wool. Specimens were successfully stained in solution or by the RuO_4 vapors. Vapor staining methodology is given elsewhere.[8]

Synthesis II: Excess of $NaIO_4$. Sodium periodate (4 g) was dissolved in deionized water (25 °C) and chilled. $RuO_2 \cdot xH_2O$ (0.6 g) was added to the aqueous $NaIO_4$ solution. All of the black ruthenium dioxide powder dissolved, producing a stable solution of RuO_4. Specimens immersed in this solution never darkened, and were eventually destroyed by RuO_4 oxidation.

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Concentration Dependence of the Mutual Translational Diffusion Coefficient of Polystyrene in Good Solvents

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The mutual translational diffusion coefficient D of a polymer chain in solution can be observed by the dynamic light scattering (DLS) technique, where the relaxation of concentration fluctuation of polymer is measured. Especially the concentration dependence of D in dilute solutions is sensitive to hydrodynamic and thermodynamic interactions of polymer chains. In this paper, we collected the data of the coefficient k_D of the concentration dependence of D obtained by DLS for dilute solutions of narrow molecular weight distribution polystyrenes in good solvents and compared them with the theoretical predictions proposed hitherto. It is shown that the relationship between k_D and weight-average molecular weight M_w is expressed by $k_D \propto M_w^{0.76}$ below $M_w = 4 \times 10^6$ but deviates downward in the higher molecular weight region and that the latter behavior is not predictable from any theory at present.

The irreversible thermodynamics gives the concentration dependence of D in the zero limit of the scattering vector q as[1]

$$D(q = 0)/D_0 = (f_0/f)(M/RT)(\partial\Pi/\partial c)_{T,\mu_1} \quad (1)$$

where D and the collective friction factor f at concentration c are expressed in the volume-fixed frame of reference and the subscript zero denotes the values at infinite dilution. Π is the osmotic pressure of the solution, c the polymer weight concentration, μ_1 the chemical potential of the solvent, and M the molecular weight of the polymer. Thus, D depends on both hydrodynamic (f_0/f) and thermodynamic $[(\partial\Pi/\partial c)_{T,\mu_1}]$ interactions of polymers. Moreover, it should be noticed that[2] for the limit $q \to 0$ one observes relaxation of concentration fluctuation with wavelength larger than the polymer dimension.

In the dilute solution region, we may expand D and f as a series of c as

$$D/D_0 = 1 + k_D c + \ldots \quad (2)$$

$$f/f_0 = s_0/s = 1 + k_s c + \ldots \quad (3)$$

We can then obtain from eq 1 the relation[3]

$$k_D = 2A_2M - k_s \quad (4)$$

where s is the sedimentation coefficient at concentration c and A_2 the second virial coefficient of the polymer. The coefficient k_s of the concentration dependence of f is expressed theoretically in the forms

$$k_s = BN_AV_H/M \quad \text{(Ba, Fe, PF)} \quad (5)$$

$$k_s = 1.2A_2M + N_AV_H/M \quad \text{(Y)} \quad (6)$$

$$k_s = (6/4^{2/3})(A_2M)^{2/3}(N_AV_H/M)^{1/3} \quad \text{(AB)} \quad (7)$$

where N_A is the Avogadro number and V_H the hydrodynamic volume of the polymer. B in eq 5 is a quantity which depends on the hydrodynamic interactions acting on the polymer segments. Only for hard-spherical interactions can B be treated rigorously: Batchelor[4] (Ba) and Felderhof[5] (Fe) gave $B = 6.55$ and 6.44, respectively, for hard spheres of radius R_a with the particle volume $V_e = V_H = (4\pi/3)R_a^3$. In the case of soft-spherical interactions, Pyun and Fixman[6] (PF) gave $B = 7.16 - K(A)$ for interpenetrable spheres of uniform density. $K(A)$ is a function of the thermodynamic parameter A and becomes zero, i.e., $B = 7.16$, for the good solvent limit (=hard sphere) at $A = \infty$. Equation 6 was proposed by Yamakawa[7] (Y) for Gaussian chains with the Flory–Krigbaum potential, and eq 7 was calculated by Akcasu and Benmouna[8,9] (AB) for Gaussian chains with an effective hard-spherical radius $\bar{S}$ related to A_2.

