Optical Anisotropy and Orientational Dynamics of Polycarbonate Dilute Solutions†

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ABSTRACT: Absolute depolarized intensity for Bisphenol A polycarbonate dilute solutions in dioxane has been obtained from the low-frequency depolarized Rayleigh spectra. The effective optical anisotropy, $\langle\gamma^2\rangle/x$ (=117 Å^6), of polycarbonate with degree of polymerization x in the range 8–163, calculated from the measured intensity at 25 °C, is consistent with rotational isomeric state model calculations. The measured optical anisotropy, β^2 (=57 Å^6), of the monomer $CH_3OC_6H_4C(CH_3)_2C_6H_4OCOOCH_3$ used to estimate the extent of internal pair correlations in the chain agrees well with that calculated from the molecular geometry and group anisotropies. The depolarized Rayleigh spectra, $I_{VH}(\omega)$, of the monomer and two oligomers, which were well represented by a single Lorentzian line, arise from overall and segmental orientation, respectively. Alternatively, a sum of two Lorentzians with roughly equal intensities was necessary to fit the experimental $I_{VH}(\omega)$ of polycarbonate dilute solutions with $x \geq 18$. The relaxation time of the broad Lorentzian is virtually x independent and can be associated with local segmental motions probed by ^{1}H and ^{13}C NMR experiments. The width of the narrow component of the $I_{VH}(\omega)$ spectrum exhibits an x dependence and can be related to the normal-mode motion of the chain. However, due to polydispersity effects, a downturn is observed at $x > 44$.

Introduction

There has long been a great deal of interest in the elucidation of molecular motion in polymers. Dynamic mechanical,[1] dielectric relaxation,[2] NMR,[3] time-resolved optical spectroscopy,[4] and dynamic light scattering[5,6] can probe local chain dynamics. Among the scattering techniques, depolarized Rayleigh scattering is a valuable tool for probing fluctuations in the anisotropic part $\hat{\alpha}$ of the polarizability tensor. For polymer chains composed of optically anisotropic monomer units, both the configurational average optical anisotropy $\langle\gamma^2\rangle$ and the relaxation times for segmental and overall orientation can be obtained from the depolarized Rayleigh spectrum, $I_{VH}(\omega)$.[5,7-9]

The contribution of two Lorentzian components of roughly equal intensity to the experimental $I_{VH}(\omega)$ has been shown only for dilute polystyrene (PS) solutions so far.[5] The narrow component is connected with overall rotation in agreement with the relaxation time of the first normal mode, whereas the broad Lorentzian is related to the rotation of the phenyl groups about the main-chain axis and therefore is virtually independent of the molecular weight. Theoretical models were subsequently proposed to account for these observations.[10,11] Two unequally weighted Lorentzians are predicted for a rodlike arrangement of cylindrically anisoptropic segments with the ratio of the weighting factors depending on the components of the segmental polarizability tensor. Despite its artificiality, this model suggests that the experimental features reported for PS so far may not be characteristic of the $I_{VH}(\omega)$ of other dilute polymer solutions. Further experimental work is necessary to show the applicability of the depolarized Rayleigh spectroscopy to study macromolecular and local dynamics and access their importance to relax the laboratory-fixed optical anisoptropy. The latter is strongly affected by intersegmental correlations and can be used to elucidate the conformation of chain molecules by using rotational isomeric state calculations.[12,13]

Poly[2,2-bis(4-hydroxyphenyl)propane carbonate] (PC), which possesses a high impact strength, has intrigued many investigators over the last years. Its dilute-solution local dynamics has been the subject of numerous NMR studies;[3,14-16] its effective anisotropy per segment, $\Delta\alpha$, was furnished from strain-birefrigence measurements on net-works;[17] its effective optical anisotropy per monomer, $\langle\gamma^2\rangle/x$, is about 4 times larger than that of PS as shown by rotational isomeric state calculations.[18,19] We therefore chose PC for a dynamic depolarized light-scattering study aiming mainly at the elucidation of the nature of the relaxation processes that affect the anisotropy fluctuations and the estimation of internal orientation correlations of the polymer chain. We have measured $I_{VH}(\omega)$ spectra of PC solutions at different temperatures over the molecular weight range 1200–46 300 using a plane Fabry–Perot interferometer. To estimate the optical anisotropy of the repeating unit and the magnitude of the interchain orientation correlations, the $I_{VH}(\omega)$ spectra of 4-methoxy-α,α-dimethyl-p-tolyl methyl carbonate and bulk PC have also been measured. The solvents used in this study are p-dioxane, acetone, CH_2Cl_2, $CHCl_3$, and CCl_4.

