Optical Anisotropy of Polysiloxanes in Bulk and Solution by Depolarized Rayleigh Scattering

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ABSTRACT: Absolute depolarized intensities R_{VH} for poly(phenylmethylsiloxane) (PPMS) and poly(dimethylsiloxane) (PDMS) in bulk and solution in CCl_4 have been obtained from the depolarized Rayleigh spectra recorded with a plane Fabry–Perot interferometer. In addition, the R_{VH} of PPMS has been measured as a function of molecular weight and temperature. The results show very weak intermolecular orientation correlation in favor of the random coil model for amorphous polymers. The measured optical anisotropy β (=4.4 Å^3) of the monomer unit of PPMS agrees well with that calculated from the molecular geometry and bond anisotropies. The value of the internal pair correlation factor $1 + F$ is consistent with strain–birefringence data and rotational isomeric-state model calculations. The markedly low R_{VH} scattering intensity from PDMS leads to the vanishingly small value of $\beta = 0.2$ Å^3 for the repeating unit $SiO(CH_3)_2$.

Introduction

The local conformation of polymer chains in the amorphous state is a subject of considerable interest. The models proposed[1–6] for amorphous polymers require different amounts of orientational correlations. Thereby, the configurational average optical anisotropy is a sensitive probe of intra- and interchain correlations of optically anisotropic subunits. Internal correlations can be used to elucidate the conformation of chain molecules by using rotational isomeric-state calculations.[7] Among scattering techniques, depolarized Rayleigh scattering spectroscopy is a valuable tool for probing fluctuations in the anisotropic polarizability tensor of the scattering moieties.[8]

Despite the widespread use of polarized Rayleigh scattering in polymer solutions, there have been few applications of depolarized Rayleigh spectroscopy partially due to the much weaker signal. Total intensity measurements have been reported for undiluted polystyrene (PS),[9–11] polycarbonate (PC),[9–12] and poly(methyl methacrylate) (PMMA).[13] These results showed no evidence for intermolecular orientation correlations in the bulk polymers. However, these intensities were probably affected by anisotropic collisional scattering,[8] which should be deducted from the total depolarized Rayleigh scattering in order to evaluate the intrinsic molecular scattering. The much broader collision-induced scattering from molecular liquids[14,15] can be excluded either by recording the low-frequency depolarized Rayleigh spectrum $I_{VH}(\omega)$ with Fabry–Perot interferometry[16] or by measuring the Rayleigh wing of the depolarized Raman scattering. The latter technique has successfully been applied for studying the orientational correlation in n-alkane melts.[17] Fabry–Perot spectra have been reported for PS solutions[8,9] bulk poly(propylene glycol),[20] and poly(phenylmethylsiloxane).[21] The latter was found to exhibit a liquid crystal type of orientational order.

In order to examine the applicability of depolarized Rayleigh spectroscopy to measure the intrinsic optical anisotropy of polymers in bulk and solution and determine the magnitude of the intra- and interchain orientation correlations, we have measured the $I_{VH}(\omega)$ spectra of atactic poly(phenylmethylsiloxane) over the molecular weight range 1900–19 000 and poly(dimethylsiloxane) with M_W = 50 000 using a plane Fabry–Perot interferometer. The depolarized scattering intensity of the latter polymer is expected to be very weak due to the vanishingly small anisotropy of the monomer unit.[22] To estimate the anisotropy of the repeating unit in PPMS, the $I_{VH}(\omega)$ spectrum of dimethoxyphenylmethylsilane has also been measured. The solvent used in our study is carbon tetrachloride.