In the good solvent limit, the thermodynamic interaction term A_2M becomes

$$A_2M = 4N_AV_e/M = 4N_AV_H/M \quad (8)$$

Then we obtain for the above-mentioned theories (eq 5–7) the same molecular weight dependence of k_D

$$k_D = (8 - B)N_AV_H/M = (2 - B/4)A_2M \quad \text{(Ba, Fe, PF; hard spheres)} \quad (9)$$

$$k_D = 2.2N_AV_H/M = 0.55A_2M \quad \text{(Y; hard spheres)} \quad (10)$$

$$k_D = 2.0N_AV_H/M = 0.50A_2M \quad \text{(AB; hard spheres)} \quad (11)$$

If we use the relation $V_H = (4\pi/3)R_H^3$, where R_H is the hydrodynamic radius of the polymer, the second equality of eq 8 leads an equivalence to setting a parameter $X = 1$, X being introduced by Akcasu and Benmouna[8,9] as a ratio $\bar{S}/R_H$; i.e., $X^3 = 3A_2M^2/16\pi N_AR_H^3$. A relation $R_H \propto M^{\nu}$ or $A_2 \propto M^{\beta}$ then may give the M dependence of k_D as $k_D \propto M^{3\nu-1}$ or $k_D \propto M^{1+\beta}$ at $X = 1$.

In Figure 1 we show the logarithmic plot of k_D data against M_w. The data were summarized from DLS measurements made so far for dilute solutions of narrow molecular weight distribution polystyrenes (PS) under the good solvent–temperature conditions[10–15] given in Table I. The k_D value for the highest molecular weight sample in Figure 1 was estimated at $qR_G = 0.713$, where the scattering angle was 10°. The data points exhibit a clear M dependence below the molecular weight $M_w \cong 4 \times 10^6$ as

$$k_D = 4.60 \times 10^{-3}M_w^{0.76\pm0.01} \ (\text{cm}^3/\text{g}) \quad (M_w < 4 \times 10^6) \quad (12)$$

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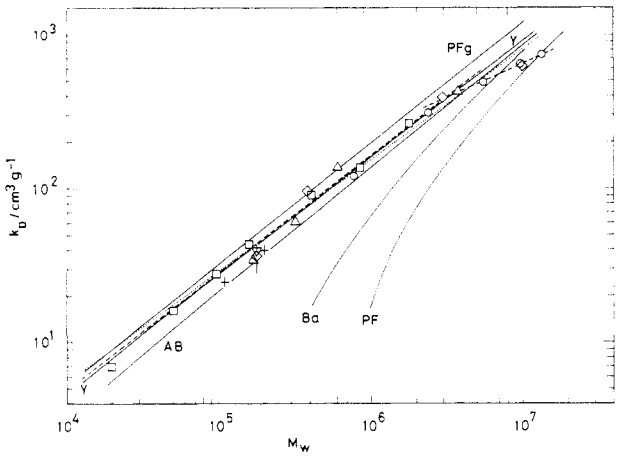

Figure 1. Logarithmic plot of the coefficient k_D for the concentration dependence of the mutual translational diffusion coefficient against M_w for linear narrow molecular weight distribution polystyrene in good solvents. The six symbols represent the dynamic light scattering data: (○) Nemoto et al;[10] (□) Mandema and Zeldenrust;[11] (▽) Han and Akcasu;[12] (◇) Yu et al;[13] (△) Adam and Delsanti;[14] (+) Pusey et al.[15] The data uncertainties are shown by vertical bars attached to the symbols if references indicated the magnitudes. If not, the uncertainties are usually kept within the symbol sizes at $k_D > 10^2$. The broken lines are the fitting curves represented by eq 12 and 13; solid curves Y,[7] AB,[8] Ba,[4] and PF[6] are the theoretical ones calculated from eq 4 by using the k_s expression shown in eq 6, 7, and 5, respectively, where the B values in eq 5 for Ba and PF are 6.55 and 7.16, respectively; the dotted line is the AB expression for hard spheres (eq 11), combined with the A_2–M_w relation of eq 14; the solid line PFg is the PF expression for hard spheres (eq 9) with $B = 7.16$, where the relation $V_H = V_e = (4\pi/3)R_G^3$ is used.

