules which are arranged parallel to each other in the liquid state. An exothermic contribution to ΔH^{M} was found in this oligomer liquid.

The author is indebted to Professor Ryoichi Fujishiro of Osaka City University, Dr. Kazuo Amaya of Government Chemical and Industrial Research Institute of Tokyo, and Dr. Hisashi Uedaira of this Institute for their valuable advice and encouragement.