Theoretical Background

The depolarized Rayleigh spectrum $I_{VH}(\omega)$ from dilute solutions of macromolecules composed of optically anisotropic monomer units is an unshifted central component usually recorded by using the Fabry–Perot interferometer. Under suitable experimental conditions the high-frequency collision-induced scattering appears as a background component that can readily be subtracted. The remaining VH spectrum (where V and H indicate a vertical and horizontal polarization of the incident and scattered light) will consist of contributions from the intramolecular function and pair orientational correlation between segments of different chains. If the latter part is neglected for sufficiently dilute solutions in isotropic solvents, the spectrum is given by the Fourier transform of the correlation function $C_{VH}(t)$[18]

$$C_{VH}(t) = \sum_{i,j}^{X} \langle a_{yz}(j,t)\, a_{yz}(i,0)\, \exp[i\mathbf{q}(r_j(t) - r_i(0))] \rangle \qquad (1)$$

where x is the number of monomer units per macromolecule, $a_{yz}(j,t)$ represents the yz component of the laboratory-fixed polarizability tensor associated with the monomer unit j at time t, $\mathbf{q}$ is the scattering vector, and r_j is the position of the jth monomer unit. Both i and j are on the same chain; i.e., interchain correlations are ignored.

Two mechanisms are generally responsible for VH scattering: segmental orientation for flexible coils and overall macromolecular rotation if the polymer is rigid. This paper will be restricted to the integral depolarized intensity I_{VH}, which is a measure of average local conformation as manifested in the mean-square optical anisotropy $\langle \gamma^2 \rangle$ of the polymer chain.

$$I_{VH} = A\rho^* \sum_{i,j} \langle a_{yz}(j,0)\, a_{yz}(i,0) \rangle = A\rho^* \langle \gamma^2 \rangle \qquad (2)$$

ρ^* is the number density of the polymer in solution, and A is a constant. The VH intensity can also be expressed

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in terms of the optical anisotropy β of the monomer unit and the factor $1 + F$, which is a measure of the internal pair correlations of the polymer chain and is defined as[18]

$$1 + F \equiv \frac{\langle \gamma^2 \rangle}{X \langle a_{yz}(i,0)\, a_{yz}(i,0) \rangle} = \frac{\langle \gamma^2 \rangle}{X\beta^2} \quad (3)$$

From eq 2 and 3 the total integrated VH intensity can be written as

$$I_{\mathrm{VH}} = A\rho(1 + F)\beta^2 \quad (4)$$

where ρ ($=\rho^* X$) is the number density of monomer units. The ratio in eq 3 can be calculated by using monomer or bond anisotropies and the rotational isomeric-state (RIS) model.[1,7] According to RIS calculations for flexible coils, intrachain correlations are relatively short, and the ratio $\langle \gamma^2 \rangle / X$ rapidly attains its asymptotic value with increase in X. At fixed volume concentration the intensity I_{VH} should therefore approach a constant value at relatively low molecular weights. The effective optical anisotropy $\langle \gamma^2 \rangle / X$ can be computed from the excess Rayleigh ratio R_{VH} attributed to the solute molecules according to

$$\langle \gamma^2 \rangle / X = 15(\lambda_0/2\pi)^4 f(n)^{-1} (R_{\mathrm{VH}}/\rho)_{\rho \to 0} \quad (5)$$

where λ_0 is the wavelength of the incident light in vacuo and $f(n)$ is the local field correction, with n being the refractive index of the solution. For undiluted polymer, static pair orientational correlation between monomer units on different chains cannot be ignored. Rigorous calculation of $C_{\mathrm{VH}}(t)$ including interchains correlations is extremely difficult. However, I_{VH} can still be given by eq 4, but now the ratio $1 + F$ may strongly depend on the concentration.[21] In fact, one of the main aims of the present study is the differentiation between inter- and intramolecular contributions by measuring the concentration dependence of I_{VH} from polysiloxanes.

Experimental Section

The depolarized Rayleigh spectra $I_{\mathrm{VH}}(\omega)$ for the bulk polymers and their solutions in CCl_4 were taken at a scattering angle of 90° by using apparatus described elsewhere.[23] The free spectral range of the plane Fabry–Perot interferometer was 40 cm^{-1}, which was sufficient to record the narrow Lorentzian line due to the intrinsic optical anisotropy of the scattering moiety. Under these conditions, the high-frequency component of the collision-induced anisotropy appears as an unresolved broad background due to overlap of several orders. The integrated depolarized intensities for the narrow spectra were obtained from numerical integration. Alternatively, the intensities for the broad spectra of the CCl_4 and the standard benzene were calculated from a Lorentzian fit of the spectra taking into account the overlap of neighboring orders. The intensity I_{VH} attributed to the polymer molecules was then converted to the absolute Rayleigh ratio R_{VH} by comparison with the depolarized intensity of benzene according to

$$R_{\mathrm{VH}} = (I/I_{\mathrm{B}})(n/n_{\mathrm{B}})^2 R^{\mathrm{B}}_{\mathrm{VH}} \quad (6)$$