Table I
Data Sources of k_D for Narrow Molecular Weight Distribution Polystyrenes in Good Solvents

$M_w \times 10^{-5}$	solvent	temp, °C	k_D, cm^3 g^{-1}	$A_2 \times 10^5$, mol cm^3 g^{-2}	ref
7.75	benzene	30	120 ± 8	32.5	10
24.2			310 ± 10	23.3	
55.3			490 ± 10	18.9	
97.0			640 ± 30	16.0	
134			740 ± 25	15.0	
0.510	THF	24	16	*a*	11
0.972			28		
1.60			44		
4.11			91		
8.6			136		
18			246		
1.79	toluene	55	38.9 ± 2	35	12
1.8	THF	30	36 ± 8	*a*	13
3.9			96 ± 7		
30			390 ± 9		
100			620 ± 30		
1.71	benzene	20	35	*a*	14
3.2			61		
6.1			138		
38			426		

[a] Experimental data were not shown.

and deviate downward above $M_w \cong 4 \times 10^6$. Force-fitted, the data in this region can be represented by

$$k_D = 0.519 M_w^{0.44\pm0.02} \quad (\mathrm{cm^3/g}) \qquad (M_w > 4 \times 10^6) \quad (13)$$

Two broken lines in the figure denote these equations. As indicated by Table I, the data points for each molecular weight are not necessarily for equivalently good solvent states. The differences are however reflected in k_D values through A_2 and V_H for a given M_w as expressed in eq 5–7. We can thus predict the M dependence of k_D by using the reliable empirical M dependences of A_2 and R_H. Curves Y, AB, Ba, and PF were calculated from eq 4 by substituting into eq 5–7 the empirical relations of A_2–M_w[16] and R_H–M_w[10] which were obtained for PS in benzene at 30 °C as follows:

$$A_2 = 1.45 \times 10^{-2} M_w^{-0.28} \quad ((\mathrm{mol\ cm^3})/\mathrm{g}) \quad (2 \times 10^5 < M_w < 1.4 \times 10^7) \quad (14)$$

$$R_H = 1.60 \times 10^{-9} M_w^{0.55} \quad (\mathrm{cm}) \qquad (2 \times 10^4 < M_w < 1.4 \times 10^7) \quad (15)$$

In the range $M_w < 4 \times 10^6$, curves Y and AB seem to well represent the data points. Recently, Akcasu and Han[12] and Van den Berg and Jamieson[17] have discussed k_D in terms of X, which varies from $X = 0$ at the Θ temperature to slightly over unity in the good solvent limit by changing solvents and temperature. They concluded that the AB expression seems to be favored at $X = 1$. If we force to compare the data in Figure 1 with the k_D expression at $X = 1$ (eq 9–11), the combination of A_2 (eq 14) with AB (eq 11) seems to be favored, as shown in Figure 1 by the dotted line with slope 0.72, rather than that with Y (eq 10), though the estimated Y line is not shown in Figure 1. Moreover, according to eq 8 we can use R_G, the radius of gyration of the polymer ($V_e = (4\pi/3)R_G^3$), instead of R_H in eq 9–11 at $X = 1$. Only one combination of PF (eq 9 with $B = 7.16$) with an empirical R_G–M_w relation[18]

$$R_G = 1.47 \times 10^{-18} M_w^{1.19} \quad (\mathrm{cm^2}) \qquad (16)$$

which was obtained for PS in benzene at 25 and 30 °C in the range $2 \times 10^5 < M_w < 6 \times 10^7$, represents the data points roughly. The line is shown in Figure 1 as PFg with slope 0.785. The experimental exponent of M_w, 0.76 ± 0.01, which was obtained in eq 12, is between 0.72 and 0.785 or 0.764 at $X = 1$, the third value being estimated from the renormalization group theory.[19]

On the other hand, the downward feature of k_D in the range $M_w > 4 \times 10^6$ is new experimental evidence which is in conflict with theoretical predictions. The slower convergence of R_H compared with R_G to the asymptotically large-M limit, proposed by Weill and des Cloizeaux[20] (WD), may give a possibility for explaining the downward curvature qualitatively, if we pay attention to the k_D expression of eq 4. However, the constant exponent $\nu' = 0.55$ for $R_H \propto M_w^{\nu'}$ in eq 15, which holds also in the M range $4 \times 10^6 < M_w < 1.4 \times 10^7$ in question, rejects strongly and quantitatively the possibility. The WD idea is based on the k_D^Θ–$M_w^{1/2}$ relationship at the Θ temperature. The experimental result in the Θ state[21] has shown that the relation $k_D^\Theta \propto M_w^{0.43\pm0.02}$ holds over the entire M region of $2 \times 10^4 < M_w < 1 \times 10^7$. Experimentally the exponent of M in the range $M_w > 4 \times 10^6$ is very close to that in Θ solvent. The analysis of k_D values for our three highest molecular weight samples[10] (open circles in Figure 1) made in terms of X indicated that these points locate between AB (eq 7) and AB*,[17] which is obtained by adding $N_A V_H/M$ to the right-hand side of eq 7. In any case, all the data points in Figure 1 could never be represented satisfactorily by a single curve over the entire region of M_w measured.

