A Method for Studying Optical Anisotropy of Polymers As a Function of Molar Mass

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Optical properties of polymers are extremely important in many end-use applications, as is the ability of anisotropic polymers to depolarize incident radiation. To date, most light-scattering studies of the optical anisotropy of macromolecules have dealt with the bulk state or measured ensemble properties of dilute solutions. Here, we introduce a method to determine the optical anisotropy as a continuous function of molar mass. By direct, on-line coupling of size-exclusion chromatography and depolarization multiangle light scattering (SEC/D-MALS), molar mass averages, polydispersities, molar mass distributions, and the distribution of the optical anisotropy as a function of molar mass may all be determined. To quantify the anisotropy, it has been expressed in terms of the Cabannes factor, thus permitting the Rayleigh ratio necessary for light-scattering calculations to be corrected for anisotropy. The effects of tacticity, heavy atom substitution on the main chain, and chain helicity on the depolarization behavior of polymers have been studied using atactic and isotactic PMMA; atactic and brominated PS; and the semiflexible polypeptide PBLG, which maintains an extended structure in solution. An introduction to the theory of SEC/D-MALS is given.

Optical properties are extremely important in the end-use application of polymers such as polystyrene, polycarbonate, and poly(methyl methacrylate), among others. As such, the interaction of macromolecules with radiation in the visible range of the electromagnetic spectrum is a subject of intense study. In polymers for which optical performance is desired, molecular anisotropy and the ability to depolarize incident radiation play an important role.

To date, most light-scattering studies of polymer anisotropy have dealt with the bulk state or measured ensemble properties of dilute solutions.[1−3] The dependence of molecular anisotropy on molar mass as a continuous function of the latter does not appear to have been studied in the literature. To determine said molar mass dependence, experiments must be performed in nearly infinitely dilute solutions, in which the influence of other macromolecules is negligible. Because most polymers are polydisperse with respect to molar mass, this type of study would per force benefit from a separation technique that discriminates on the basis of molar mass or a related property (e.g., hydrodynamic volume). To this end, the combination of size-exclusion chromatography (SEC) and multiangle light scattering (MALS) offers the benefit of determining absolute molar mass averages, polydispersities, and distributions.

In this paper, we present a novel type of light-scattering experiment, termed depolarization multiangle light scattering (D-MALS), such that by the direct, on-line coupling of SEC and D-MALS, the optical anisotropy of polymers can be determined as a function of molar mass. The information obtained from this technique has been cast here in terms of classical light-scattering theory to yield a parameter, the Cabannes factor, as a function of molar mass. This factor is not only convenient for representing the anisotropy data, but its quantitation is also essential for extremely accurate (i.e., >1% accuracy) molar mass calculations via light scattering.[4,5] We present the theory behind the SEC/D-MALS experiment as well as initial data from our laboratory on variations in the optical anisotropy of polymers as a function of molar mass.

EXPERIMENTAL SECTION

Materials. Polystyrene (PS) standard (30 kg/mol) was obtained from Pressure Chemical Co. (Pittsburgh, PA); atactic poly(methyl methacrylate), from Polymer Laboratories (Amherst, MA); isotactic poly(methyl methacrylate) and poly(γ-benzyl-L-glutamate), from Polysciences (Warrington, PA); atactic polystyrene, from Scientific Polymer Products (Ontario, NY); and brominated polystyrene, from American Polymer Standards (Mentor, OH). *N,N'*-dimethyl acetamide (DMAc) and LiCl were purchased from Fischer (Pittsburgh, PA). (See Table 1 for polymer abbreviations).

For preparing DMAc/0.5% LiCl, the salt was oven-dried overnight at 150 °C and maintained in a desiccator. After dissolving 5 g of LiCl in 1 L of DMAc at 100 °C, the solvent (DMAc/0.5% LiCl) was allowed to cool to <50 °C and then was filtered through a 0.45-μm PTFE (Teflon) filter membrane (Phenomenex, Torrance, CA).