The value $R^{\mathrm{B}}_{\mathrm{VH}}$ at $\lambda_0 = 488$ nm and 25 °C amounts to 2.67×10^{-6} cm^{-1}.[23] Refractive indices of the samples were measured with an Abbe refractometer. The experimental $I_{\mathrm{VH}}(\omega)$ values of benzene and bulk poly(phenylmethylsiloxane) are shown in Figure 1. The atactic poly(phenylmethylsiloxane) (PPMS) samples and the dimethoxy phenylmethylsilane (PMS) were synthesized and characterized at the Max-Planck-Institut according to the method outlined previously,[24] whereas the dimer (1,3-diphenyl-1,1,3,3-tetramethyldisiloxane)[25] and poly(dimethylsiloxane) (PDMS) were purchased from Petrarch systems. Three PPMS' with weight-averaged molecular weights M_{W} of 1.9×10^3, 5×10^3, and 1.9×10^4 ($M_{\mathrm{W}}/M_{\mathrm{n}} \sim 1.1$) and one PDMS sample ($M_{\mathrm{W}} = 4.9 \times 10^4$) were used for the present investigation. The solvents CCl_4 and benzene were analytical grade and were used without further purification.

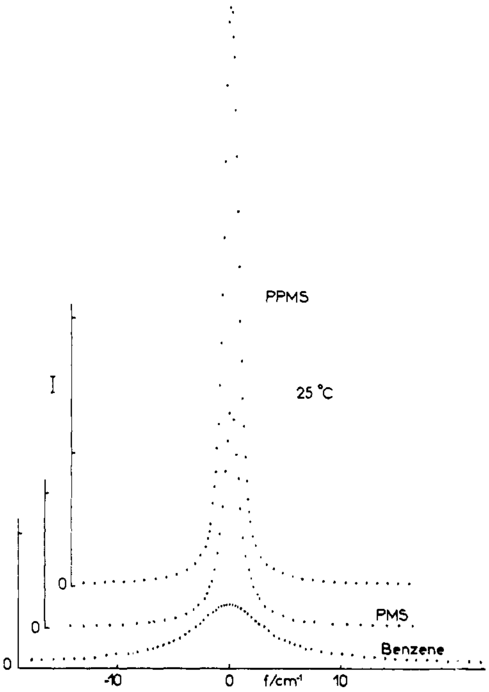

Figure 1. Depolarized Rayleigh spectra of bulk poly(phenylmethylsiloxane) (PPMS) (M_{W} = 1900), dimethoxyphenylmethylsilane (PMS), and benzene at 25 °C.

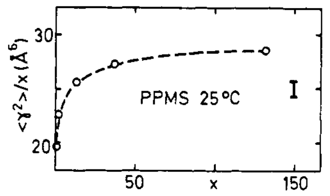

Figure 2. Effective optical anisotropy $\langle \gamma^2 \rangle / X$ per monomer unit in PPMS at 25 °C versus the degree of polymerization X.

Dust-free samples were obtained after filtration through 0.5-μm Teflon Millipore filters directly into the dust-free rectangular (1 × 1 cm) cells. The procedure to prepare dust-free high-MW PPMS is described elsewhere.[26]

