Light Scattering by Oligostyrene Solutions

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Light-scattering photometers were partially modified in order to measure light scattering by low molecular-weight molecules. Corrections to the molecular weights were then theoretically estimated, when the light scattering due to fluid density fluctuations were approximated by that due to the density fluctuations of a pure solvent. The molecular weight of benzene was determined, in an ethyl methyl ketone solvent, using the light-scattering method prior to the determination of the molecular weights of oligostyrene molecules. Measurements of light scattering by oligostyrene molecules with molecular weights from 600 to 20000 were then carried out. The weight-average molecular weight observed by the light-scattering method was compared with the number-average molecular weights which were determined by the vapor-phase osmometric and NMR methods. The molecular-weight heterogeneity of the specimen is discussed. The second virial coefficient, in the ethyl methyl ketone solvent system, was found to change from negative to positive with increasing molecular weight. It is also shown that the molecular optical anisotropy changes markedly in the range of molecular weights between 2000 and 3000, the change being considered to reflect the conformational changes of oligostyrene molecules.

Oligomers are not only useful for practical uses but are also attracting considerable interest in the study of solution properties. It is especially interesting to determine the range of molecular weights in which the recent theory of solutions for high molecular-weight polymers can be applied. For this purpose it is desirable to measure molecular weights in the range from oligomers to high molecular-weight compounds using the same technique, because mean values should be compared on the same basis. The light-scattering method is most suitable for the measurement of molecular weights over such a wide range. There are several technical problems in the measurement of low molecular weights as noted below:

(1) Minute amounts of scattered light must be accurately measured, because the scattering intensity may be very weak.

(2) Scattering due to a fluctuation in the fluid density cannot be approximated by that due to the fluctuation of the solvent density.

(3) The correction to the degree of depolarization of the scattered light due to a fluctuation in the orientation of anisotropic molecules should be made accurately when unpolarized light is used as the incident light.

The method for measuring molecular weights utilizing minute amounts of scattered light has already been reported by Kamata and Nakahara.$^{1)}$ In the present paper, a method for correcting the observed molecular weights, as the result of density fluctuations and methods for correcting the depolarization are reported. In addition, the characteristic behavior of oligomer molecules in solution are discussed based on the results of light-scattering measurements of oligostyrene.

Experimental

Materials. Polystyrenes, batch 16a, 15a, 12b, 11b, 8b, and 2b, obtained from the Pressure Chemical Co., were used. Dibenzyl of G.R. grade, used as the substance corresponding to the dimer for the measurement of the specific refractive index increment, was obtained from the Tokyo Kasei Kogyo Co. The solvent, ethyl methyl ketone (special grade), was purchased from the Kanto Chemical Co. and used after distillation. The benzene (DOTITE Primazol) used, after distillation, for the calibration of the light-scattering photometers was purchased from the Dojin Chemical Co.

Light-Scattering Measurements. It is difficult to accurately measure the depolarization and the scattered light produced by a solution containing a low molecular-weight substance using a single light-scattering photometer. Thus, the Rayleigh factor and the depolarization were separately measured using two photometers. A light-scattering photometer, Shimadzu Model PG-21, was used for measuring the Rayleigh factor, and a high-gain photomultiplier, Hamamatsu TV. Co. Model R-105 UH, having an anode sensitivity= 1530 μA/μlm, was used for accurately measuring weakly scattered light. A Shimadzu Model DL-10A light scattering photometer was used with some modifications for the depolarization measurements. It is necessary that the zero point be easy to monitor during the experiments and the observed values be stable in order to accurately determine the depolarization of the weakly scattered light. For this purpose, a solenoid shutter was placed in front of the photomultiplier. This shutter can be opened and closed by means of an external switch. The zero point was very easily checked using this shutter, which also rendered the observed values very stable, since there was no need to shut off the power supply for the photomultiplier during the course of the experiments. A Glan-Thompson prism was also used as a polarizer and an analyzer.

