Some Thermodynamic Properties of Polymer–Solvent Systems. Comparison between Deuterated and Undeuterated Systems

Claude Strazielle and Henri Benoit*

Centre de Recherches sur les Macromolécules (CNRS), 67083 Strasbourg Cedex, France.

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ABSTRACT: Determinations of "θ" temperatures of poly(protostyrene) in deuterated cyclohexane, poly(deuteriostyrene) in cyclohexane, and poly(deuteriostyrene) in deuterated cyclohexane have been made and compared to the "θ" temperature of the classical poly(protostyrene)–cyclohexane system. The "θ" temperatures are slightly different from one system to another. The viscosimetric behavior in a good solvent (benzene) of poly(deuteriostyrene) and poly(protostyrene) is also examined. The results are explained by considering the cohesive energy density of each substance.

In order to do neutron scattering experiments, intensive use has been made of deuterio polymers in proto solvents, proto polymers in deuterio solvents, or mixtures of deuterio and proto polymers.[1–3] It has always been assumed that, if the use of deuterated substances affects the neutron-scattering length (a large difference in neutron scattering cross-sections between hydrogen and deuterium atoms), this deuteration does not affect the thermodynamic properties of polymer–solvent systems. In dilute solution, especially, the unpertubed dimensions and the θ conditions are considered to be identical for deuterio polymers and for proto polymers. This assumption has never been verified experimentally. On the other hand, a recent study[4] on the separation of phases and melting point of proto systems and deuterio systems (paraffin in C_{34} and polyethylene) shows differences in the melting temperatures: the melting temperature is greater for polyethylene than for poly(deuterioethylene).

For these different reasons, it would be interesting to study the deuterium effect on the thermodynamic properties by considering the well-known polymer–solvent systems: polystyrene in cyclohexane or in benzene.

The thermodynamic properties which are very sensitive to temperature near Flory's θ temperature have been investigated by a systematic study of the second virial coefficient A_2 as a function of temperature in the poly(protostyrene) (PSH)–deuterated cyclohexane (C_6D_{12}), poly(deuteriostyrene) (PSD)–hydrogenated cyclohexane (C_6H_{12}), and PSD–C_6D_{12} systems.

We have also determined the viscosity of some PSD and PSH samples in benzene, which is a good solvent for both polymers.

PSH and PSD samples have been synthesized by anionic polymerization from proto- and deuteriostyrene, respectively. The degree of polydispersity (i.e., the ratio M_w/M_n of these samples) is about 1.1.

1. Second Virial Coefficient A_2 and "θ" Temperature

The molecular weights of PSD and PSH samples were determined by using light scattering in undeuterated solvents (cyclohexane or benzene). For these measurements, we have determined values of the refractive index increment dn/dc of PSD in benzene, cyclohexane and methylethylketone (at λ = 546 nm). These values are given in Table I and compared to the corresponding values for PSH.

We have also shown that dn/dc of PSH in benzene and cyclohexane is not modified by the use of deuterated solvent; the same remark is valid for PSD.

The "θ" temperatures have been determined by means of light scattering from the temperature dependence of the second virial coefficient A_2. In pure solvent, the "θ" temperature is the temperature at which $A_2 = 0$. Figure 1 shows the variation of A_2 as a function of $1/T$ for PSH–C_6H_{12}, PSH–C_6D_{12}, PSD–C_6H_{12}, and PSD–C_6D_{12} systems. The "θ" temperatures have been obtained also from the critical miscibility temperature measurements[5] by plotting $1/T_c$ *vs.* $M^{-1/2}$ (see Figure 2). The "θ" temperature and the ψ_1 parameter are obtained according to the relation

$$1/T_c = 1/\theta \left\{1 + \left(\frac{V_1}{\bar{V}_2}\right)^{1/2} \frac{1}{\psi_1 M^{1/2}}\right\} \tag{1}$$