Results and Discussion

Poly(phenylmethylsiloxane). The depolarized Rayleigh spectra $I_{\mathrm{VH}}(\omega)$ (Figure 1) allow the computation of the I_{VH} intensities as the area under the measured Lorentzian line as well as an estimation of the collision-induced contribution, which appears as a flat background. The absolute R_{VH} values (eq 6) of the undiluted samples were used in eq 5 to yield the effective optical anisotropy $\langle \gamma^2 \rangle / X$ of the monomer unit. For the local field correction we used the form $f(n) = [(n^2 + 2)/3]^2$.[27] The values of $\langle \gamma^2 \rangle / X$ are plotted in Figure 2 against the degree of polymerization X of PPMS chains at 25 °C. The invariant $\langle \gamma^2 \rangle / X$ is the result of RIS model calculations for polymer chains in dilute solutions.[1,7] Asymptotic values of strain birefringence in atactic PPMS[28] and of $\langle \gamma^2 \rangle / X$ in PS[7,29] are closely approached for $X \approx 60$, in qualitative agreement with the data of Figure 2. This resemblance suggests that no significant interchain orientation correlations exist in amorphous PPMS at 25 °C, and hence the depolarized Rayleigh intensity exhibits a weak temperature dependence. This situation is shown in Figure 3, where the observed temperature dependence of R_{VH} results mainly from the product $\rho f(n)$ in eq 5. In the case of liquid-crystal-like orientational order ($\sim T/(T - T_0)$) there is a strong decrease of R_{VH} with increasing temperature, as has been observed for n-alkanes[17] and for a PPMS sample.[21]

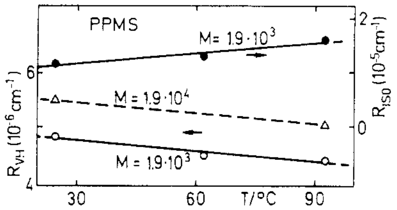

Figure 3. Isotropic (R_{iso}) and anisotropic (R_{VH}) part of the polarized scattered intensity from bulk PPMS versus temperature.

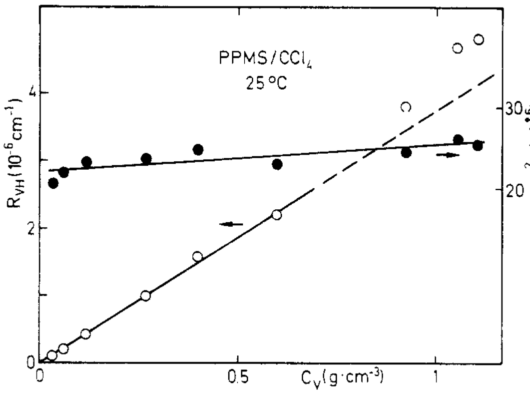

Figure 4. Absolute depolarized Rayleigh intensity R_{VH} and optical anisotropy $\langle\gamma^2\rangle/X$ of PPMS (M_W = 1900) at 25 °C plotted versus volume concentration in CCl$_4$.

The latter, however, was found to contain about 10% oligomers, mainly dimer.

The intensity of the depolarized light scattering from amorphous PS,[9-11] PMMA,[13] and PC[12] investigated so far has been measured without the use of a Fabry–Perot interferometer. These measurements were probably affected by the inclusion of the collision-induced anisotropy. Nevertheless, the results show that I_{VH} is independent of the probing wavelength q^{-1} and exhibits a weak temperature dependence. There is therefore no indication of intermolecular orientation correlations present in the bundle and meander models proposed for amorphous solid polymers.[3,4]

The isotropic part R_{iso} of the polarized scattered intensity can be calculated from the measured depolarized and polarized component of the scattered light, $R_{iso} = R_{VV} - {}^4/_3 R_{VH}$. The R_{iso} intensity arising from local density fluctuations in undiluted polymers is grossly affected by the isothermal compressibility χ_T according to[11]

$$R_{iso} = \frac{\pi^2}{9\lambda_0^{\,4}}(n^2 - 1)^2(n^2 + 2)^2 kT\chi_T \qquad (7)$$

The values of R_{iso} for the bulk PPMS with $M_w = 1.9 \times 10^3$ are plotted versus temperature in Figure 3. The observed temperature dependence is that predicted by eq 7. In addition, there is a good agreement between the experimental value of R_{iso} (1.18×10^{-5} cm^{-1} at 25 °C) and that (1.28×10^{-5} cm^{-1}) computed from eq 7 by setting χ_T equal to the low-frequency adiabatic compressibility χ_S ($=4.7 \times 10^{-11}$ cm^2/dyn). The latter was obtained from the ultrasonic sound velocity u_0 ($=1391$ ms^{-1}) of PPMS at 25 °C, i.e., $\chi_S = (\rho u_0^{\,2})^{-1}$. This agreement further suggests that the isotropic scattering from amorphous PPMS is attributable to local density fluctuations with no evidence of an excess light scattering.