The solvents and solutions used were all centrifuged for 1 h at about 60000 g using a Beckman (Spinco) Model L_4 preparative ultracentrifuge, and then directly filtered into the light-scattering cell through a Corning ultrafine glass filter.

The light scattering was measured using mercury radiation at a wavelength of 436 nm in vacuo at room temperature. Calibration of the light-scattering photometer was carried out using the Rayleigh ratio, $R_{90}=45.88\times10^{-6}$ cm^{-1}(20.0 °C), for benzene. Depolarization was measured using the Shimadzu Model DL-10A light-scattering photometer with the cell containing the specimen the same as that used for the Rayleigh factor measurements. The isotropic part was calculated from the Cabannes factor.$^{2)}$

The determination of the specific refractive index increment was carried out at room temperature using a Shimadzu differential refractometer.

Measurement of the Number Average Molecular Weight. The number average molecular weight was determined from values of the vapor pressure which was obtained using a

Hitachi-Perkin Elmer Model 115 vapor pressure osmometer and from the NMR spectra obtained in a CCl_4 solvent system using a JEOL Model HL-60 NMR spectrometer.

Gel Permeation Chromatography. Gel permeation chromatography was carried out at 35 °C using a Waters Ana-Prep GPC with four columns (4 feet long with pore sizes of 3×10^5, 10^4, 10^3, and 10^2 nm) connected in series, tetrahydrofuran being used as the solvent.

Results and Discussion

Light Scattering Due to Fluctuations in the Fluid Density and Its Influence on Molecular Weight Determination. The total isotropic light scattering of the binary solution is expressed by

$$R_{is} = R_c + R_d + R^*, \tag{1}$$

where R_c and R_d indicate the scattering intensity due to fluctuations in the densities of solute concentrations and those of the densities of the pure solvent, respectively. R^* is the cross term. The scattering due to fluctuations in the solute concentrations, which is necessary for determining the molecular weight using the light-scattering method, is usually obtained by subtracting the scattering by a pure solvent from that by the solution. As indicated by Eq. 1, the scattering due to fluctuations in the binary solution density is not equal to that due to fluctuations in the pure solvent density. The influence of this difference causes no problem for determining molecular weights larger than 10^4. The determination of low molecular weights, such as those in the range between several tens and several hundreds, however, is considerably affected by this difference.

According to Bullough,[3] when the scattering due to fluctuations in the solution density is approximated by the scattering due to fluctuations in the density of the pure solvent, a correction of the molecular weight obtained by the light-scattering method is given approximately by

$$\Delta M \approx N_A\lambda_0^2(\tau_0\kappa_0 kT/8\pi^3)^{1/2}/n_0(dn/dc), \tag{2}$$

where N_A is Avogadro's constant, λ_0 the wavelength of the incident light in vacuo, τ_0 the turbidity, κ_0 the isothermal comressibility, k Boltzmann's constant, T the absolute temperature, n_0 the refractive index of the solvent, and dn/dc the specific refractive index increment. For isotropic molecules, $\tau_0=(16/3)\pi R_{90}$. Therefore, Eq. 2 becomes

$$\Delta M \approx \{(N_A\lambda_0^2/n_0(dn/dc)\}(2R_{90}\kappa_0 kT/3\pi^2)^{1/2}. \tag{3}$$

The values of ΔM obtained from measurements at $\lambda_0=436$ nm in several solvents are given in Table 1.

The contribution to the light scattering due to the density fluctuation was found to be rather large when a determination of the molecular weight of benzene was attempted in an ethyl methyl ketone (EMK) solvent using the light-scattering method. The displacement of the estimated molecular weight was up to 13% and was not negligible when the scattering due to fluctuations in the solution density was approximated by that due to fluctuations in the pure solvent density. The influence of such as approximation on estimations of the molecular weights of oligostyrenes, which are larger than 1000, in an EMK solvent using the light-scattering technique, however, was found to be negligible when compared with the experimental errors in the light-scattering measurement.