SEC/MALS. For SEC/MALS experiments, 25 mg of sample was dissolved in 10 mL of DMAc/LiCl by shaking in a laboratory shaker for 1 h then allowing it to sit overnight with gentle swirling. The *i*-PMMA sample was heated to 125 °C for ~1 h in order to destroy solution aggregates, which were observed in the MALS

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Table 1. Molar Mass Data and Cabannes Factors for Polymers

polymer[a]	M_n ($\times 10^5$ g/mol)	M_w ($\times 10^5$ g/mol)	M_z ($\times 10^5$ g/mol)	M_w/M_n	$C^v(R_{90})$
a-PS	1.42 (0.11)[b]	3.05 (0.16)	5.22 (0.06)	2.15	1.010 (0.002)[c]
PSBr	3.26 (0.05)	6.74 (0.01)	11.7 (0.00)	2.07	V^d
a-PMMA	1.07 (0.03)	1.07 (0.03)	1.08 (0.03)	1.00	1.011 (0.007)[e]
i-PMMA	0.896 (0.033)	2.80 (0.01)	6.86 (0.20)	3.12	V
PBLG	0.754 (0.023)	1.48 (0.05)	2.31 (0.10)	1.96	1.018−1.006[f]

[a] a-PS = atactic polystyrene, PSBr = brominated polystyrene, a-PMMA = atactic poly(methyl methacrylate), i-PMMA = isotactic poly(methyl methacrylate), PBLG = poly(γ-benzyl-L-glutamate). [b] Values in parentheses correspond to standard deviations. [c] For molecular mass range: 40.8 kg/mol ≤ M ≤ 635 kg/mol. [d] V = Cabannes factor varies with molecular mass. See text for details. [e] For molecular mass range: 77.1 kg/mol ≤ M ≤ 94.6 kg/mol. [f] Value decreases linearly with molecular mass in the region 78 kg/mol ≤ M ≤ 297 kg/mol.

trace of the unheated sample. A 400-μL portion of unfiltered solution was injected into a system consisting of a Waters 590 programmable HPLC pump (Waters, Milford, MA), a Shodex degassing unit (the mobile phase was also degassed by He sparging in addition to vacuum degassing), a Waters 717+ autosampler, a DAWN EOS multiangle light-scattering photometer (Wyatt, Santa Barbara, CA), and an Optilab DSP interferometric differential refractive index detector (Wyatt). The detectors were connected in series, with the refractometer last because of back-pressure considerations in this detector's cell. The detectors were maintained at 35.0 ± 0.1 °C. Separation occurred over a column bank consisting of four analytical SEC columns (three PSS GRALlinear 10-μm columns and one PSS GRAL10000 10-μm column) preceded by a guard column (PSS Polymer Standards Service, Mainz, Germany). Column temperature was maintained at 35.0 ± 0.1 °C with a Waters TCM column temperature system. The mobile phase was DMAc/0.5% LiCl at 1.0 mL/min. For all chromatographic determinations, the results are averages of four runs from two separate dissolutions, with 2 injections/dissolution.

The MALS detector, which measures scattered light at 17 different angles simultaneously, was calibrated by the manufacturer using toluene. Normalization of the photodiodes was performed in-house using a small, monodisperse ($M_w/M_n \leq 1.06$), isotropic scatterer, linear polystyrene with M_p = 30 kg/mol. This PS was also used to determine the interdetector delays for SEC/MALS. Data acquisition and manipulation was performed using Wyatt's ASTRA for Windows software (V. 4.73.04).

Specific refractive index increments, $\partial n/\partial c$, were determined using the Optilab DSP refractometer off-line, under the same solvent/temperature/wavelength conditions as the SEC/MALS experiments, using Wyatt's DNDC for Windows software (V 5.20 (build 28)). Values for $\partial n/\partial c$ for the polymers studied here are as follows (all data in mL/g, with uncertainties of ±0.001): a-PS, 0.146; PSBr, 0.110; a-PMMA, 0.052; i-PMMA, 0.056; PBLG, 0.104. Data were obtained from at least five dissolutions of each sample, ranging from 0.3 to 3.0 mg/mL.