The lack of appreciable intermolecular orientation correlations in bulk PPMS in favor of the random coil model(1,6) can be crucially verified by performing a concentration-dependent study of the R_{VH} intensity. This dependence is depicted in Figure 4 for the PPMS with $M_w = 1.9 \times 10^3$ dissolved in CCl$_4$ with an extremely low value of R_{VH} ($\sim 3.5 \times 10^{-8}$ cm^{-1})[23] at 25 °C. The R_{VH} increases linearly with polymer concentration up to about 60% PPMS and shows positive deviations from the linear dependence at higher concentrations resulting partially from the refractive index correction $f(n)$ in eq 5. The weak concentration dependence of R_{VH} is better demonstrated in the plot of $\langle\gamma^2\rangle/X$ vs C_V, also shown in Figure 4. To compute $\langle\gamma^2\rangle/X$ from eq 5 we have used the same function $f(n)$ introduced above. Assuming the same intrachain correlations in bulk and solution, the difference between the values of $\langle\gamma^2\rangle/X$ in the undiluted and very dilute PPMS amounts only to 12%. This small contribution from intermolecular effects is obscured by the uncertainties in the refractive index correction. Besides the values of $\langle\gamma^2\rangle/X$ in Table I we have therefore reported the absolute valus of R_{VH}/ρ too.

Table I
Depolarized Rayleigh Intensities and Optical Anisotropies

sample	R_{VH}/ρ, 10^{-28} cm^2	$\langle\gamma^2\rangle/X$, Å^6
benzene	4.0	10.7
PMS	6.8	19.1
dimer[a]	8.5	22.6
PPMS[b]	11.1	28.8
PDMS	0.038	0.12

[a] Reference 25. [b] High molecular weight.

To estimate the intramolecular correlation factor 1 + F (eq 3) the anisotropy of the monomer is needed. The latter can be either computed from the bond anisotropies or measured for molecules having a structure very similar to that of the repeating unit. First we attempt to calculate β defined by

$$\beta^2 = {}^3/_2 \text{ trace } (\hat{\mathbf{a}}\hat{\mathbf{a}}) \qquad (8)$$

where $\hat{\mathbf{a}}$ is the traceless part of the polarizability tensor $\mathbf{a}$ for the repeating unit of the chain. Assuming additivity of group polarizability tensors, the $\mathbf{a}_i$ for the skeletal bond Si–O with the attached side groups methyl (Me) and phenyl (Ph) can be written as[7]

$$\mathbf{a}_i = \mathbf{a}_{SiO} + \Omega_0 \mathbf{a}_{SiPh} \Omega_0^{\,T} + \Omega_0 \mathbf{a}_{SiMe} \Omega_0^{\,T} \qquad (9)$$

or after resolving the tensors into cylindrical Δa and acylindrical $\Delta\alpha^+$ parts[29]

$$\hat{\mathbf{a}}_i = \Delta a_{SiO} J + \Omega_0(\xi,-\psi) \times (\Delta a_{SiPh} J + \Delta a^+{}_{SiPh} J^+)\Omega_0{}^+(\xi,-\psi) + \Delta a_{SiMe} \Omega_0(\xi,\psi) J \Omega_0{}^+(\xi,\psi) \qquad (10)$$

where $J = \text{diag}({}^2/_3, -{}^1/_3, -{}^1/_3)$, $J^+ = \text{diag}(0, {}^1/_2, -{}^1/_2)$, and

$$\Omega_0(\xi,\psi) \equiv \Xi_z(\xi)\ \Psi_{y'}(\psi) \qquad (11)$$

$\Xi_Z(\xi)$ and $\Psi_{y'}(\psi)$ are transformations for rotation ξ about Z and ψ about y', respectively (see Figure 1, ref 7), required to transform the coordinate systems attached to the Si–Ph and Si–Me bonds to the reference frame affixed to the bond Si–O, e.g.

$$\Xi(\xi) = \begin{bmatrix} c & s & 0 \\ -s & c & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad \Psi(\psi) = \begin{bmatrix} c & 0 & s \\ 0 & 1 & 0 \\ -s & 0 & c \end{bmatrix} \qquad (12)$$

where $c = \cos \varphi$, $s = \sin \varphi$, and $\varphi \equiv (\xi, \psi)$. The phenyl ring is taken to be perpendicular to the plane defined by the adjoining pair of skeletal bonds SiO.