It has been clear that the fluctuating hydrodynamic interaction between monomers, which causes the coupling between the translational and internal motions of the polymer, decreases D only to be more than 1.67% for flexible chains consisting of point particles having no volume.[22] This interaction becomes much more complicated for segments with finite size. The effect of this interaction on k_D is thus still ambiguous theoretically. The hydrodynamic coupling between translational and rota-

tional motions of the polymer[23] may also play a somewhat unexpected role on k_D as well as D since the translating finite-size particle will exert both a force and a torque on a second particle within its velocity field. Moreover, some kind of inner structure of a particle (or coil), e.g., self-knots,[24] may not be neglected, though this effect on k_D is minor in good solvents compared to the case for Θ solvent.

As described already, $D(q = 0)$ reflects mainly the long-range hydrodynamic interaction. However, the experimental k_D value for the hard spheres[25] has been explained completely by only the theories of Batchelor[4] and Felderhof,[5] who calculated the hydrodynamic interaction by taking into account the short-range potential as well as long-range one without using the Kirkwood–Riseman approximation. The short-range force may play a much more complicated role especially for a very low concentration system of high molecular weight polymers.[4,5,26] These may indicate that in the high molecular weight range $M_w > 4 \times 10^6$, $D(q = 0)$ and k_D have to be calculated by taking into account the short-range hydrodynamic interaction as well as the long-range one between segments of finite size.

The deviation of the k_D value from AB observed for the highest molecular weight ($=1.34 \times 10^7$) is about 40% and exceeds clearly from the data uncertainties (±4%). Experimentally this deviation, however, should be tested further. We are now carrying out similar experiments to those described here using polyisoprene (PIP) with molecular weights as high as 8×10^7, since PIP is more flexible than PS.

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Chiral Novolacs. Enantiocontrolled Synthesis of Alkylidene-Linked Binuclear Phenolic Compounds

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Recent studies from this laboratory have emphasized the cardinal role played by the coordinating metal phenolates in providing regio- and diastereoselectivity in the synthesis of alkylidene-bridged oligomers related to novolac resins.[1-3] We now communicate that chirally modified aluminum phenolates[4] permit the asymmetric and regiospecific synthesis of alkylidene-bridged binuclear oligomers to be reached for the first time via chirality transfer from the auxiliary located at the metal to the bridging moiety.

Treatment of (−)-menthoxyphenoxyaluminum chlorides **1**, prepared in situ from (−)-menthoxyethylaluminum chloride and the corresponding phenol, with racemic α-substituted 2-hydroxybenzyl alcohols **2** in anhydrous toluene at room temperature (Scheme I) gave unsymmetrical binuclear novolacs **3** in good chemical yield with varying enantiomeric excess (ee). Yields, optical rotations, and ee's for the prepared dimers are presented in Table I.

Some features about this reaction are worthy of mention. While the steric requirement of the phenolic substrates had little effect on the degree of enantioselection, changes in the steric environment of the reactive site of **2** produced a pronounced effect on the asymmetric induction. Thus, while α-methylcarbinol **2a** (entries 1, 4, and 9) and α-phenylcarbinol **2c** (entries 3 and 6–8) exhibited remarkable differentiating ability (28–41% ee), an enantiomeric excess of only 12–18% was observed by using the quite congested α-isopropyl derivative **2b** (entries 2 and 5).

Strict observance to a precise reaction protocol was required to obtain optimum stereocontrol. In a typical procedure, 1.0 equiv of natural (−)-menthol[5] was added to a stirred solution of 1.0 equiv of Et_2AlCl.[6] After this solution was stirred for at least 1 h at 20 °C, 0.3 equiv of the appropriate phenol was added, and the resulting solution was stirred for an additional hour. Salicyl alcohol (0.3 equiv) was finally added, and the mixture was allowed to react at 20 °C for the indicated period (Table I). All manipulations were done under anhydrous conditions. The final reaction mixture was quenched by stirring with saturated aqueous NH_4Cl. Dimers **3** were then isolated by chromatography while (−)-menthol was recovered unracemized (80% recovery) and recycled if necessary.

If the addition sequence of the reactants was reversed or shorter equilibration times were allowed, the enantiomeric excess of the reaction was greatly diminished. Furthermore, a 10-fold increase in concentration from 0.1

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