Measurement of Light Scattering of Benzene in an EMK Solvent. Since styrene polymers contain phenyl groups which are strongly optically anisotropic, it is believed that oligomers may strongly be affected by the phenyl groups and exhibit strong optical anisotropy. It is, therefore, important to correct for the degree of depolarization in the light-scattering measurements of anisotropic molecules using unpolarized incident light. In the present study, as mentioned above, two photometers were used for measurements of the light-scattering intensity and the degree of depolarization. In order to verify the method adopted in this study, a measurement of the molecular weight of benzene dissolved in an EMK solvent was carried out prior to measurements on oligostyrenes.

The equation which is well known for the calculation of molecular weights,

$$Kc/R_\theta = 1/(M_w P(\theta)) + 2A_2c + \cdots, \tag{4}$$

was used. When unpolarized incident light is used, K and $P(\theta)$ are given respectively by

$$K = 2\pi^2 n_0^2(dn/dc)^2/(N_A\lambda_0^4) \tag{5}$$

and

$$P(\theta) = 1-(1/3)(4\pi/\lambda)^2R_G^2\sin^2(\theta/2) + \cdots, \tag{6}$$

where R_θ is the isotropic excess light scattering, c the solution concentration (g/cm³), M_w the weight average molecular weight of the solute, A_2 the second virial coefficient and R_G the radius of gyration. R_θ in Eq. 4

Table 1. Molecular weight corrections calculated for various solutions of low molecular-weight substances

Substance	Solvent	n_0[a]	dn/dc[a] (cm³/g)	$R_{90}\times10^6$[a] cm^{-1}	$\kappa_0\times10^{12}$ (cm²/dyne)	ΔM	M[b]	δ[c] (%)
Benzene	EMK[d]	1.388	0.154	12.0	108[e]	10.1	78.1	13
Benzene	Cyclohexane	1.436	0.100	12.5	112[g]	15.6	78.1	20
Toluene	EMK	1.388	0.150	12.0	108[e]	10.3	92.1	11
Carbon tetrachloride	EMK	1.388	0.055	12.0	108[e]	28.2	153.8	18
Oligostyrene (16a)	EMK	1.388	0.222	12.0	108[e]	7.0	600[f]	1
Oligostyrene (16a)	Benzene	1.523	0.082	45.9	95[g]	31.6	600[f]	5
Sucrose	Water	1.340	0.149	2.84	45.7[h]	3.4	342.3	1

a) Experimental conditions: 20 °C, $\lambda_0=436$ nm. b) Calculated from molecular formula. c) $\delta=(\Delta M/M)\times100$. d) Ethyl methyl ketone. e) Ref. 8. f) Nominal molecular weight. g) Ref. 9. h) Ref. 10.

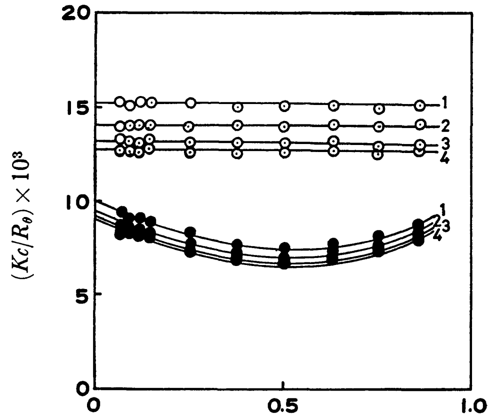

Fig. 1. Light Scattering diagram for benzene in ethyl methyl ketone.