The anisotropy tensor $\mathbf{a}$ of the repeating unit is the sum of the contributions $\mathbf{a}_i$ and $\mathbf{a}_{i+1}$ ($=\Delta \mathbf{a}_{SiO} J$), both tensors being expressed in the reference frame of the ith Si–O bond. Substitution of $\xi = \psi = 54.75°$, which has been proven to reproduce some conformational properties of

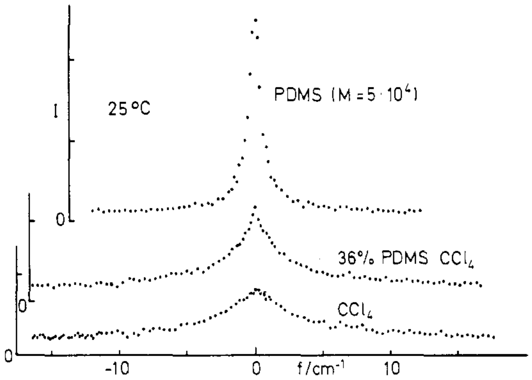

Figure 5. Depolarized Rayleigh spectra of poly(dimethylsiloxane) (PDMS) ($M_W = 4.9 \times 10^4$) in bulk and solution at 25 °C. The spectrum of the solvent CCl_4 at 25 °C is also shown.

PPMS,[30] and the values[28] 5.1, 1.3, 1.25, and −3 Å^3 for the anisotropies Δa_{SiPh}, Δa_{SiO}, Δa_{SiMe}, and Δa^+_{SiPh}, respectively, into eq 8 yields $\beta^2 = 21.1$ Å^6. The variation $\delta(\beta^2)/\delta p$ is 5.5, −5, and −3.6 when p is identified with Δa_{SiPh}, Δa_{SiO}, and Δa^+_{SiPh}, respectively.

Alternatively, the measured optical anisotropy of PMS used to estimate the depolarized scattering intensity of the monomer unit amounts to 19.1 ± 0.9 Å^6. This value obtained from the R_{VH} intensity for a 51.1% PMS solution in CCl_4 at 25 °C agrees reasonably with the calculated value of 21.1 Å^6. The former would be nicely reproduced, for instance, by decreasing $\Delta \mathbf{a}_{SiPh}$ about 7% or increasing $\Delta \mathbf{a}_{SiO}$ by 17%. The value of $1 + F$ for the high-M_W PPMS used in the present study is 1.5 ± 0.1. The value for atactic PS calculated by using RIS[29] levels off for M_w 5000 at 1.9 ± 1. The RIS theory was used to calculate the characteristic ratio $\langle r^2 \rangle / nl^2$ ($\langle r^2 \rangle$ is the mean square end-to-end distance, n the number of bonds, and l the bond length) for PPMS; it resembles the ratio $1 + F$ in that it is determined only by bond angles and internal potentials. For atactic PPMS with $X > 60$ the conformational property $\langle r^2 \rangle / nl^2$ amounts to 5.8 at 30 °C.[30] This value corresponds to about two monomer units per statistical segment. An independent estimate of this number follows from the comparison between $\langle \gamma^2 \rangle / X$ and the effective anisotropy per segment $(\Delta \alpha)^2$ obtained from strain–birefringence measurements of networks. For swollen PPMS at 25 °C the reported value[28] $\Delta \alpha = -8$ Å^3 leads to $(\Delta \alpha)^2 / (\langle \gamma^2 \rangle / X) = 2.2$, which agrees with that obtained from the characteristic ratio.