SEC/D-MALS. In SEC using depolarization multiangle light scattering (SEC/D-MALS), two strips of Polaroid film (Wyatt) are placed around the sides of the flow cell of the MALS unit and maintained tightly in place by a grooved cell retainer attached to the cell. One strip is vertically polarized and the other horizontally polarized. Data were initially taken with the former facing the odd-numbered photodiodes and the latter, the even-numbered photodiodes. This procedure was then reversed. Normalization was effected in both modes with the 30 kg/mol PS standard. The same dissolutions of polymers and standard were analyzed in both

polarization modes. Chromatographic conditions were the same as those detailed above. Minor flow rate fluctuations were corrected manually by using the retention times of the solvent/air peaks common to the refractometer traces of the samples.

Theory of SEC/D-MALS. The incident light from the GaAs laser (λ = 685 nm) in the MALS unit is vertically polarized. As mentioned in the previous section, in depolarization multiangle light scattering (performed as an on-line experiment with SEC, or SEC/D-MALS), the flow cell is covered with two polarizing filters (Polaroid strips). We first placed the filter with a vertical transmission axis facing the odd-numbered photodiodes of the MALS unit and the filter with a horizontal transmission axis facing the even-numbered photodiodes. After obtaining data in this mode, the placing of the filters was reversed. (It should be noted that the 90° photodiode is an odd-numbered photodiode). The filters play the role of analyzer in the optical train of the system. If the scattering particle is completely isotropic, the induced dipole will be parallel to the electric vector (E_0) of the incident light.[4] Assuming no absorption, only the component of the scattered light parallel to the transmission axis of the analyzer (polarizing filters), $E_0 \cos \phi$, will be passed on to the photodiodes. (Here, ϕ is the angle between the transmission and polarization axes, *not* the angle at which the photodiodes of the MALS detector are placed around the flow cell with respect to the direction of propagation of the laser light). The intensity of scattered light reaching the photodiodes is given by eq 1,

$$I(\phi) = \frac{c\epsilon_0}{2}E_0^2 \cos^2 \phi \qquad (1)$$

where c is the speed of light in a vacuum and ϵ_0 is the permittivity of free space. The intensity of the scattered light transmitted by the analyzer will reach a maximum, $I_{max} = (c\epsilon_0 E_0^2)/2$, at $\phi = 0°$ and is zero when $\phi = 90°$. Equation 1 can be rewritten as eq 2,

$$I(\phi) = I_{max} \cos^2 \phi \qquad (2)$$

which is known as Malus's law.[6] Therefore, when an isotropic molecule in the flow cell scatters the (vertically polarized) light from the laser, none of the scattered radiation should reach the photodiodes facing the horizontal-polarization strip, and all of the scattered radiation should reach the photodiodes facing the vertical-polarization strip. Another way of putting this is that the

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depolarization ratio at 90° should be zero. The ratio is given the symbol ρ^v and is defined as[7,8]

$$\rho^v = \frac{I^v_h}{I^v_v} \tag{3}$$

The superscript v in this paper will refer to the fact that the incident radiation is vertically polarized. I^v_h and I^v_v are the intensities of the horizontally and vertically polarized components of the scattered light, respectively. The above derivations relied on the assumption that the scattering particle was completely isotropic. If it is not, fluctuations in the orientation of the scattering particle offer the possibility of additional scattering, because the induced moment is generally not parallel to the electric vector of the incident light.[4]

Cabannes showed that the excess scattering due to anisotropy is related to the depolarization ratio. Thus, the Rayleigh ratio (the light scattered by a solution at angle θ in excess of that scattered by the pure solvent, divided by the incident light intensity) for a system of anisotropic particles, $R_\theta^{v,tot}$, is

$$R_\theta^{v,tot} = R_\theta^{v,iso}\left(\frac{3 + 3\rho^v}{3 - (4 + 7\cos^2\theta)\rho^v}\right) \tag{4}$$

where $R_\theta^{v,iso}$ is the Rayleigh ratio for isotropic particles. At an observation angle θ of 90°,

$$R_{90}^{v,tot} = R_{90}^{v,iso}\left(\frac{3 + 3\rho^v}{3 - 4\rho^v}\right) \tag{5}$$

The correction term is known as the Cabannes factor and has a slightly different form for unpolarized incident radiation.[8] Because the determination of molar mass via light scattering is dependent upon determination of the excess Rayleigh ratio of a polymer in solution, an increased accuracy in R_θ will lead to increased accuracy in the calculated molar masses.[4,9] For a more extensive review of anisotropic scattering and the cooperative effects encountered in depolarized light scattering, the reader is referred to ref 10. For a comprehensive treatment of the polarization of light, see ref 6.

