Molecular Weight Dependency of Refractive Index Increment of Polystyrene Determined by Uniform Oligomers

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ABSTRACT: Molecular weight dependency of a specific UV absorption coefficient of polystyrene in solution was determined by supercritical fluid chromatography applied to equimolar and equimass mixtures of uniform polystyrenes whose degree of polymerization was $n = 1$ to 40. From the ratio between the response from a UV detector and that from a refractometer, we determined the refractive index increment dn/dc as a function of molecular weight for polystyrene in tetrahydrofuran at the wavelength $\lambda = 633$ nm. We found that dn/dc is well expressed as a linear function of the reciprocal of molecular weight for uniform polystyrenes. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 1101–1106, 2004

Key words: refractive index (RI); polystyrene; supercritical fluid chromatography (SFC); light scattering; molecular weight distribution

INTRODUCTION

The refractive index (RI) increment dn/dc is necessary to static light scattering (SLS) measurements to determine the weight-average molecular weight M_w of polymers. The relationship between the molecular weight and dn/dc is generally assumed to be independent of molecular weights over a few thousands. Because the molecular weight of polymer determined by light scattering depends on the square of dn/dc, even a slight variation in dn/dc produces a great error in the value of M_w.

On the other hand, in the oligomeric region, a number of studies have shown that dn/dc greatly depends on the molecular weight.[1–10] Variations in dn/dc affect not only the accuracy of M_w measured by SLS, but also that of molecular weight distribution measured by size-exclusion chromatography (SEC). It is therefore important that the relationship between molecular weight and dn/dc is exactly determined. In all the previous investigations, monodisperse polymers or oligomers having molecular weight distribution were used to determine dn/dc. However, the polydispersity of these polymer samples made the dn/dc data somewhat ambiguous.

Molecular weight dependencies of dn/dc were reported experimentally, which are expressed as linear functions of reciprocal number-average molecular weight.[5–10] However, it should be verified that the molecular weight dependency is also expressed as a linear function of reciprocal molecular weight of each component (see the Appendix).

In this article, we investigate the molecular weight dependency of a specific UV absorption coefficient and dn/dc of uniform polystyrene (PS) oligomers in tetrahydrofuran (THF). Using preparative supercritical fluid chromatography (SFC), we first separated PS oligomers with degrees of polymerization $i = 2$ to 41 from monodisperse oligostyrene samples. We determined a specific UV coefficient as a function of molecular weight by measuring SFC chromatograms of equimolar and equimass mixtures of the uniform polystyrenes. Because it is difficult to obtain a large quantity of uniform polystyrene for accurate dn/dc measurement, we calculated dn/dc from the ratio of RI responses to UV responses observed at SEC chromatograms of each uniform polystyrene mixture.

THEORY

Relative UV absorption coefficient

If we assume that the UV absorption of a polystyrene molecule is proportional to the number of monomer units, the specific UV coefficient ε_i' of the ith-mer can be expressed as

$$\varepsilon_i' = \varepsilon_0' \frac{iM_0}{M_i} = \varepsilon_0' \frac{iM_0}{M_e + iM_0} \tag{1}$$

where ε_0' is a specific UV absorption coefficient of the monomer unit; and M_0 and M_e are the molecular weights of monomer unit and terminal end, respectively.

A UV sensitivity coefficient, defined as the ratio of the area fraction of a chromatogram to the mass fraction of an injected sample polymer, is expressed as follows:

$$a_i = \frac{s_i}{w_i} = \frac{1}{w_i} \frac{S_i}{\sum_i S_i} = \frac{\varepsilon_i'}{\sum_j \varepsilon_j' w_j} \tag{2}$$

where S_i, s_i, and w_i are the peak area, peak area fraction, and the mass fraction of the ith polymer, respectively. Because the coefficient a_i is not an intrinsic value but is dependent on the distribution of mass fraction, we introduce a relative sensitivity coefficient $\alpha_i(s)$, which is normalized in the following equation:

$$\alpha_i(s) = \frac{a_i}{a_s} = \frac{\varepsilon_i'}{\varepsilon_s'} \tag{3}$$

where s is the sth component chosen as a standard.