Poly(dimethylsiloxane). The depolarized scattering intensity from bulk PDMS is suprisingly very small and comparable to that of CCl_4. Figure 5 shows the $I_{VH}(\omega)$ spectra of undiluted PDMS, of 36% PDMS solution in CCl_4, and of CCl_4 at 25 °C. The low-frequency spectrum of the symmetric CCl_4 is clearly not just a broad background but an addition to that weak central Lorentzian line. This residual depolarized intensity[18,27] was considered as an intrinsic anisotropic component.[27] Very low effective anisotropy $\Delta \alpha$ per segment has also been reported from strain–birefringence measurements on PDMS networks.[22,31-33] The absolute depolarized intensity R_{VH} of bulk PDMS and two PDMS solutions in CCl_4 at 25 °C is plotted vs volume concentration of PDMS in Figure 6. The R_{VH} of the solutions is the excess intensity attributed to the solute PDMS. The effective optical anisotropy $\langle \gamma^2 \rangle / X$ per monomer unit is also shown in Figure 6. Both curves show that intermolecular effects are negligible within the limit of experimental error. The absolute value of R_{VH}/ρ for PDMS is given in Table I along with the $\langle \gamma^2 \rangle / X$ value.

The anisotropy tensor $\hat{\mathbf{a}}$ of the repeating unit in PDMS is easily derived by replacing two of the methyl groups in the optically isotropic $Si(CH_3)_4$ by oxygen atoms. Each replacement entails the formation of a Si–O bond, elimination of a Si–C bond, and removal of a methyl group, which involves a contribution $-\Delta a_{CH}$ to the anisotropy.[22] Thus, $\hat{\mathbf{a}}$ can be written as

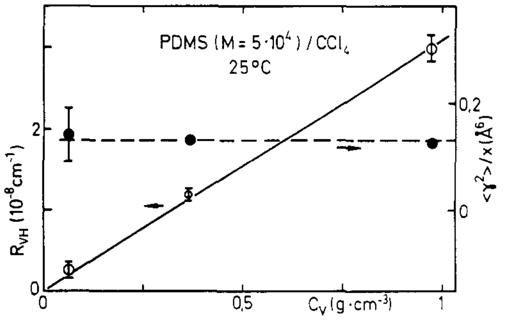

Figure 6. Absolute depolarized Rayleigh intensity and optical anisotropy $\langle \gamma^2 \rangle / X$ of PDMS at 25 °C plotted versus polymer concentration in CCl_4.

$$\hat{\mathbf{a}} = \Gamma(\mathbf{J} + \Xi(\theta)\,\mathbf{J}\,\Xi^T(\theta)) \tag{13}$$

where

$$\Gamma \equiv \Delta a_{SiO} - \Delta a_{SiC} + \Delta a_{CH} \tag{14}$$

With $\cos \theta = {}^1/_3$ for symmetrical tetrahedral bonding about the silicon atom, it follows from eq 8 and 13 that $\beta^2 = {}^4/_3\Gamma^2$. Assuming similar internal correlations for PDMS and PPMS chains we obtain $\Gamma = 0.24$ Å^3, indeed a very small value in accord with eq 14. In the framework of the RIS model, the optical configuration parameter Δa of swollen PDMS networks was approximately reproduced with a set of geometrical and conformational energies obtained from the analysis of the characteristic ratio and $\Gamma \simeq 0.23$ Å^3.[31] On the other hand, using different experimental values of $\Delta \alpha$ in PDMS networks swollen with CCl_4 at 70 °C Flory and co-workers[22] have reported the extremely small value of $\Gamma = 0.05$ Å^3, which surprisingly was found to be temperature dependent. The bond anisotropy Δa_{SiO} occurring in eq 14 is not known, and additional independent information on Γ is therefore not available. Nevertheless, the present data favor the higher Γ value, which is expected to be similar to that of Δa_{CH} for the vanishingly small difference $\Delta a_{SiO} - \Delta a_{SiC}$. Using the literature values[22] $\Delta a_{CH} = 0.21$ Å^3 and $\Delta a_{SiC} = 1.46$ Å^3 we obtain $\Delta a_{SiO} = 1.5$ Å^3. It may be noteworthy that the latter value leads to a better agreement between the calculated and measured anisotropy of the repeating unit in PPMS.