The results obtained from both methods are listed in Table II. In this table we also give the A_2 values at 35°; this temperature is taken as a reference because it is the "θ" temperature for the classical PSH–C_6H_{12} system. From A_2 values at 35° the corresponding parameter χ according to the Flory formula is

$$A_2 = \frac{\bar{V}_2^2}{V_1}\left(\frac{1}{2} - \chi\right) F(x) \tag{2}$$

In relations 1 and 2, V_1 is the molar volume of the solvent and $\bar{V}_2$ the partial specific volume of the polymer. V_1 is equal to 108 and 105.4 for C_6H_{12} and C_6D_{12}, respectively (the density of C_6D_{12} measured by pycnometry is 0.909 compared to the corresponding value for C_6H_{12} which is 0.779). The partial specific volume of polymer $\bar{V}_2$ in cyclohexane is 0.92[6] for PSH and 0.80 for PSD; the last value has been calculated from dn/dc data by using the Gladstone and Dale relation.[6]

In order to estimate the χ parameter at 35° for our systems, we have assumed in a first approximation that the function $F(x)$ is equal to unity; in fact, near the θ point $F(x)$ is slightly different from unity. These χ values are listed in Table I.

The "θ" temperatures are slightly different from one system to another. If one uses deuterated cyclohexane, there is a "θ" temperature increase for both polymers and consequently, at a given temperature (35°), the χ parameter increases. This increase is equal to 0.009 and 0.015 for PSH and PSD, respectively.

Now, if the thermodynamic properties of polymers PSD and PSH in a given solvent (C_6H_{12} or C_6D_{12}) are compared, an opposite result appears; there is a "θ" temperature lowering for deuterated PS compared to hydrogenated PS and the parameter decrease at 35° is equal to 0.013 in C_6H_{12} and 0.006 in C_6D_{12}.

The effects of the deuteration of polymer and solvent are practically opposite and will be discussed later. The θ point of PSD–C_6D_{12} (36°) is almost identical to the θ point of the undeuterated system.

The differences observed in the thermodynamic behavior of PSH and PSD in C_6H_{12} and C_6D_{12} cannot be attributed only to slight molar volume differences of the solvents or to

Table I
The Refractive Index Increment d*n*/d*c* of PSD and PSH

	d*n*/d*c*		
	C_6H_6	C_6H_{12}	MEK
PSD	0.091	0.151	0.182
PSH	0.106	0.169_5	0.215

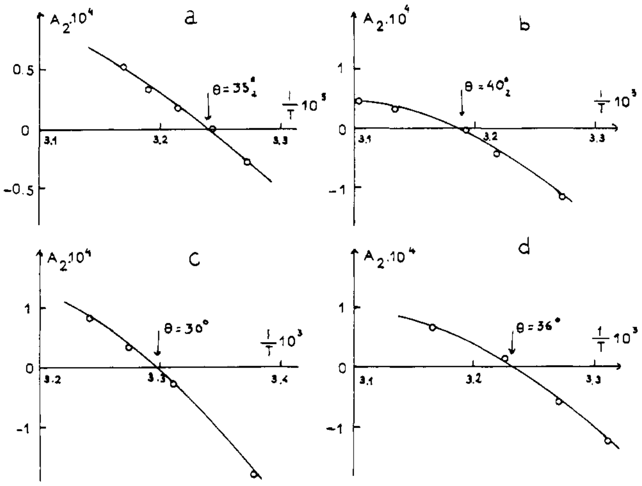

Figure 1. Temperature dependence on the second virial coefficient A_2: (a) PSH-C_6H_{12}, (b) PSH-C_6D_{12}, (c) PSD-C_6H_{12}, (d) PSD-C_6D_{12}.

the partial specific volume differences of the polymers. In fact, the experimental results can be explained by use of the relation between the χ parameter and the cohesive energy density.