RI relative sensitivity coefficient

The RI sensitivity coefficient for the ith polymeric component can be defined as

$$b_i \equiv \frac{s_i^{RI}}{w_i} \tag{4}$$

where s_i^{RI} is the peak area fraction of a SEC chromatogram measured on an RI detector for the ith component. In the same way as UV absorption coefficients, b_i can be expressed as

$$b_i = \frac{s_i^{RI}}{w_i} = \frac{1}{w_i} \frac{S_i^{RI}}{\sum_j S_j^{RI}} = \frac{v_i}{\sum_j v_j w_j} \tag{5}$$

Here v_i is the dn/dc for the ith component defined by $v_i = (dn/dc)_i$. The RI relative sensitivity coefficient can be defined as follows:

$$\beta_i(s) = \frac{b_i}{b_s} = \frac{v_i}{v_s} \tag{6}$$

where subscript s is the sth component chosen as a standard. In the literature, the RI increment has generally been written as follows[5–10]:

$$\frac{dn}{dc} = a - \frac{b}{M_n} \tag{7}$$

where a and b are constants dependent on both polymer and solvent. For the relative sensitivity coefficient β_i, an expression corresponding to eq. (7) can be given as

$$\beta_M(\infty) = 1 - \frac{d}{M_n} \tag{8}$$

where $d = b/a$. Practically, we calculated the coefficient d from the coefficients a' and b' appearing in $\beta_i(s)$:

$$\beta_M(s) = a' - \frac{b'}{M_n} \tag{9}$$

$$\beta_M(\infty) = 1 - \frac{d}{M_n} \tag{10}$$

where $d = b/a$. Because uniform polystyrenes were used in this study, we can replace M_n with M_i.

Here we consider dn/dc for a polymer having molecular weight distribution. The concentration dependency of refractive index for polymer solutions is given as follows:

$$n = n_0 + \left(\frac{\partial n}{\partial c}\right)_0 c + \cdots \tag{11}$$

Using mass fraction of each component,

$$= n_0 + \sum_{i=1} \left(\frac{\partial n}{\partial c_i}\right)_0 c_i + \cdots = n_0 + \left[\sum_{i=1} \left(\frac{\partial n}{\partial c_i}\right) w_i\right] c + \cdots \tag{12}$$

That is,

$$\left(\frac{\partial n}{\partial c}\right)_0 = \sum_{i=1} \left(\frac{\partial n}{\partial c_i}\right)_0 w_i = \left(\frac{\partial n}{\partial c}\right)_{0, i=\infty} \sum_{i=1} \frac{(\partial n/\partial c_i)_{T,P}}{(\partial n/\partial c)_{0,\, i=\infty}}$$

$$w_i = \left(\frac{\partial n}{\partial c}\right)_{0, M=\infty} \sum_{M=0} \beta_M w_M \tag{13}$$

TABLE I
Molecular Weight of the Polystyrene Samples

Sample code	M_w	M_n
PS-300	455.1	387.2
PS-500	501.7	436.2
PS-1000	1007	881.0
PS-2400	2415	2292
NIST 705a	1.79×10^5	1.67×10^5

where *dn/dc* of polydisperse polymer can be estimated with the relative sensitivity coefficient and the mass fraction of every component.

EXPERIMENTAL

Materials

The uniform PS oligomers were separated from four samples: PS-300 and PS-1000 (supplied by Tosoh Co., Tokyo, Japan), PS-500 and PS-2400 (Certified reference materials 5002-a and 5001-a; National Metrology Institute of Japan, Ibaraki, Japan) by preparative SFC. The uniform oligomer with $i = 1$ (hexylbenzene) was purchased from Fluka Chemika (Buchs, Switzerland) because it could not be separated by SFC. Mass spectral data were acquired to determine the molecular weight of the separated oligomers using a reflectron time-of-flight MALDI mass spectrometer (Shimadzu/Kratos Kompact-MALDI III; Kyoto, Japan). Each of the uniform oligomers was weighed on a differential scanning calorimetry (DSC) pan using a microbalance. The uniform oligomers on DSC pans were dissolved in THF (Wako Pure Chemicals, Tokyo, Japan) and subdivided into bottles to prepare mixed solutions. The details of the separation procedure of the uniform PS oligomers and preparation of equimolar and equiweight oligomer solution are described elsewhere.[11]

For differential refractive index measurement PS-500, PS-1000, PS-2500, and high molecular weight monodisperse polystyrene (NIST SRM 705a), as a standard at infinite molecular weight, were used. In Table I molecular weights of all samples are listed. Molecular weights of these oligomers were determined by SFC and the molecular weight of high molecular weight polystyrene referred nominal values.