Conclusions

We have measured the integrated depolarized intensity of atactic poly(phenylmethylsiloxane) in bulk and solution in the molecular weight range 1900–19 000 and the temperature range 25–90 °C. We have used a plane Fabry–Perot interferometer with a free spectral range of 40 cm^{-1} to exclude the high-frequency collision-induced scattering which appears in this case as an unresolved background. The results show weak interchain orientation correlations in favor of the random coil model for amorphous polymers. By estimating the depolarized intensity of the monomer unit we computed the internal pair correlation factor $1 + F$, whose magnitude agrees reasonably with stain–birefringence data and RIS calculations.

The depolarized spectrum of poly(dimethylsiloxane) ($M_W = 5 \times 10^4$) is very weak due to the vanishingly small anisotropy β of the monomer unit. The intensity R_{VH}, which is affected only by intrachain correlations, yields $\beta \simeq 0.28$ Å^3 in contrast to the much higher value of 4.4 Å^3 for the monomer unit in PPMS.

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pH-Dependent Equilibrium Swelling Properties of Hydrophobic Polyelectrolyte Copolymer Gels

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ABSTRACT: The aqueous equilibrium swelling properties of a series of lightly cross-linked polyelectrolyte copolymers based on *n*-alkyl methacrylate esters (*n*-AMA) of various chain lengths and (dimethylamino)ethyl methacrylate (DMA) have been measured as a function of pH at 25 °C and constant ionic strength. Swelling is highly pH dependent, with water contents ranging from less than 10% (w/w) at high pH to greater than 90% at low pH. The extent of the transition from the collapsed hydrophobic state to the hydrophilic state and the pH interval over which it occurs depend on the comonomer composition. Increasing the proportion of *n*-AMA to DMA generally reduces the extent of the transition and shifts it to lower pH. Increasing the length of the *n*-AMA side chain (at constant comonomer ratio) causes a reduction in the extent of the transition, with a less systematic effect on the transition pH. The specific ionic composition of the solution, at a given pH and ionic strength, affects the extent of swelling. The ionic strength dependence of the equilibrium swelling has also been found to be affected by the ion valencies of the buffer system, as predicted by the Donnan equilibrium theory.

Introduction

It has long been known that a cross-linked polymer gel bearing weakly acidic and/or weakly basic pendant groups will imbibe solvent to an extent that depends on the pH and the ionic composition of the solution bathing the gel. When the gel is relatively solvophilic and contains acidic pendant groups, the swelling increases as solution pH increases.[1,2] Similarly, a weakly basic solvophilic gel expands smoothly as the solvent pH decreases.[3,4]

In recent years, considerable attention has been drawn to systems in which the polyelectrolyte gel and the solvent do not interact favorably. In such cases the polyelectrolyte gel remains in a collapsed state until the external solvent reaches a critical pH, at which point the gel abruptly increases its equilibrium swelling.[5] A plot of gel weight or volume versus pH can exhibit abrupt changes. These transitions in gel volume can also be induced by varying the ionic composition,[6] temperature,[7,9,10] or solvent composition.[5,10,11] This has stimulated research on the feasibility of such gels as artificial muscles and/or switches,[5] as components in chemical separation systems,[1,8] and as physiologically sensitive drug delivery devices.[3,4,9]

In the present study, the equilibrium swelling properties of a class of lightly cross-linked, hydrophobic, tertiary-amine-containing copolymer gels in aqueous solutions of various pH and ionic strengths were studied. The copolymers consisted of *n*-alkyl methacrylate esters (*n*-AMA) and (dimethylamino)ethyl methacrylate (DMA) Copolymer characteristics were varied by altering the *n*-alkyl side chain length of the *n*-AMA comonomer and by varying the ratio of *n*-AMA to DMA.

Experimental Section

Materials. Methyl methacrylate (MMA), ethyl methacrylate (EMA), *n*-propyl methacrylate (PMA), *n*-butyl methacrylate