Light Scattering Study on Polymer Chain Conformation: Polystyrene in Good Solvents

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Solvent dependence of the static solution properties of a polymer chain was studied by static light scattering technique for polystyrene in three good solvents, toluene, tetrahydrofuran and CCl_4. The molecular parameters such as radius of gyration and second virial coefficients of polystyrene are found to be clearly larger in THF than the other two solvents and they are in the order of tetrahydrofuran>toluene>CCl_4. The radius of gyration shows the same order while the difference is smaller. Nontheless, the penetration functions are found to have a comparable value about 0.2, which confirms the universality of the penetration function in high expansion regime over different nature of solvents.

Introduction

A polymer chain in dilute solution changes its conformation depending on the interaction of chain segments with solvent molecules so that it swells in a good solvent where the excluded volume of the chain segment is large and vice versa.[1] Excluded volume effect on a polymer chain in good solvents has attracted interest of polymer chemists for a long time since Flory.[1,2] One of the most widely used methods to describe the excluded volume effect is the two parameter perturbation theory.[2] According to the two parameter theory, the dilute solution properties, such as root-mean-square radius of gyration (R_g) and second virial coefficient (A_2) can be expressed in terms of two basic parameters, unperturbed dimension of a polymer chain and the excluded volume parameter, z. The parameter z is related to the cluster integral of polymer chain segments and can be expressed as a function of the chain expansion coefficient, $\alpha_s \equiv R_g/R_{g,0}$ where $R_{g,0}$ is the radius of gyration at the unperturbed state.

There exist diverse theories sharing this feature with some difference in detail.[3-6] One of the common method to test these theories is through the penetration function, Ψ defined by

$$\Psi = \frac{A_2 M^2}{4\pi^{3/2} N_{AV} R_g^3} \tag{1}$$

where M is the molecular weight of a polymer chain and N_{AV} is the Avogadro's number.[7,8] The penetration function is another widely used parameter to express the excluded volume effect in terms of the interchain penetration, which is related to z by a functional form of $\Psi = f(z/\alpha_s^3)$. Thus it is a universal function of z, which vanishes at the theta condition and increases steeply as a chain expands from the unperturbed state. Since z cannot be determined directly by experiment, the experimentally accessible chain expansion coefficient, α_s is commonly employed to test the theories.

These perturbation theories have been evaluated in detail and this approach is found to be reliable only in the vicinity

of the theta state probably due to the asymptotic nature of the excluded perturbation series. On the other hand, there seems to be an experimental concensus that Ψ is a universal function of α_s and reaching an asymptote around 0.2 at the large α_s limit, which has not been successfully predicted by any perturbation theories.[2-6] More recent theoretical predictions by renormalization group theory on Ψ at the fully developed excluded volume limit, 0.219 by Oono and Kohmoto[9] and 0.269 by Douglas and Freed[10] are in closer agreement with experiment. However, it cannot be said that the universality has been critically tested, in particular with respect to the solvent used. For an example, Jamieson and coworkers recently reported a Ψ value of 0.315 for polystyrene in tetrahydrofuran (THF) and 0.211 in ethylbenzene.[11,12] The Ψ value determined in THF is much larger than commonly accepted values at good solvent limit and the large discrepancy found in two good solvents is in conflict with two parameter theories.

In this report, we present the result of light scattering studies on polystyrene in three good solvents having different nature, toluene, THF, and CCl_4 in order to have an insight of the solvent dependence of Ψ with respect to the conflicting results in particular.

Experimental

The light scattering apparatus uses 632.8 nm line of a He/Ne laser (Spectra-Physics, Model 127-35) as its incident light and the details of the instrument are described previously[13]. Specific refractive index increments (dn/dc) were obtained at the same wavelength by a differential refractometer, (LDC, Model KMX 16). All the measurements were carried out at the temperature of $25.0 \pm 0.1 °C$.

Solvents used are all reagent grade (Aldrich) and further purified by fractional distillations after drying with proper reagents.[14] Purified toluene served as a reference to calculate the absolute scattered intensity and its Rayleigh ratio was taken as $13.6 \times 10^{-6} cm^{-1}$ (Uv)[15] at 632.8 nm.