RESULTS AND DISCUSSION

Molar mass averages and polydispersities for the polymers in this study are given in Table 1. As can be seen, the list includes both narrow and broad polydispersity polymers. The data in the Table were calculated by SEC/MALS as described in the Experimental Section, that is, without the use of polarizing filters. DMAc/0.5% LiCl was chosen as solvent on the basis of its versatility as both solvent and chromatographic mobile phase for a large number of synthetic and natural polymers,[11-13] as well as

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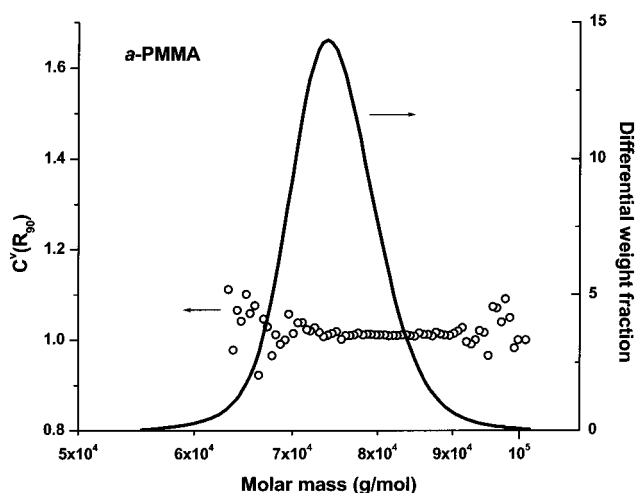(11) Striegel, A. M. *Carbohydr. Polym.* **1997**, *34*, 267−274, and references therein.

Figure 1. Distribution of the Cabannes factor, $C^v(R_{90})$, of a narrow polydispersity *a*-PMMA as a function of molar mass (open circles) overlaid upon the polymer's molar mass distribution (MMD, solid line).

for its role as a nonaggregating medium for PBLG (see PBLG section, below).

The depolarization of light by anisotropic bodies described in the previous section manifests itself most markedly for small objects, such as solvents and oligomers. Macromolecules, which normally exist as flexible chains in solution, display minimal depolarization characteristics. As the polymeric chain becomes more rigid, however, its anisotropy increases and so does its ability to depolarize incident radiation. This rigidity may be due to configuration (e.g., tacticity); to a heavy substituent on the main backbone of the polymer; or to the formation, in concentrated solutions, or ordered phases (e.g., mesophases).[14]

a-PMMA vs *i*-PMMA. To study the effect of tacticity on the depolarization behavior of polymers, atactic and isotactic PMMA were dissolved in DMAc/LiCl and analyzed by SEC/D-MALS. Figure 1 shows the molar mass distribution (MMD) of *a*-PMMA. Overlaid upon this plot is a plot of the Cabannes factor as a function of molar mass. The term $C^v(R_{90})$ is used to denote the Cabannes factor, determined by measuring the right-angle (90°) scattering of vertically polarized incident radiation that is used to correct the Rayleigh ratio for deviations due to anisotropy. From eqs 5 and 3,

$$C^v(R_{90}) = \left(\frac{3 + 3\rho^v}{3 - 4\rho^v}\right) \tag{6}$$

Deviations in the Cabannes factor in both the positive and negative directions are observed at the high and low ends of the MMD. These deviations are due to the low signal-to-noise ratios at the ends of the MMD of this narrow polydispersity polymer ($M_w/M_n = 1.005$), as well as the lower sensitivity of the MALS detector with decreasing molar mass. Over the majority of the MMD of *a*-PMMA, however, the Cabannes factor achieves a constant value of 1.011 (see Table 1).