For a given polymer–solvent system, one can write[7]

$$\chi = \chi_s + \frac{V_1}{RT}(\delta_2 - \delta_1)^2 \qquad (3)$$

where δ_1 and δ_2 are the solubility parameters of solvent and polymer. The quantity χ_s is the entropic contribution to the parameter χ. This entropic contribution, which is related to the ψ_1 parameter in Flory's theory, seems to be identical for both polymers. In fact, our results on critical temperatures as a function of M have shown that ψ_1^{-1}, which is proportional to the slope of the plot of T_c^{-1} *vs.* $M^{-1/2}$, is slightly modified by the deuteration of polymer. With neglect of this effect, at a given temperature a decrease of δ produces an increase of the χ parameter whereas a decrease of δ_2 diminishes χ.

If the solubility parameter of PSH is taken as reference,[8] $\delta_{2H} = 9.1$ cal/ml$^{1/2}$ (the index H denotes the hydrogenated product and D the deuterated product) and $\chi_s = 0.34$,[7] the other δ values can be calculated from χ values obtained, in first approximation, by supposing $F(x) = 1$ (see Table I) and we obtain $\delta_{1H} = 8.14_8$ for C_6H_{12}, $\delta_{2D} = 9.06$ for PSD, and $\delta_{1D} = 8.11_0$ for C_6D_{12}.

From these values one can write $\Delta\delta_1 = \delta_{1D} - \delta_{1H} = -0.03_8$ and $\Delta\delta_2 = \delta_{2D} - \delta_{2H} = -0.03_9$. $\Delta\delta_1$ and $\Delta\delta_2$ are practically identical even with a ratio C/H different for PS and cyclohexane.

Another way of looking at the results is to evaluate the relation between the $\Delta\chi$ and $\Delta\delta$ when one goes from undeuterated to deuterated samples. For the deuteration of the solvent, we have, using eq 3

$$\Delta\delta_1 = \delta_{1D} - \delta_{1H} = \frac{\delta_{2H} - \delta_{1H}}{2}\left\{\frac{\Delta V_{1H}}{V_{1H}} - \frac{\Delta\chi^{(1)}}{\chi_{HH} - \chi_s}\right\} \qquad (4)$$

where $\Delta\chi^{(1)} = \chi_{DH} - \chi_{HH}$ represents the variation of the χ parameter due to the deuteration of solvent. The term $\Delta V_{1H}/V_{1H}$ is the contribution of the change in the molar volume of the solvent.

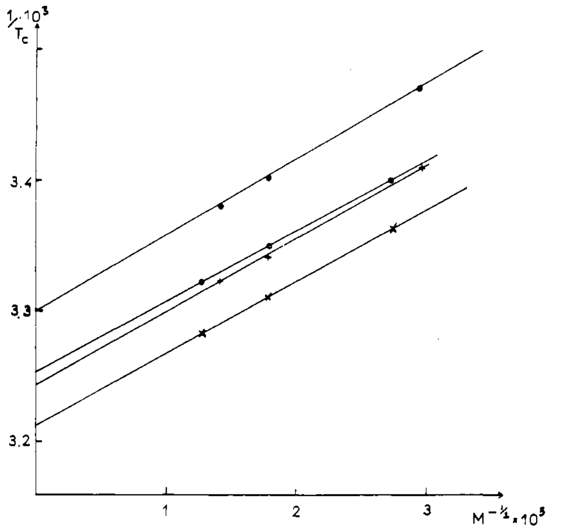

Figure 2. Plot of $1/T_c$ *vs.* $M^{-1/2}$: ⊙, PSH-C_6H_{12}; x, PSH-C_6D_{12}; ●, PSD-C_6H_{12}; +, PSD-C_6D_{12}.

Similarly, we can write for the polymer

$$\Delta\delta_2 = \delta_{2D} - \delta_{2H} = \frac{\delta_{2H} - \delta_{1H}}{2}\left(\frac{\Delta\chi^{(2)}}{\chi_{HH} - \chi_s}\right)$$

$\Delta\chi^{(2)}$ represents here the variation of the χ parameter after deuteration of the polymer.