●: Uncorrected, ○: corrected for optical anisotropy. Concentration of benzene: (1) 0.293, (2) 0.219, (3) 0.146, (4) 0.0974 (g/cm³).

was calculated, using the King equation (Eq. 8),[4] from the Rayleigh factor $(R_\theta)_u$, which was measured with unpolarized light,

$$R_\theta = (R_\theta)_u/f_u(\theta) \tag{7}$$

with

$$f_u(\theta) = [6+6\rho_u\{(1-\cos^2\theta)/(1+\cos^2\theta)\}]/(6-7\rho_u), \tag{8}$$

where ρ_u is the degree of depolarization. The scattering diagram for benzene in an EMK solvent is shown in Fig. 1. Since the benzene molecule is optically anisotropic, the curves in Fig. 1 curve downward sharply. A straight line was obtained after correction for depolarization, indicating a proper correction for depolarization. In addition to this, the value of Kc/R_θ in Eq. 4 exhibited no angle dependency and the value of $P(\theta)$ is approximately equal to 1, since the benzene molecule is considerably smaller than the wavelength of the incident light. Thus, the molecular weight of benzene can be calculated from only the 90° scattering.

TABLE 2. MOLECULAR WEIGHT OF BENZENE ESTIMATED FROM LIGHT-SCATTERING MEASUREMENTS

M_{app}	ΔM	M(expt)[a]	M(formula)[b]
88.5	10.1	78.4	78.1

a) $M(\text{expt}) = M_{app} - \Delta M$. b) Calculated from molecular formula of benzene.

Since the contribution from the cross term, in Eq. 1, is rather large for the benzene molecule, the molecular weight estimated using the conventional double extrapolation method (Zimm plot) resulted in a considerable deviation from the true value. The measured values of the molecular weight of benzene are shown in Table 2. M_{app} indicates the apparent molecular weights evaluated by the conventional extrapolation method. ΔM gives the correction to the molecular weights, calculated using Eq. 3 and neglecting the cross term in Eq. 1. M is the molecular weight compensated for by the cross term. M(formula) is the molecular weight calculated from the molecular formula of benzene. The corrected molecular weights of benzene agree well with the formula weight of this compound, although Eq. 3 can only give a rough correction. The results given in Table 2, therefore, suggest that molecular weights of low molecular-weight substances may be determined with sufficient accuracy by means of the light-scattering method, if the solvent system is so chosen as to make the molecular weight correction due to the cross term as small as possible.

Light-Scattering Measurements of Oligostyrenes in an EMK Solvent. The scattering diagram of polystyrene (16a) is given in Fig. 2, showing a rather intense optical anisotropy.

The results of measurements on oligostyrene are

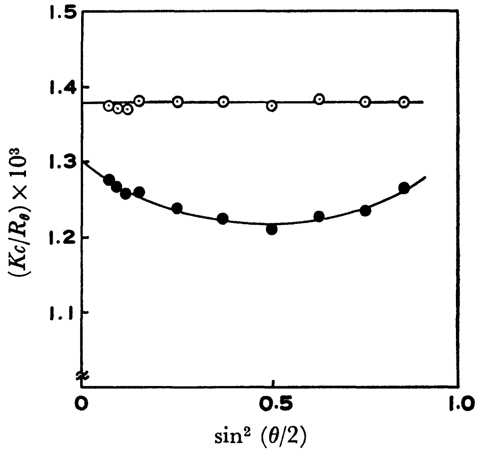

Fig. 2. Light scattering diagram for oligostyrene(16a) in ethyl methyl ketone.

●: Uncorrected, ○: corrected for optical anisotropy. Concentration of oligostyrene: 2.05×10⁻² (g/cm³).

TABLE 3. EXPERIMENTAL RESULTS FOR OLIGOSTYRENES IN AN ETHYL METHYL KETONE SOLVENT

Oligostyrene sample[a]	dn/dc[b] (cm³/g)	ΔM	$(M_w)_{app}$	M_w	M_n	$A_2\times10^4$ (mol cm³/g²)	$f_u(90°)$	M_w/M_n Exptl	Calcd[c]	Ref[d]
16a	0.2221	7.0	702	695	580	−11	1.115	1.20	1.18	<1.10
15a	0.2257	6.9	1780	1770	1230	3.8	1.156	1.14	1.09	<1.10
12b	0.2297	6.7	2250	2240	2100	−3.3	1.178	1.07	1.05	<1.10
11b	0.2297	6.7	3790	3780	3100[d]	0.12	1.038	1.22[e]	1.03	<1.10
8b	0.2309	6.7	11000	11000	9800[d]	1.0	1.019	1.12[e]	1.01	<1.10
2b	0.2309	6.7	20800	20800	20200[d]	2.0	1.019	1.03[e]	1.005	<1.06