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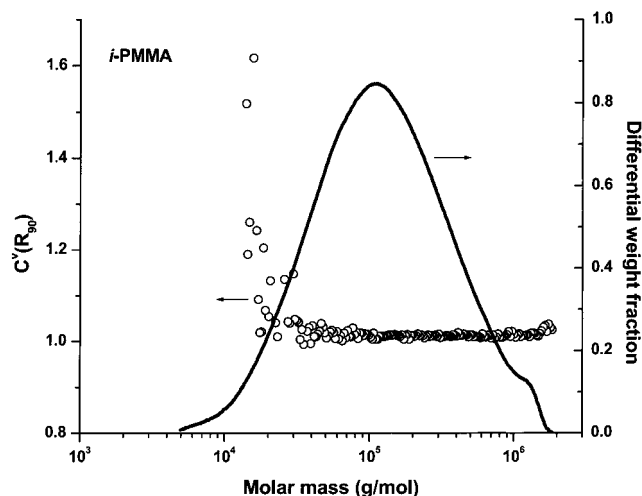
Figure 2. Distribution of the Cabannes factor of *i*-PMMA as a function of molar mass (open circles) overlaid upon the polymer's MMD (solid line).

Figure 3. Cabannes factor and molar mass distributions of *a*-PS (solid triangles) overlaid upon the Cabannes factor and molar mass distributions of PSBr (open circles).

Figure 2 overlays the Cabannes factor distribution atop the MMD of isotactic PMMA. It may clearly be observed that as this polymer's molar mass decreases, $C'(R_{90})$ increases, reflecting the increased rigidity of the chain. As the degree of polymerization becomes larger, the polymeric backbone becomes more flexible, and the Cabannes factor for *i*-PMMA becomes equal to that of its atactic counterpart (1.012). This occurs at $M \approx 100$ kg/mol. The shoulder at the high end of the MMD of *i*-PMMA is due to a small amount of residual aggregation in solution. Heating of solutions of *i*-PMMA was performed as described in the Experimental Section to destroy/decrease aggregation. Extended heating was not attempted so as to not induce thermal degradation of the polymer. Thus, a small amount of aggregates remained in solution, clearly observed with the light scattering detector. The aggregates appear to depolarize light more than the high-molar-mass *i*-PMMA does, although the aggregate region of the MMD is too small for a constant value of the Cabannes factor to be achieved there.

It should be noted that the MMDs in the Figures in this paper do not correspond exactly to the molar mass averages given in Table 1 for the respective polymers. This is due to the following: In order for the $C'(R_{90})$ values to be overlaid with their corresponding molar mass slices, the MMDs were calculated from data from the odd-numbered photodiodes when these faced the vertical-transmission axis Polaroid film (i.e., vertical-polarization mode). However, even in this mode, the intensity of the light reaching the photodiodes was 10−20% less than when the strips were not present because of absorption of light by the Polaroid (also, only data from 8 scattering angles were employed). Therefore, a 10−20% shift to lower molar masses is observed in the MMD. As mentioned previously, the data in Table 1 were calculated without the Polaroid strips, using data from all 17 scattering angles. To calculate the data plotted in the Figures, scattering intensities in the vertical- and horizontal-polarization modes, as well as molar mass data from the vertical-polarization mode experiment, were compared for the same elution volumes after manually correcting for minor flow rate fluctuations. This ensured that the same elution slices from the SEC columns were being compared with respect to depolarization behavior and molar mass. The shape of the MMD calculated from SEC/D-MALS is identical to that from
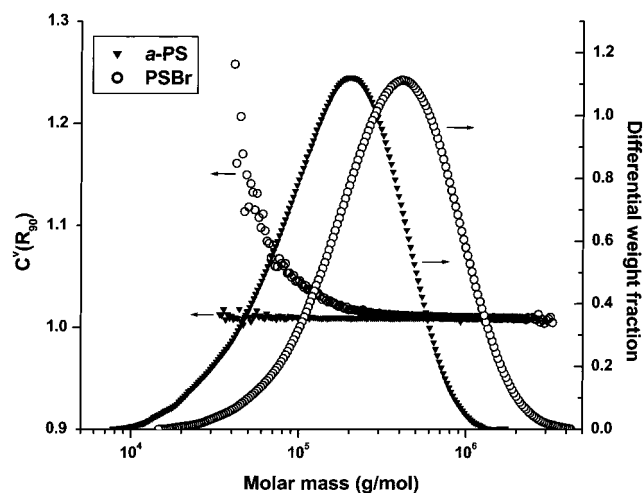
SEC/MALS, only shifted toward lower masses by 10−20%. The effect seems to be reproducible, such that a correction appears possible in order to eliminate the dual need for MALS and D-MALS experiments. Future experiments in this regard are planned.