Six commercial polystyrene samples (Tosoh Corp. and Polymer Lab.) were used and their characteristics are listed

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Table 1. Values of M_w, A_2, and R_g of Polystyrenes in Different Solvents

Sample code	M_w^c ($\times 10^3$)	M_w/M_n^c	Solvent	M_w ($\times 10^3$)	A_2 ($\times 10^{-4} cm^3 mol/g^2$)	R_g (nm)
F-80[a]	706	1.05	toluene	697	2.94	39.2
			THF	710	3.23	39.5
			CCl$_4$	721	2.77	38.7
F-128[a]	1090	1.08	toluene	1130	2.53	50.2
			THF	1120	2.95	51.4
			CCl$_4$	1150	2.57	49.0
P-180[b]	1800	1.06	toluene	1650	2.36	61.9
			THF	1650	2.59	64.3
			CCl$_4$	1650	2.24	60.7
F-288[a]	2890	1.09	toluene	2930	2.06	89.2
			THF	2950	2.09	91.7
			CCl$_4$	2980	1.97	88.7
F-380[a]	3840	1.04	toluene	3840	1.87	104
			THF	3710	2.06	105
			CCl$_4$	3970	1.84	102
F-700[a]	6770	1.14	toluene	6070	1.66	137
			THF	6270	1.91	138
			CCl$_4$	6310	1.63	135

[a] from Tosoh Corp. [b] from Polymer Laboratories LTD. [c] manufacturer's value.

in Table 1. At least 4 different concentrations were prepared by weight and clarified by filtration through PTFE membrane filters (Gelman). In order to avoid the shear degradation of the polymer during the filtration, pore size of the filter was chosen to be at least 4 times larger than R_g of the polymer and the rate of filtration was kept low. Also the molecular weights as well as polydispersities of the specimen were carefully monitored for any symptoms of the degradation. With our clarification procedure, we have not found any change in molecular weights indicating sample degradation. The 21 mm ϕ sample vials with PTFE lined caps (Wheaton) served as scattering cells.

The scattered light intensities were analyzed by the square root plot[16] in the Guinier region, *i.e.*, at the scattering angle $qR_g < 1$, where q is the magnitude of scatteing wave vector given as follows.

$$q \approx \frac{4\pi n}{\lambda_o} \sin(\theta/2) \qquad (2)$$

where n the refractive index of the scattering medium, λ_o the wavelength *in vacuo* and θ is the scattering angle. The Rayleigh ratios were calculated from the scattered intensities through the normalization by use of toluene as the reference material and an n^2 refraction correction.[17]

Results and Discussion

Most of measured specific refracitve index increments conform to the values available in the literature[18] except that of CCl$_4$ solution. We obtained 0.146 cm^3/g while the literature value is 0.156 cm^3/g. We have no explanation for this discrepancy, but the molecular weight in CCl$_4$ would yield consis-
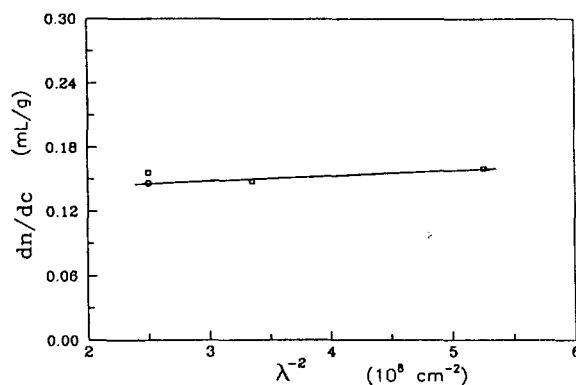

Figure 1. Wavelength dependence of the specific refractive index increments of polystyrene in CCl$_4$. Squares are from the literatures[18,19] and a circle from this work.

tently values smaller by about 5% than those determined in other solvents if we used the literature value.[18,19] Also the literature values[18] obtained at other wavelengths are consistent with the values measured in this work in terms of the dispersion relation as shown in Figure 1.

The square root plots for F-80 in three good solvents are given in Figure 2 from which the values of M_w, A_2 and R_g are obtained. As shown in the figures, the range of the scattering angle was $30°$-$100°$ fulfilling the condition of $qR_g < 1$. Molecular weights determined in these solvents coincide within 5%, which may be regarded as an indication that our determination of other single coil parameters are also reliable.