a) Commercial samples obtained from the Pressure Chemical Co. were used. b) Experimental conditions: 20 °C, λ_0=436 nm. c) Calculated from Eq. 10 on the assumption that living polymerization proceeded under ideal conditions. d) Pressure Chemical Co. data sheet. e) The values of M_n given on the Pressure Chemical Co. data sheet were used for the calculation of M_w/M_n.

summarized in Table 3. The factor indicating the optical anisotropy, $f_u(90°)$, was calculated with

$$f_u(90°) = [(Kc/R_{90})_u]_{c\to0}/(Kc/R_{90})_{c\to0} = [(R_{90})_u/R_{90}]_{c\to0}, \qquad (9)$$

where $(R_{90})_u$ is the excess light scattering observed at an angle of 90°, without correction for depolarization, and R_{90} is the isotropic excess light scattering calculated from the King equation. Values in the "exptl" column for M_w/M_n were calculated from the values obtained using the light-scattering and vapor-pressure measurements. The values under "calcd" in the table indicate the heterogeneity of the molecular weights of polymers calculated, for conditions under which living polymerization would ideally be performed, using

$$M_w/M_n = 1 + 1/P_n, \qquad (10)$$

where P_n is the number average polymerization degree. When the observed, reference, and calculated values were compared with each other, the reference value for specimen 16a turned out to be markedly smaller than the calculated value. Since the calculated values were estimated assuming ideal polymerization, the heterogeneity of the molecular weights of real specimens should not be lower than this calculated value. The observed value for specimen 16a, on the other hand, was not in disagreement with the calculated value.

In addition to specimen 16a, there exist considerable discrepancies between the observed values and the reference values for specimens 15a and 11b, the discrepancy being marked for 15a. The heterogeneity of the molecular weights of this specimen is extremely high when compared with other specimens. This appears to be due to incomplete living polymerization. Since the calculated value of the heterogeneity of molecular weights is dependent upon the number average polymerization degree, it is important to accurately measure the number average molecular weight. The number average molecular weight of specimen 16a was estimated from the NMR spectrum of this compound, which is given in Fig. 3. The chemical structure of this substance was thought to contain a terminal butyl group based on its polymerization mechanism. Thus, the degree of polymerization may be estimated by taking the ratio of the H_ϕ contributed by protons in the phenyl group to that, the H_b, from protons in other groups in the expression

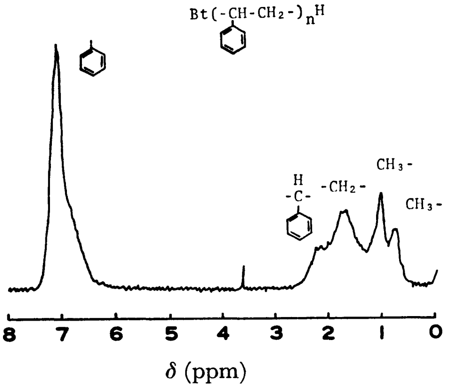

Fig. 3. NMR spectrum of oligostyrene(16a) in carbon tetrachloride.

$$H_\phi/H_b = 5P_n/(10+3P_n). \qquad (11)$$

The value of H_ϕ/H_b was estimated from the areas occupied by each spectrum and then the value of P_n for oligostyrene was calculated. The P_n value was calculated to be 4.64, and the number average molecular weight estimated from the P_n was found to be 541.