a-PS vs PSBr. Heavy substituents restrict the configurational entropy of polymers in solution. This decrease in entropy should result in an increase in anisotropy. To test this, we compared atactic PS and brominated PS, both polydisperse with respect to molar mass (Table 1). Results of the SEC/D-MALS experiments are shown in Figure 3. The increased anisotropy of PSBr, as compared to *a*-PS, with decreasing molar mass is clearly reflected in the steadily increasing values of the Cabannes factor of PSBr as the degree of polymerization of this molecule becomes smaller. For *a*-PS, $C'(R_{90}) = 1.010$ across its entire MMD (from 41 to 635 kg/mol), whereas for PSBr, the Cabannes factor never achieves a constant value. The insolubility of *i*-PS in DMAc/LiCl (and, indeed, in most other solvents with the notable exception of butyl phthalate)[1] prevented comparisons for PS of the type performed for PMMA above.

PBLG. Poly(γ-benzyl-L-glutamate), or PBLG, is a semiflexible polypeptide that can phase-separate in solution above a certain critical concentration. One of these phases is liquid crystalline and believed to resemble a nematic structure. It is well-known that *N,N*-dimethyl formamide (DMF) is a nonaggregating solvent for PBLG, one in which the polymer retains an α-helix conformation. As such, in dilute solution, PBLG in DMF resembles more the "wormlike chain" model of Kratky and Porod than the "rigid rod" model of Kuhn.[15,16] No evidence of aggregation was observed for PBLG in the present experiments using DMAc/0.5% LiCl, as witnessed by the lack of early elution volume peaks or shoulders in the MALS traces at all angles. Moreover, the extended nature of the polymer appears to have been preserved. This last conclusion is based on the value of the slope (α) of the configuration plot (log root-mean-square radius vs log *M*) of PBLG, 0.93, corresponding to a fractal dimension ($\alpha = 1/d_f$) for the

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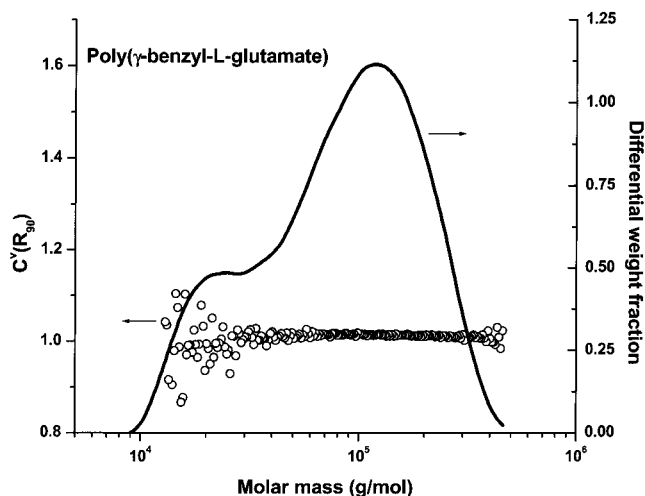
Figure 4. Distribution of the Cabannes factor of PBLG as a function of molar mass (open circles) overlaid upon the polypeptide's MMD (solid line).

polymer of 1.08. This is slightly above the fractal dimension of a rigid rod ($d_f = 1$), as expected for a semiflexible polymer in dilute solution. The constancy in the slope of the configuration plot is taken as further evidence of the lack of solution aggregates of the polymer.