The integrated depolarized intensity measurements have shown that the magnitude of the internal pair correlation agrees very well with RIS calculations,[19] whereas interchain correlations in the undiluted PC are experimentally negligible. The $I_{VH}(\omega)$ spectra of monomer and oligomers are well presented by a single Lorentzian line associated with overall rotation. Alternatively, the $I_{VH}(\omega)$ spectra of the higher molecular weight PC show strong evidence of two spectral components. The broad Lorentzian line with relaxation time $\tau_f \approx 10^{-10}$ s was found to be insensitive to molecular weight variations and can be ascribed to segmental motion studied by NMR spin–lattice relaxations.[3,14-16] The narrow component with relaxation time $\tau_s \approx 10^{-9}$ s exhibits a molecular weight dependence, which, however, is weaker than that predicted for

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† Dedicated to Prof. E. W. Fischer on the occasion of his 60th birthday.

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Table I
Molecular Characteristics of Polycarbonate Samples

x	$M_w \times 10^{-3}$, g/mol	M_w/M_n	$[\eta]$, cm^3/g
5	1.27	1.06	
8	2.0	1.57	
18	4.57	1.80	15.2
44	12.6	2.03	26.6
87	24.9	2.16	31.1
163	46.3	3.70	51.1

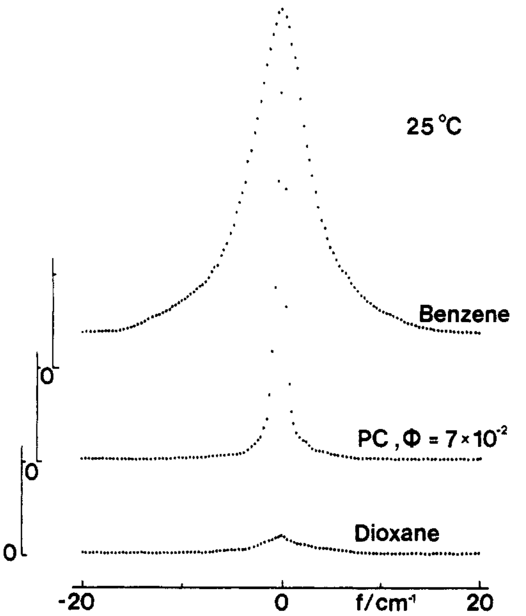

Figure 1. Depolarized Rayleigh spectra of 7.5% polycarbonate (M_w = 2000) in dioxane, neat dioxane, and benzene at 25 °C.

the first normal-mode time mainly because of the polydispersity of PC samples. The experimental ratio of the depolarized intensity associated with the segmental motion to that of the overall rotation is of the order of 1.

Experimental Section

The Bisphenol A polycarbonate samples and the monomer 4-methoxy-α,α-dimethyl-p-tolyl methyl carbonate were synthesized, and their weight- and number-average molecular weight, M_w and M_n, respectively, were determined at the Max-Planck-Institut at Mainz, FRG. The characteristics of the samples along with their intrinsic viscosities, $[\eta]$, are given in Table I. Dust-free samples were obtained after filtration through 0.5-μm Teflon Millipore filters directly into the dust-free rectangular (1 × 1 cm) cells.