The results obtained for specimen 16a are summarized in Table 4. The values of M_w/M_n were calculated using the number average polymerization degrees obtained from the number average molecular weights observed using various methods and from Eq. 10 on the assumption that living polymerization proceeded under ideal conditions. The values of M_w/M_n are in the range between 1.18 and 1.20. Therefore, the true M_w/M_n value of specimen is thought to be greater than 1.18 and is unlikely to be smaller than 1.10. Although the value of M_w/M_n obtained using the GPC method was slightly higher than those obtained from the light-scattering and VPO methods, it appears to be reasonable judging from the calculated value.

Molecular Optical Anisotropy of Oligostyrene. It is interesting to study the dependency of the molecular optical anisotropy of styrene polymers on their molecular weights because this involves a phenyl group which exhibits strong optical anisotropy. The relation between the molecular optical anisotropies, $f_u(90°)$, and the

TABLE 4. MOLECULAR WEIGHTS AND MOLECULAR WEIGHT HETEROGENEITIES OF OLIGOSTYRENE (16a)

Method		M_w	M_n	M_w/M_n	
				Exptl	Calcd[a]
LS[b]	Present work	695	—	1.20	—
VPO[c]		—	580	—	1.18
NMR		—	541	—	1.19
GPC		684	544	1.26	—
VPO(A)[d]	Pressure Chemical Co. data sheet	—	524±7%	—	1.20
VPO(B)[e]		—	585±7%	—	1.18
Rast[f]		—	581±5%	—	1.18
Kinetic		—	550±10%	—	1.19

a) Calculated from Eq. 10 on the assumption that living polymerization proceeded under ideal conditions. b) Light scattering. c) Vapor pressure osmometry. d) Analysis performed at the Mellon Institute. Experimental conditions: benzene solvent, duplicate determinations. e) Crobaugh Laboratories, chloroform solvent, duplicate determinations. f) Camphor solvent, duplicate determinations.

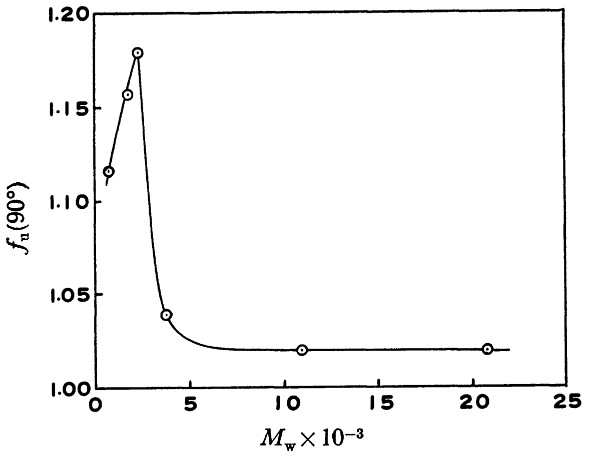

Fig. 4. Molecular weight dependence of the molecular optical anisotropy for oligostyrene in ethyl methyl ketone.

molecular weights of oligostyrenes is shown in Fig. 4. Values of $f_u(90°)$ most fluctuated in the range between molecular weights of 2000 and 3000 and became almost constant at about 10000. This tendency has been observed by Nomura and Miyahara⁵⁾ who reported the dependency of the partial specific compressibility on the molecular weight. This phenomenon has been considered to reflect the transition process of conformation of the polystyrene molecule from a rod-like rigid form to a random coil caused by internal rotation of the molecular chain.

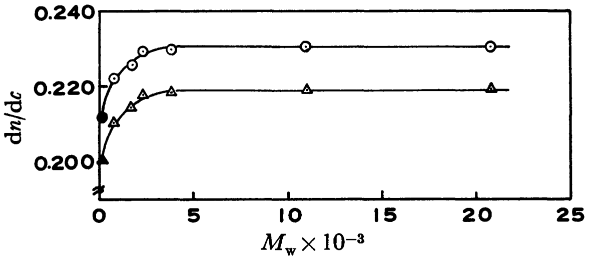

Fig. 5. Molecular weight dependence of the specific refractive index increment for oligostyrene in ethyl methyl ketone.

○: $\lambda_0=436$ nm, △: $\lambda_0=546$ nm, ●▲: data for dibenzyl.