The $\Delta\delta_1$ and $\Delta\delta_2$ quantities have been calculated by using the relations 4 and 5 from the χ values obtained with the approximation $F(x) = 1$. These values are given in Table III. Theoretically, even near the "θ" point, the function $F(x)$ is different from unity. We have taken into account the excluded volume effect in order to determine the parameter χ from relation 2. For the PSD-C_6H_{12} and PSH-C_6D_{12} systems we have estimated $F(x)$ to be 1.4 and 0.80, respectively. These values have been obtained from the experimental data for A_2 by considering the universal function $A_2M^{1/2}$ *vs.* z (where z is the parameter of pertubation theory) given by Berry[9] and the modified Flory–Krizbaum–Orofino theory.[10]

The χ values calculated in this way are slightly lower (see Table III) and the corresponding $\Delta\delta$ values are now respectively $\Delta\delta_1 = -0.032$ and $\Delta\delta_2 = -0.048$.

By combining the relations 4 and 5, one can write for the completely deuterated system (solvent and polymer)

$$\Delta\chi = \frac{2}{\delta_{2H} - \delta_{1H}}(\chi_{HH} - \chi_s)\left[(\Delta\delta_2 - \Delta\delta_1) + \frac{\Delta V_{1H}}{V_{1H}}\right]$$

From this relation we can determine the variation of the χ parameter and estimate the "θ" point for the PSD-C_6D_{12} system. With the data of Table III, the $\Delta\chi$ value is about -7×10^{-3} by supposing $F(x) = 1$ and -12×10^{-3} with $F(x)$ different from unity. These $\Delta\chi$ values lead to a decrease of the "θ" point of about 2 and 4°; experimentally the θ point of the deuterated system is 36°. Qualitatively, this difference can be explained by the fact that we have neglected the effect of the χ_s parameter.

2. Viscosimetry of PSD and PSH in Benzene

The intrinsic viscosities of six PSD samples in the range of M_w from 20,000 to 500,000 have been measured in benzene (C_6H_6) at 25° and compared to $[\eta]$ of PSH samples in the same range of molecular weight. The coefficients K and a of the classical viscosity–molecular weight relationship $[\eta] = KM^a$ are reported in Table IV. In particular, one can see that the exponent a is lower ($a = 0.67_5$) in the PSD–

Table II
Thermodynamic Properties of PS-Cyclohexane (Deuterated and Undeuterated) Systems

System	M_w	θ,[a] deg	θ,[b] deg	ψ_1	A_2 (at 35°)	χ at 35° with $F(x) = 1$
PSH–C_6H_{12}	130,000	35[2]	34[5]	0.68	0	0.500
PSH–C_6D_{12}	130,000	40[2]	38[5]	0.61	-7×10^{-5}	0.508_7
PSD–C_6H_{12}	115,000	30	30	0.65	$+8 \times 10^{-5}$	0.487
PSD–C_6D_{12}	115,000	36	35[5]	0.64	-1.5×10^{-5}	0.502_4

[a] θ from A_2 measurements. [b] θ from critical miscibility temperatures.

Table III
Effect of the Deuteration of Solvent and Polymer on the Solubility Parameter

Systems	$F(x)$	χ	$\Delta\delta$[a]
PSH–C_6D_{12}	1	0.508_1	$\Delta\delta_1 = -0.037_3$
	1.4	0.506_2	$\Delta\delta_1 = -0.032$
PSD–C_6H_{12}	1	0.487	$\Delta\delta_2 = -0.038$
	0.8	0.484	$\Delta\delta_2 = -0.048$

[a] $\Delta\delta$'s are calculated from the relations 5 and 6 with $\chi_{HH} = 0.500$, $\chi_s = 0.34$, and $\delta_{2H} - \delta_{1H} = 0.95_2$.

C_6H_6 system.

If PSH and PSD molecules have the same dimensions, one should obtain the same law for both polymers after correction due to the differences in the mass m of the chain unit. Even plotting the intrinsic viscosity $[\eta]$ as a function of the number x of chain units is not sufficient (see Figure 3); one has to correct also the viscosity index values since they are based on weight concentration.