For integrated intensity measurements the depolarized Rayleigh spectra, $I_{VH}(\omega)$, of the samples and of the liquid used as a standard (benzene) were taken at a scattering angle of 90° using a plane Fabry–Perot interferometer with the free spectral range of 40 cm^{-1}. The polarizers used for the incident and scattered light have extinction coefficients better than 10^{-6} and 10^{-7}, respectively. The experimental $I_{VH}(\omega)$ spectra of the solvent dioxane, dilute PC (M_w = 2000) solution and benzene at 25 °C are shown in Figure 1. The integrated depolarized intensities for the narrow spectra were obtained from numerical integration. The intensity attributed to the solute molecules with volume fraction φ, $I_{VH} = I_{solu} - (1 - \varphi)I_{solv}$, is calculated from the measured intensities of the solution and the inert neat solvent. The intensity I_{VH} is then converted to the absolute ratio R_{VH} by comparison with the depolarized intensity of benzene according to

$$R_{VH} = (I/I_B)(n/n_B)^2 R_{VH}{}^B \tag{1}$$

The $R_{VH}{}^B$ at λ = 488 nm and 25 °C amounts to 2.67 × 10^{-6} cm^{-1}.[7,13] Refractive indices, n, of the samples were measured with an Abbe refractometer. The intrinsic optical anisotropy per monomer unit, $\langle\gamma^2\rangle/x$, can then be computed from

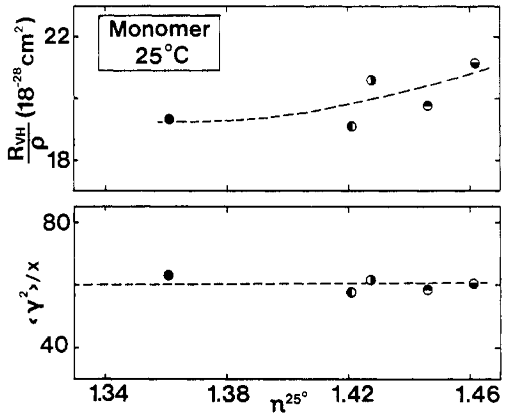

Figure 2. Depolarized Rayleigh ratio and optical anisotropy of monomer solutions in different solvents (●, acetone; ◐, dioxane; ◑, CH$_2$Cl$_2$; ⊖, CHCl$_3$; ◒, CCl$_4$) plotted versus their refractive indices of 25 °C.

$$\langle\gamma^2\rangle/x = 15(\lambda_0/2\pi)^4 f(n)^{-1}\left(\frac{R_{VH}}{\rho}\right) \tag{2}$$

where x is the degree of polymerization, λ_0 the wavelength of light in vacuo, ρ the number density of monomer units, and $f(n) = [(n^2 + 2)/3]^2$ is the local field correction.[13,20] To check for the correct substraction of the collision-induced depolarized scattering, which appears as an unresolved background in the $I_{VH}(\omega)$ spectra, we have measured the I_{VH} of the monomer in different solvents. Figure 2 shows that while R_{VH}/ρ increases with increasing n, the optical anisotropy is insensitive to the variation of n. This behavior also suggests that form anisoptropy is very small.

To study the orientational dynamics of the PC solutions, two free spectral ranges of 9.1 and 5.6 GHz were used to analyze the spectral distribution of monomer and PC solutions, respectively. The $I_{VH}(\omega)$ spectra obtained from monomer and oligomers (M_w < 4000) were found to be well represented by a single Lorentzian function plus a base line, considering the overlap of neighboring orders. On the other hand, two Lorentzians plus a base line were used to fit the higher molecular weight PC solutions in dioxane. At a free spectral range of 5.7 GHz the spectrum of dioxane appears, through the overlap of different orders, as an unresolved background. The true spectral width was obtained after correction for the instrumental width corresponding to a finesse of about 75. The correction was done by comparing the measured widths with those obtained from the convolution of the instrumental line shape with a set of Lorentzians of varying widths.

Results

The absolute depolarized intensity, R_{VH}, was measured for different solute concentrations to check for the presence of appreciable intermolecular orientation correlations in $\langle\gamma^2\rangle/x$. The concentration dependence of R_{VH}/ρ (eq 2) is depicted in Figure 3 for solutions of PC in dioxane and bulk PC at 25 °C. For comparison, the ratio R_{VH}/ρ for dioxane amounts to 1.4 × 10^{-29} cm^{-1} at 25 °C. The $\langle\gamma^2\rangle/x$ is insensitive to concentration variations in the considered dilute range. Similar behavior was recently reported for polysiloxanes[7] and linear and star polyisoprenes.[21] Values of $\langle\gamma^2\rangle/x$ thus calculated are listed in Table II together with the ratio R_{VH}/ρ at 25 °C.