Apparatus

Supercritical fluid chromatography

Supercritical fluid chromatography (SUPER-201, Jasco Co., Tokyo, Japan) with silica gel column Superpak SIL60–5 (pore size 60 Å, particle size 5 μm, 10 mm i.d. ×250 mm; Jasco Co.) was carried out to separate the uniform PS oligomers and to determine the UV absorption coefficient. The mobile phase was a mixture of carbon dioxide with modifier solvents, run at a constant flow rate under a constant pressure of 200 kg/cm². The modifier solvents were mixtures of chloroform and ethanol. Every sample was dissolved in chloroform to inject, and a UV–vis detector was used at the wavelength of 254 nm. Figure 1 shows a typical SFC chromatogram. The conditions of SFC measurements were varied for each oligomer sample. The molar fraction for each ith polymeric component was estimated from these chromatograms with a correction of UV absorbance coefficient.

Size-exclusion chromatography

The SEC system consisted of a Tosoh pump (DP-8020), two TSK columns (TSK gel GMHHR-H with a TSK-guard column HHR-H; Tosoh Co.) with a column oven operated at 40°C, a UV–vis detector (UV-8010 or UV-8020 at 254 nm; Tosoh Co.), and a RI detector [Optilab DSP, $\lambda_0 = 632.8$ nm, at 25°C (Wyatt Technology Corp., Santa Barbara, CA) or RI-8020, tungsten light, at 40°C (Tosoh Co.)]. The flow rate of mobile phase (THF) was 1 mL/min. To obtain approximately the same area for every peak, equimolar and equiweight mixture solutions were prepared. Every measurement was carried out at least three times.

Differential refractive index measurement

An Otsuka (Tokyo, Japan) DRM-1030 differential refractometer ($\lambda_0 = 632.8$ nm) of ordinary type was used to determine the *dn/dc* value of high molecular weight polystyrene as standard for infinite molecular weight and oligomer samples having molecular weight distribution. Because this instrument needs abundant solutions for precision measurements, it is difficult to measure *dn/dc* of uniform polystyrene oligomer. The oligomer samples having molecular weight distribu-
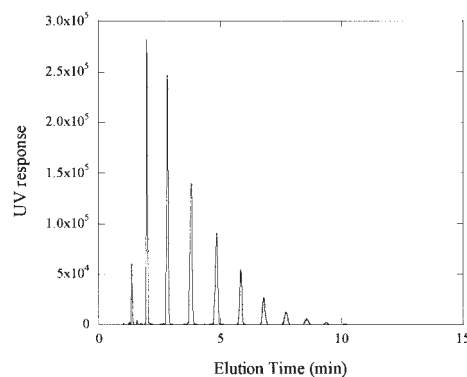

Figure 1 Typical SFC chromatogram for PS-300. The modifier composition is 4 : 1 (ethanol : chloroform). Flow rates of carbon dioxide and modifier are 2.5 and 0.4 mL/min, respectively. A temperature gradient from 130 to 40°C at constant rates of −5°C/min is used.
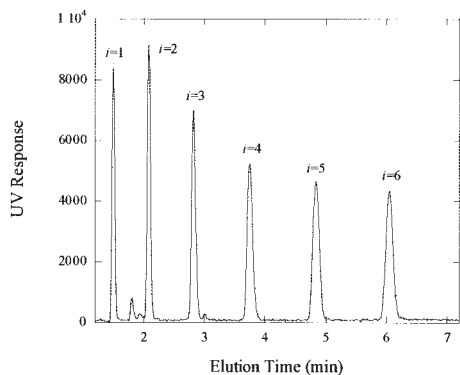
Figure 2   SFC chromatogram of equimass mixture (i = 1, 2, 3, 4, 5, and 6) in THF. A correction coefficient of molecular weight dependency of UV detector response for each component was determined from the ratio of these peak areas.

tion were measured to verify our method. Each oligomer's dn/dc was determined by five solutions with various concentrations.