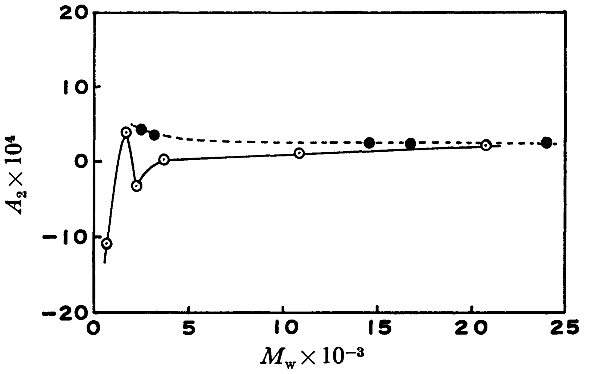

Fig. 6. Molecular weight dependence of the second virial coefficient for oligostyrene.

○: Present work, ●: Outer *et al.*⁶⁾

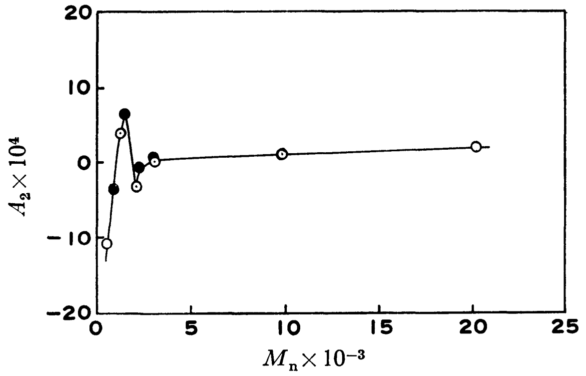

Fig. 7. Molecular weight dependence of the second virial coefficient for oligostyrene.

○: Present work, ●: Nomura and Miyahara.⁵⁾

Dependency of the Specific Refractive Index Increment and the Second Virial Coefficient on Molecular Weight. The data given in Table 3 are plotted in Figs. 5 and 6. The values of d*n*/d*c* show considerable fluctuations for molecular weights smaller than 20000. The second virial coefficient of the oligostyrene–EMK solution changed from negative to positive and exhibited a maximum with increasing molecular weight. It has been reported by Outer *et al.*⁶⁾ that the second virial coefficient monotonically decreases with increasing molecular weight when light scattering by polystyrenes of molecular weights from 2460 to 1770000 were measured in an EMK solvent. The results obtained in the low molecular-weight range, in the present study, are thus different from their results. Sotobayashi and Ueberreiter⁷⁾ have measured the second virial coefficient by means of a cryoscopic method. Nomura and Miyahara⁵⁾ have also measured this using vapor-pressure osmometry. They obtained results similar to those reported here. Figure 7 shows the plots of the second virial coefficients against the number average molecular weights, M_n, and also compares the results obtained in the present study with those of Nomura and Miyahara.⁵⁾ Since, in the present study, the second virial coefficients were obtained from light-scattering measurements, they could not be compared with those of Nomura and Miyahara⁵⁾ because of the influence of the molecular-weight distribution. The overall tendency, however, showing a conversion from negative to positive of the value of A_2 with the molecular weight and the appearance of a maximum, agree well with their results. It has been suggested by Sotobayashi and Ueberreiter,⁷⁾ as mentioned above, that this may be due to the transition of the molecular conformation of styrene polymers from rod-like rigid molecules to random coil structures. It appears improper to discuss the nature of this phenomenon in further details, because there is no evidence to prove the homogeneity of the chemical structure of terminal groups and because the heterogeneity of the molecular weights of oligostyrenes are slightly different for each of the specimens used in the present study.

Since the properties of oligomers in solution are greatly influenced by the chemical structure of the terminal groups of the oligomer molecules, it may be necessary, first of all, to prepare specimens with homogeneous molecular weights and with identical terminal groups in the molecules and then to measure these properties, in order to discuss them in detail over the oligomer molecular-weight range.

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