Figure 4 shows representative experimental $I_{VH}(\omega)$ spectra of different molecular weight PC solutions in dioxane at 85 °C. From the satisfactory fit of a single Lorentzian function plus base line to the PC samples with x < 18, we obtained the depolarized Rayleigh relaxation time, $\tau = (2\pi\Gamma)^{-1}$, with Γ being the true half-width at half-height. However, a systematic deviation is evident from

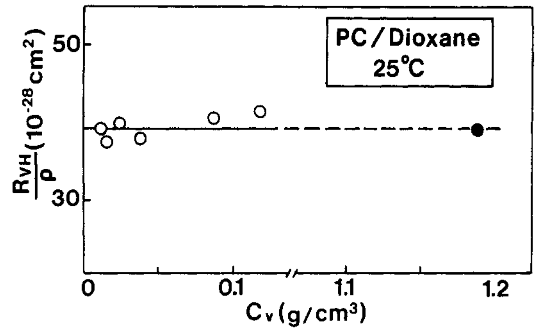

Figure 3. Absolute ratio R_{VH}/ρ of PC solutions (○) and bulk PC (●) versus solute concentration in dioxane at 25 °C.

Table II
Depolarized Intensities and Optical Anisotropies at 25 °C

sample	R_{VH}/ρ, $\times 10^{-28}$ cm^2	$\langle\gamma^2\rangle/x$, Å^6
$x = 1$	19.1	57.3
$x = 5$	37.1	111.3
PC solution	39.1	117.3
PC bulk	39	115.0
dioxane	0.14	0.4

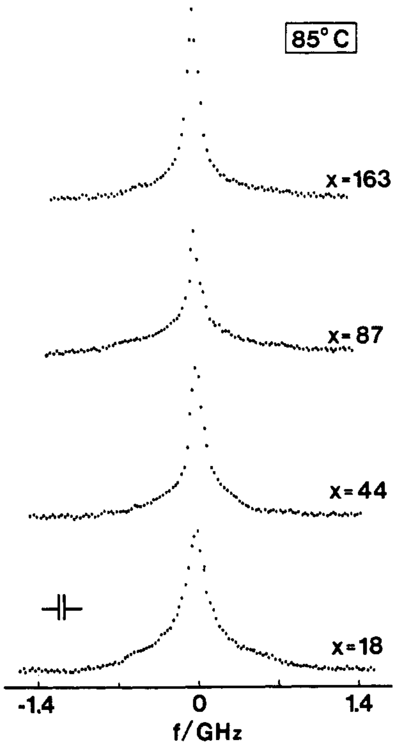

Figure 4. Experimental $I_{VH}(\omega)$ spectra of different molecular weight polycarbonate solutions in dioxane at 85 °C. The symbol -||- denotes the full-width of the instrumental function.

the single Lorentzian fit to the experimental spectra of PC with higher x. Figure 5 illustrates this situation for $x = 44$ at 85 °C. The present results mirror those reported for polystyrene solutions in CCl_4. We have also chosen a sum of two Lorentzians plus base line to fit the $I_{VH}(\omega)$. The resulting deviation plot and the relative contribution of the two components are also shown in Figure 5. We found that the broad and narrow Lorentzians make roughly equal contribution to the observed spectrum. The ratio I_s/I_f of the intensities in the narrow and broad spectral components, respectively, amounts to 0.9 ± 0.1 and is independent of molecular weight in the temperature range 65–95 °C.