RESULTS AND DISCUSSION

Relative UV absorption coefficient

Figure 2 shows a typical chromatogram of mixture of uniform PS oligomer. The areas of each peak were calculated and UV absorption coefficients were estimated, shown in Figure 3 as a function of degree of polymerization with fitting curve and theoretical curve. The fitting curve, which is normalized to unity for infinity molecular weight, for UV sensitivity coefficients acquired experimentally, is expressed as follows:

$$\alpha_i(\infty) = \frac{i}{0.48194 + i} \qquad (14)$$
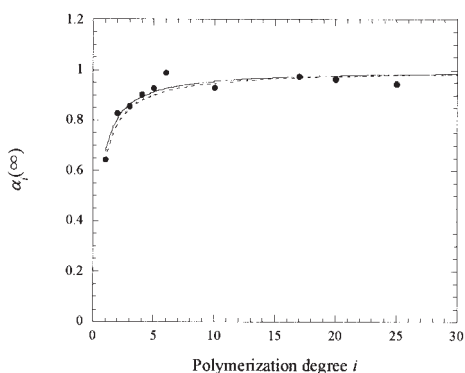

Figure 3   Relative UV absorption coefficient as a function of degree of polymerization i. Dotted and solid lines are experimental and theoretical curves, respectively. These data are normalized to unity at infinite molecular weight.
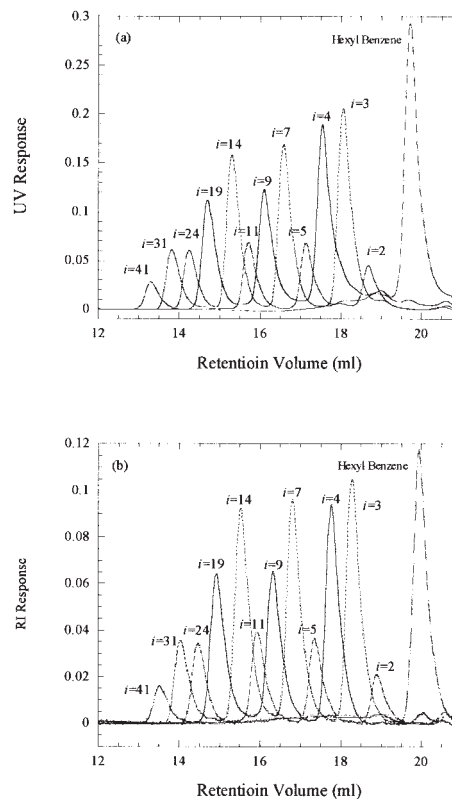

Figure 4   UV response (a) and RI response (b) of SEC chromatograms for mixtures of uniform polystyrene in THF. These measurements were carried out with mixtures of i = 2, 5, 11, 24; 3, 7, 14, 31; 4, 9, 19, 41, and hexyl benzene as i = 1, respectively.

Theoretically, molecular weight dependency of UV sensitivity coefficients is represented using by eq. (1) as follows:

$$\alpha_i(\infty) = \frac{\varepsilon_i'}{\varepsilon_\infty} = \frac{i}{(M_e/M_0) + i} = \frac{i}{0.55806 + i} \quad (15)$$

Although this curve has a slight gap, especially in the small molecular weight region, it is essentially in good agreement.

RI relative sensitivity coefficient

Figure 4 shows UV and RI chromatograms of SEC. The RI relative sensitivity coefficients were estimated form the area of each peak. The RI relative sensitivity coefficients are shown as a function of reciprocal molecular weight in Figure 5. In this case the RI relative sensitivity coefficients are normalized to unity at infinite molecular weight. By linear fitting, equations of RI relative sensitivity coefficient are given as follows:

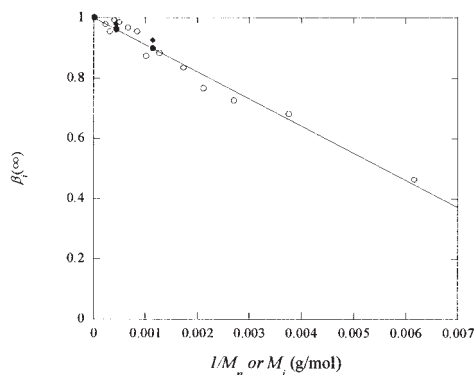$$\beta_M(\infty) = 1 - \frac{89.94}{M_i} \quad (\lambda_0 = 632.8 \text{ nm, at } 25°\text{C}) \quad (16)$$

Figure 5 Relative RI sensitivity coefficient as a function of reciprocal molecular weight (M_i and M_n) in THF for each ith component ($\bigcirc$) and for oligomeric standard samples having a molecular weight distribution, ($\bullet$) calculated data, and ($\blacklozenge$) experimental data from conventional *dn/dc* measurements.

In the same way,

$$\beta_M(\infty) = 1 - \frac{88.54}{M_i} \quad \text{(tungsten light, at 40°C)} \quad (17)$$

These results show the evidence that $\beta_M(\infty)$ can be fitted by linear functions as a function of reciprocal M_i.

Here we discuss the effects of wavelength and temperature on the RI response. It is known that *dn/dc* depends on concentration and temperature. Nevertheless, there is no significant difference between eq. (16) and eq. (17). The temperature and wavelength dependencies of *dn/dc* could be attributable to their change in the value of $(\partial n/\partial c)_{0,M=\infty}$.

To verify our results by this procedure, we estimated *dn/dc* for PS oligomers standards having molecular weight distribution by two methods. Substituting eq. (16) and measured mass fraction distribution of the standard samples into eq. (13), we first calculated their *dn/dc* values. Second, we measured their *dn/dc* by use of a refractometer. These results are shown in Figure 5 with the line of eq. (16). These results show good agreement.

Chance et al.[7] reported the following relation:

$$\beta_M(\infty) = 1 - \frac{83}{M_n} \quad (\lambda_0 = 632.8 \text{ nm, at 27°C}) \quad (18)$$

Their result differs only slightly from our data. They used nominal M_n values or those measured by SEC. However, it is generally difficult to determine M_n value with high precision. On the other hand, because our PS sample is uniform, without distribution of molecular weight, its molecular weight can be used as an exact M_n. Therefore our equations of molecular weight dependency of *dn/dc* for polystyrene oligomer

in THF could be very useful and better than previously reported values.

CONCLUSIONS

Molecular weight dependencies of *dn/dc* were investigated for PS in THF using uniform PS oligomers, which were separated from monodisperse oligostyrene samples by means of SFC. To estimate the refractive index increments, a UV relative absorption coefficient and RI relative sensitivity coefficient were measured. At lower i values (less than $i = 5$) the UV sensitivity coefficients decreased with decreasing molecular weight, consistent with theoretical expectation. The RI sensitivity coefficients could be fitted by a linear function of reciprocal molecular weight of each ith component as well as number-average molecular weight. Values of *dn/dc*, calculated from the RI relative sensitivity coefficients, were consistent with results of usual *dn/dc* measurements.

In this article we do not discuss wavelength and temperature dependencies of *dn/dc* in detail. However, our results show that the difference is not more significant than that of other previous investigations, where monodisperse standard samples having molecular weight distribution were used.

APPENDIX

Refractive index increments of polymer having molecular weight distribution are generally written in the form expressed by eq. (7). However, the relation is verified only when the same relationship can apply to the ith component with molecular weight M_i:

$$\beta(M_i) = 1 - \frac{d}{M_i} \quad (A.1)$$

Here, for a polymer having molecular weight distribution, we have

$$\left(\frac{dn}{dc}\right) = \left(\frac{dn}{dc}\right)_{M=\infty} \int \beta(M_i)w(M_i)dM_i \quad (A.2)$$

where $w(M_i)$ is the differential molecular weight distribution, which satisfies

$$\int w(M_i)dM_i = 1 \quad (A.3)$$

Substitution of eq. (A.1) into eq. (A.2) gives

$$\left(\frac{dn}{dc}\right) = \left(\frac{dn}{dc}\right)_{M=\infty}\left(1 - \frac{d}{M_n}\right) \qquad (A.4)$$

However, it has not been confirmed whether eq. (A.1) is valid.

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