Based on the above, a large $C^v(R_{90})$ value was expected for PBLG. To the contrary, the Cabannes factor for PBLG was barely differentiated from those of the two atactic polymers described above (Table 1 and Figure 4). Although a steady decrease in $C^v(R_{90})$ was observed for PBLG between 78 kg/mol and 297 kg/mol, this decrease was merely from 1.018 to 1.006. A definitive explanation for this unexpected phenomenon is not clear at this point. Several effects may be at play simultaneously, however. First, the design of the flow cell in the light-scattering photometer is such that the flow path is aligned in a parallel, line-of-sight geometry with the optical path of the laser.[9] In its passage through the flow cell, a flexible macromolecule will normally experience a number of solution layers moving with different velocities as part of a laminar, parabolic flow profile. The torque thus applied to the molecule will force it to rotate and tumble, with the incoming laser beam irradiating a number of possible statistical conformations of the molecules in the flow cell at the time. A polymer with limited flexibility, such as PBLG, can align with the streamlines of flow, its solutions displaying non-Newtonian, "slip-stick"-type behavior.[17] From an optical standpoint, the long axis of the α helix of the polypeptide is aligned in the flow cell with the axis of propagation of the laser beam; although the PBLG molecule may rotate about this axis, no other rotations are likely to occur. The fluctuations in the orientation of the anisotropic scattering particle, which in the Theory section were shown to be responsible for depolarization, are absent for PBLG, and thus, the scattered light reaching the photodiodes is barely depolarized.

Second, it has been observed that the depolarization ratio of poly(ethylene oxide), PEO, is 1 order of magnitude higher in tetralin ($\rho^v = 6.3$) than in isoamyl acetate ($\rho^v = 0.40$), and nearly 2 orders of magnitude higher in ethyl benzene ($\rho^v = 19.0$) than

in isoamyl acetate.[1] These large differences appear to be related to the differences in the refractive indices of the solvents with respect to the refractive index of PEO and, more specifically, to differences in the polarizabilities of the various solvents with respect to the in-plane and out-of-plane polarizabilities of PEO. Therefore, it is possible that the optical anisotropy of PBLG will be observed in another solvent system. The difficulty lies in finding another nonaggregating solvent for this polymer that can also be used as a mobile phase in SEC to study the anisotropy as a function of molar mass.

A third contributing factor for the lack of observed anisotropy in dilute solutions of PBLG is that the 90° observation angle may not be the optimal angle to study the depolarization characteristics of the molecule. This was demonstrated by Picot et al. for PEO, *i*-PS, and a block copolymer of PEO and *a*-PS.[1] Current work in our laboratory is concentrating on simultaneously measuring the Cabannes factor as a function of molar mass at a variety of scattering angles.

Finally, it is worth noting the extremely dilute nature of the solutions being studied here, which lie in the dilute, nonentangled viscoelastic regime.[18] As the volume fraction of polymer in solution decreases (i.e., the solvent fraction increases) the librational oscillations of PBLG will be facilitated until, below a certain critical concentration, the solution becomes isotropic.[15] Below this critical concentration, the orientation of the helices will be uncorrelated in the isotropic solution. For solutions of PBLG in dioxane, the critical concentration appears to occur at a volume fraction of 0.058.[19] Because PBLG displays a higher order in dioxane than in DMF,[20] a higher critical concentration should be expected in the latter; it is reasonable to extrapolate this expectation to DMAc/LiCl.

CONCLUSIONS

A method has been presented that enables study of the optical anisotropy of polymers as a continuous function of molar mass. This appears to be the first publication demonstrating this novel technique, termed here SEC/D-MALS. Examined were the effects of tacticity, heavy-atom substituents, and molecular helicity on optical anisotropy. In the first two cases, the effect was quite large, increasing with a decrease in the molar mass of the polymers. The effect of molecular helicity for a semiflexible polypeptide was surprisingly small, however, likely due to a combination of non-Newtonian behavior in solution as well as to polarizability, observation angle, and solution concentration effects.

The SEC/D-MALS data can be used to study the molar mass dependence of the optical anisotropy of polymers. Once issues regarding absorption of light by the Polaroid film have been dealt with, the method can also be used to increase the accuracy in molar mass determinations of highly anisotropic polymers performed using light scattering photometry. This technique should also be applicable to other separation methods that discriminate on the basis of molar mass, size, or related properties. Coupling with field flow fractionation, hydrodynamic chromatography, etc., in the form of FFF/D-MALS or HDC/D-MALS should yield information about the optical anisotropy of macromolecules as it

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relates to a variety of fundamental polymeric properties. Current work in this laboratory is focusing on the angular dependence of the anisotropy/molar mass relationship as well as on different homo- and copolymers.