By definition, $[\eta]$ is the limit of the ratio $(\eta - \eta_0)/\eta_0 c$. Since one should have the same behavior for two solutions with the same number of molecules, one has to multiply the ratio $(\eta - \eta_0)/\eta_0 c$ obtained for PSD by the ratio m_{PSD}/m_{PSH}. This means that one has to multiply the intrinsic viscosities measured for PSD by 1.077 in order to compare with those for PSH. The same result could be obtained from the assumption that the intrinsic viscosity is proportional to V/M, where V is the volume of the polymer molecule of molecular weight M.

The results are shown on Figure 3. There is a difference in the slope of the two lines a and c (PSH and corrected PSD) which lies outside of the experimental error. It seems therefore that, in contrast to C_6H_{12}, benzene is a better solvent for PSH and PSD.

Since the two lines cross at low molecular weight, the deuterated molecules should have larger unperturbed dimensions than PSH. In order to check this point we have used the Stockmayer–Fixman relation

$$[\eta]/M^{1/2} = K_\theta + 0.51 B \phi_0 M^{1/2}$$

with

$$B = \frac{2\overline{V_2}^2}{V_1 N_A}(1/2 - \chi) \text{ and } K_\theta = \phi_0(\overline{r_0^2}/M)^{3/2}$$

ϕ_0 is the Flory's constant: $\phi_0 = 2.7 \times 10^{23}$. The K_θ value and the χ parameter obtained from this relation are given in Table IV. The parameter K_θ decreases when polystyrene is deuterated, but the unperturbed dimensions increase. In order to examine the effect of the deuteration on the dimensions of the coil, one has to take into account the ratio of the mass of the chain unit. We can write

$$(\overline{r_0^2})^{3/2}_{PSD} = (\overline{r_0^2})^{3/2}_{PSH} \frac{(K_\theta m^{3/2})_{PSD}}{(K_\theta m^{3/2})_{PSH}}$$

From our experimental results, we obtain: $(\overline{r_0^2})^{3/2}_{PSD} = 1.035\ (\overline{r_0^2})^{3/2}_{PSH}$. The dimensions of the PSD chain are slightly greater than those of the PSH chain. The same result is obtained from the Stockmayer–Fixman relation by plotting $[\eta]/x^{1/2}$ *vs.* $x^{1/2}$, where $[\eta]$ is the corrected viscosity intrinsic of PSD; we obtain $K_\theta = 8.5 \times 10^{-2}$.

Table IV
Viscosity Data on PSD and PSH at 25°

System	K	a	K_θ	χ
PSH–C_6H_6	11.4×10^{-3}	0.725	8.1×10^{-2}	0.448
PSD–C_6H_6	17×10^{-3}	0.675	7.5×10^{-2}	0.452

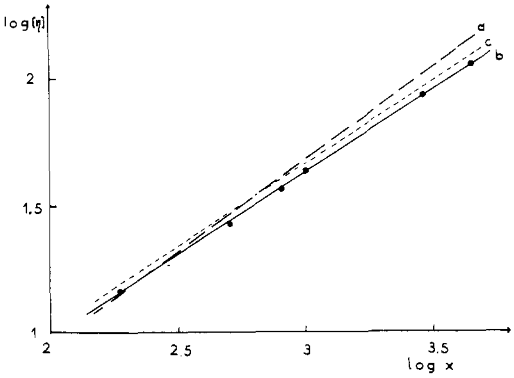

Figure 3. Plot of the intrinsic viscosity versus the degree of polymerization x: curve a is for PSH, curve b is for PSD, curve c is for PSD after correction of $[\eta]$ (see text).

These differences in the viscometric behavior between PSD and PSD should be confirmed by other experimentalists.

In conclusion, these experiments have been made in order to show the thermodynamic differences between deuterated and undeuterated polystyrene. These polymers are not exactly identical but they are characterized by very small χ parameter differences at 35° in cyclohexane. Therefore, one can guess that their enthalpy of mixing in the absence of solvent will be very small, which justifies the absence of segregation which has been assumed for the interpretation of neutron-scattering experiments.

References and Notes

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