The values of M_w, R_g, and A_2 thus determined are also listed in Table 1. The log R_g and A_2 are plotted against logM_w
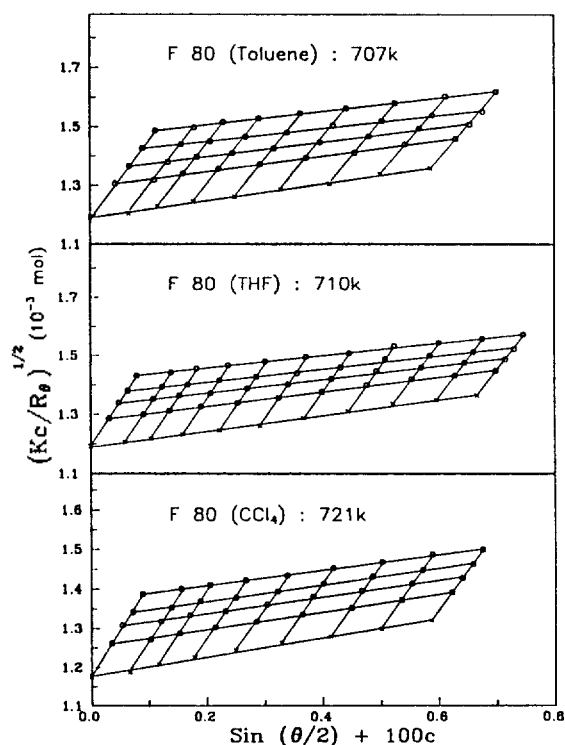
Figure 2. Results of static light scattering on F-80 in 3 different solvents represented by square root plots.
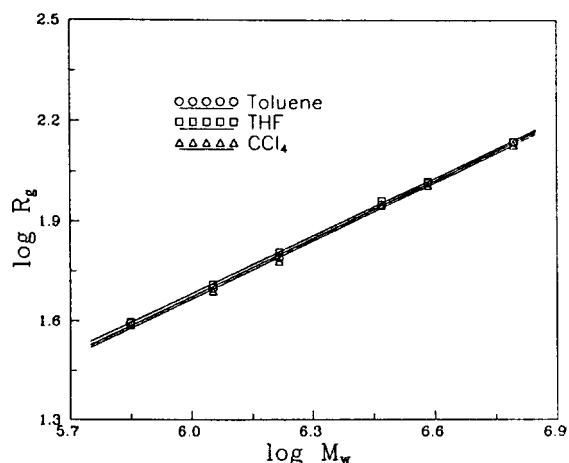

Figure 3. Molecular weight dependence of the radii of gyration of polystyrene in 3 good solvents.

as shown in Figure 3 and 4 and good linear relationships are observed. Their molecular weight dependences are obtained from the plots as follows.

$$R_g = 0.0150 \times M^{0.583 \pm 0.01} \text{ nm (toluene)}$$
$$0.0160 \times M^{0.580 \pm 0.01} \text{ nm (THF)}$$
$$0.0144 \times M^{0.585 \pm 0.02} \text{ nm (CCl}_4)$$

$$A_2 = 0.00933 \times M^{-0.26 \pm 0.01} \text{ cm}^3 . \text{mol/g}^2 \text{ (toluene)}$$
$$0.0109 \times M^{-0.26 \pm 0.02} \text{ cm}^3 . \text{mol/g}^2 \text{ (THF)}$$
$$0.00811 \times M^{-0.25 \pm 0.01} \text{ cm}^3 . \text{mol/g}^2 \text{ (CCl}_4)$$

Uncertainties are the one standard deviation from the least square analysis. First, we can compare our results with existing literature values in toluene and in THF. Data in CCl₄
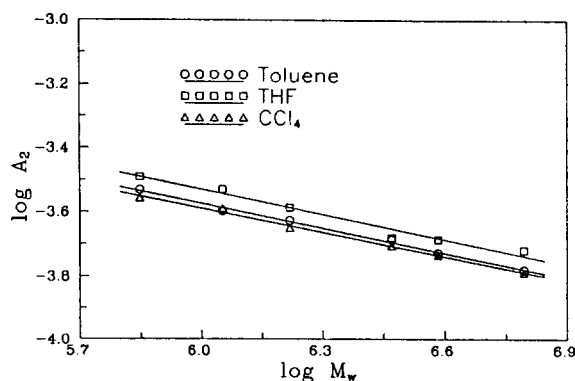

Figure 4. Molecular weight dependence of the 2nd virial coefficients of polystyrene in 3 good solvents.