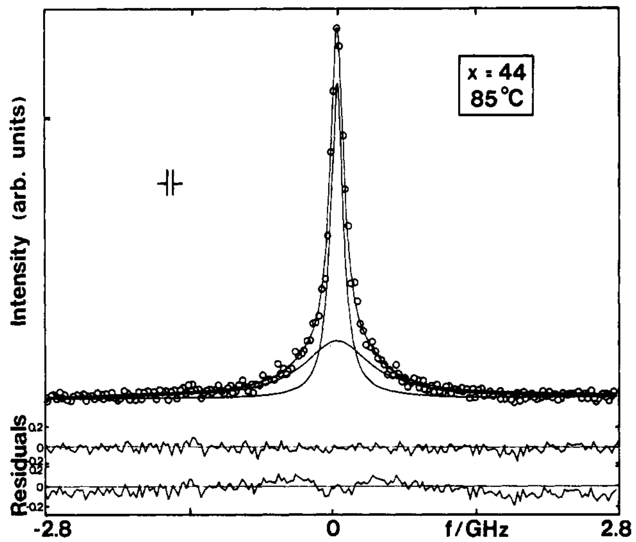

Figure 5. $I_{VH}(\omega)$ spectrum of 2% solution of polycarbonate ($x = 44$) in dioxane at 85 °C. The narrow and broad components are indicated by the solid lines. The quality of the fit represented by percent deviation for single and double Lorentzian functions are also given.

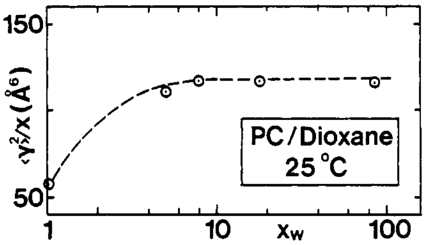

Figure 6. Effective optical anisotropy per monomer unit, $\langle\gamma^2\rangle/x$, in dilute PC solutions at 25 °C versus the degree of polymerization, x.

Discussion

1. Optical Anisotropy. The values of the configurational average optical anisotropy per monomer unit, $\langle\gamma^2\rangle/x$, are plotted in Figure 6 versus the degree of polymerization, x, of PC chains in dilute solutions at 25 °C. The invariant $\langle\gamma^2\rangle/x$ is the result of RIS model calculations for individual polymer chains. According to these calculations for flexible coils, intrachain orientation correlations are relatively short and the ratio $\langle\gamma^2\rangle/x$ rapidly attains its asymptotic value with increase in x; for PS[18] and poly(phenylmethylsiloxane) (PPMS)[7] asymptotic values are closely approached for $x \approx 60$. The latter is even shorter ($x \approx 10$) for PC chains (Figure 6) in nice agreement with theoretical calculations for PC.[19] This behavior further suggests that no significant interchain orientation correlation should be expected for amorphous bulk PC. We indeed measured experimentally the same $\langle\gamma^2\rangle/x$ in an undiluted PC sample with that obtained in dilute solutions (Table II).

The intensity of the depolarized light scattering from amorphous PC has previously been measured without the use of a Fabry–Perot interferometer.[22] The reported value of $\langle\gamma^2\rangle/x = 136$ Å^6 is probably somewhat overestimated due to the inclusion of collision-induced anisoptropy. Under similar experimental conditions the reported[19] value of $\langle\gamma^2\rangle/x$ in a dilute PC ($x \approx 11$) solution amounts to 120 ± 5 Å^6.

A measure of the internal pair correlations of the polymer chain is the intramolecular correlation factor, $1 + F$,

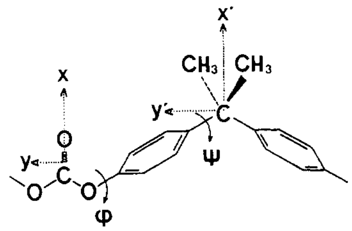

Figure 7. Structure of the repeat unit of the polycarbonate chain.

defined as[5]

$$1 + F = \frac{\sum_{ij}^{x} \langle a_{yz}(i,0) a_{yz}(j,0) \rangle}{x \langle a_{yz}(i,0) a_{yz}(i,0) \rangle} = \frac{\langle \gamma^2 \rangle}{x \beta^2} \qquad (3)$$

where the static $a_{yz}(i,0)$ represents the yz component of the laboratory-fixed polarizability tensor associated with the ith monomer unit. The optical anisotropy, β^2, of the monomer can be either computed or measured for molecules having a structure very similar to that of the repeating unit. We attempt to compute β defined by

$$\beta^2 = 3/2 \text{ trace } (\hat{a}\hat{a}) \qquad (4)$$

where $\hat{a}$ is the traceless part of the polarizability tensor **a** of the repeating unit. Its geometry for the PC chain is shown in Figure 7. Assuming additivity of group polarizability tensors

$$\hat{a} = \hat{a}_c + R_x(\varphi)\, \hat{a}_{\text{DPP}}\, R_x^{-1}(\varphi) \qquad (5)$$

where $\hat{a}_c$ and $\hat{a}_{\text{DPP}}$ ($=\hat{a}_{\text{ph,a}} + \hat{a}_{\text{ph,b}}$) are the traceless anisotropy tensors for the carbonate and diphenylpropane, respectively (both tensors being expressed in the reference frame of the carbonate group), and R_x is the transformation for rotation. When the procedure described in ref 23 is followed, the symmetric tensor $\hat{a}_{\text{DPP}}$ expressed in the reference frame affixed to the $C(CH_3)_2$ group is written as

$$\hat{a}_{\text{DPP}} = \begin{bmatrix} -0.07 & 0 & 0 \\ & 0.667\Delta a - 0.03 & \\ & \pm 0.577\Delta a & -0.667\Delta a + 0.1 \end{bmatrix} \qquad (6)$$

We made use of the tetrahedral angle for the quaternary carbon, the angle $\psi = \pm 46°$, (Figure 7), and the value $\Delta a^+ = 3.0$ Å^3 for the acylindrical part of the $\hat{a}_{\text{ph}}$ given in ref 23. The cylindrical part, Δa, depends on the substitution of the phenyl ring; $\Delta a = 5.2$ Å^3 for the phenyl in DPP[23] and $\Delta a = 7.4$ Å^3 for the phenylene group in PC.[19] The anisotropy tensor $\hat{a}$ of the repeating unit is then obtained from eq 5 after transformation of a_{DPP} from the coordinate system ($x'y'z'$) into the reference frame (xyz) using discrete values $\varphi = \pm 46°$ (ignoring fluctuations) and substitution of $\hat{a}_c = \text{diag}\ (0.17, 1.04, -1.21)$ Å^3.

$$\hat{a} = \begin{bmatrix} 0.1 & 0 & 0 \\ & -0.023\Delta a - 0.654 & \\ & \pm(0.667\Delta a - 0.13) & 0.023\Delta a + 0.554 \end{bmatrix} \qquad (7)$$

The optical anisotropy β^2 of the monomer computed from eqs 4 and 7 using $\Delta a = 7.4$ Å^3 for the phenylene group amounts to 71 Å^6, which depends critically on Δa. For comparison, the value $\Delta a = 5.2$ Å^3 for the phenyl group in DPP leads to the calculated value $\beta^2 = 35$ Å^6.

Table III
Orientation Times of PC Oligomers

monomer (37 vol %)		$x = 5$ (8.2 vol %)		$x = 8$ (7.5 vol %)	
T, K	τ, ns	T, K	τ, ns	T, K	τ, ns
283	0.35	298	2.20	298	3.05
293	0.25	313	1.50	313	2.56
295	0.21	326	1.65	326	2.33
313.5	0.17	359	1.11	333	1.78
315.5	0.12			359	1.34
337	0.09				

Alternatively, the measured optical anisotropy of the monomer $CH_3OC_6H_4C(CH_3)_2C_6H_4OCOOCH_3$ used to estimate the depolarized scattering intensity of the repeating unit of the PC chain amounts to 57.3 ± 2 Å^6 at 25 °C. This value is very different from the calculated values of 71 and 35 Å^6, which are insensitive to the acylindrical part Δa^+. This disparity, however, suggests that the effect of oxygen to the phenyl ring is overestimated. The experimental β^2 is reproduced exactly by using $\Delta a = 6.7$ Å^3 for the phenylene group in the monomer. The higher reported[19] value of 7.4 Å^3 may partially arise from the value of R_{VH} of carbon tetrachloride used, which exceeds our value at 488 nm.[36] The final agreement between calculated and experimentally determined β^2 suggests furthermore that the previously calculated value of 32 Å^6 should be wrong.[17]