Table 2. Values of Ψ of Polystyrenes in Good Solvents

Sample	Toluene	THF	CCl₄
F-80	0.183	0.196	0.179
F-128	0.190	0.207	0.208
P-180	0.202	0.198	0.203
F-288	0.188	0.176	0.183
F-380	0.183	0.196	0.191
F-700	0.186	0.210	0.191
Mean*	0.19	0.20	0.19
	± 0.01	± 0.01	± 0.01

* The uncertainties of the mean values indicate the one standard deviations.

are not available to the best of our knowledge. It was found that our R_g values in toluene are in good agreement with the values of Appelt and Meyerhoff[20] while about 5% and 15% larger than those reported by Varma et al.[21] and by Utiyama et al.,[22] respectively. On the other hand, our A_2 values are well consistent with the values of Utiyama et al.,[22] while about 15% smaller than Varma et al.[21] For THF solutions, our A_2 values are in good agreement with those of Schulz and Baumann[23] and of Jamieson et al.[21] while R_g values of Jamieson et al. are about 15% smaller the Schulz and Baumann and ours. All these discrepancy may illustrate a persistent problem associated with the characterization of polymer solutions. These deviations are mainly due to the polydispersity of the polymer, which is inherent in a synthetic polymer system and difficult to control. However, a self-consistency in a given set of polymers are thought to exist. Our Ψ values, tabulated in Table 2, are slightly smaller but consistent with the asymptotic Ψ value reported by others within experimental uncertainty.[22,24]

We note from Figure 3 and 4 that A_2's in THF are distinctively larger than those in the other two solvents and toluene solution shows a slightly larger A_2 than CCl₄ solution. The same sequence is also observed for R_g in the three good solvents that THF>toluene>CCl₄ while the difference is much smaller than the case of A_2. From this result, it can be said that the thermodynamic solvent quality of THF is better than other two good solvents consistent with the results of Jamieson et al.[11,12] as far as the trend is concerned.

Polystyrene Conformation in Good Solvents

Bull. Korean Chem. Soc., Vol. 12, No. 6, 1991 685

However, Ψ values listed in Table 1 are quite similar regardless of the solvent used because the large A_2 found in THF is largely compensated by the inverse cube dependence on R_g in Eq. (1). This results contradict with the anomalously large Ψ value reported for THF solutions.[11,12] Although we cannot elucidate this discrepancy, the major difference in two sets of data is in R_g values which differ by 15% while A_2 values are consistent each other. The third power dependence of Ψ on R_g results in such a large discrepancy. Although the available R_g data of polystyrene in THF is scarce, we concern that their R_g values are too small compared to existing R_g values in THF.[23] We reached the similar conclusion through the study on comparison of static and hydrodynamic size of polystyrene chains.[25]

Lastly, it is pertinent to mention the molecular weight dependence of Ψ. For low molecular weight polymer, a large deviation from the typical excluded volume behavior has been observed. This has been explained by taking into account of chain stiffness.[26,27] Also, even for a long chain, Ψ passes through a flat maximum at intermediate α_s before reaching the asymptotic value.[22,24] We did not observe these behavior probably because our molecular weight range is high and relativley narrow so that volume expansion factor, α_s^3 spans over 4.2-6.9. In this range, Ψ is already close to the asymptotic value. The decreasing trend was discussed previously in relation to the convex-downward curvature found in the plot of log A_2 against log M.[28,29] The linear relationship of log A_2 vs. log M displayed in Figure 4 also illustrates that such a trend is not visible in this study.

In summary, we can conclude from this study that there does not seem to exist a peculiar property in THF solution of polystyrene, and their conformation in three good solvents namely, toluene, tetrahydrofuran and carbon tetrachloride are well described by the two parameter concept in terms of the universal Ψ value.

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