Substitution of the measured values of β^2 and $\langle \gamma^2 \rangle / x$ (Table II) in eq 3 yields the intramolecular correlation factor, $1 + F = 2.1$. The measured values for atactic PPMS[7] and PS,[5,18] respectively, are 1.5 ± 0.1 and 2.6 ± 0.4 whereas RIS calculations for PS yield 1.9 ± 1. The factor $1 + F$ resembles the charateristic ratio $\langle r^2 \rangle / x l^2$ in that both are determined only by bond angles and internal potentials. From small-angle neutron-scattering measurements of the average end-to-end distance, $\langle r^2 \rangle$, of an amorphous PC with $x = 71$ the conformational property $\langle r^2 \rangle / x l^2$ with monomer length $l = 8.8$ Å amounts to 4.8.[24] This value, which is in agreement with recent RIS calculations,[25] corresponds to 2.2 monomer units per statistical segment. A rough estimate of this number follows from the comparison between $\langle \gamma^2 \rangle / x$ and the effective anisotropy per segment, $(\Delta a)^2$, obtained from strain-birefringence measurements of networks.[17] The reported value $\Delta a^2 = 215$ Å^6 for PC at 25 °C exceeds the value of $\langle \gamma^2 \rangle / x$ by a factor 1.84.

2. Orientational Dynamics. Oligomer Solutions. The depolarized Rayleigh spectra of the monomer were recorded in the temperature range 10–65 °C using a free spectral range of 9.1 GHz. The spectra can fit well to a single Lorentzian, and the orientation time, τ, is a decreasing function of temperature (Table III). For small molecules, it is well established that τ can be given by the modified Stokes–Debye–Einstein relation[26,27]

$$\tau = V_h \eta_s / kT + \tau_0 \qquad (8)$$

where η_s is the shear viscosity of the solution, V_h is the effective hydrodynamic volume of the reorienting moiety, and the nonzero intercept τ_0 is necessary to fit the relaxation times. The volume V_h can depend on the static pair orientational correlations.

Figure 8 shows a plot of τ versus η_s/T for the 37 vol % monomer solution in dioxane. The data are well represented by eq 8 with $\tau_0 = 12$ ps and $V_h = 213 \pm 20$ Å^3. The latter value is in contrast to the molecular volume, $V_m = 357$ Å^3, calculated by using the bond geometries in Figure 7. Rigorously, this volume cannot be identi-

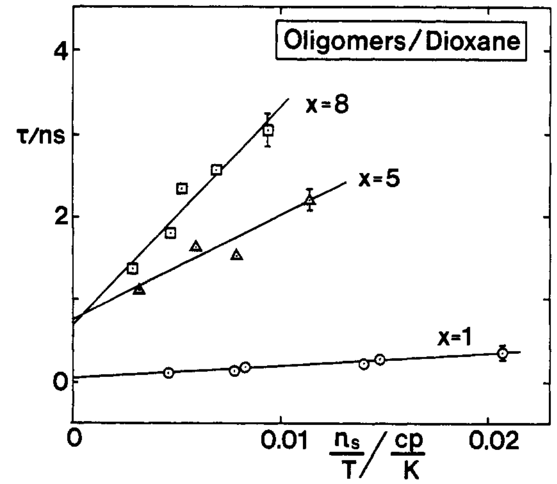

Figure 8. Orientational relaxation times for polycarbonate oligomers versus η_s/T.

fied with the molecular volume, but it is rather the volume swept out during molecular rotation. In this context, it is worth mentioning that the molecular volume of the ester $CH_3OCOOC_6H_4C(CH_3)_2C_6H_4OCOOCH_3$ is recently reported[28] to be 288 Å^3. This estimate is based on van der Waals radii for all atoms in the ester and then on a numerical integration over the resulting volume. If the effect of orientational pair correlations is negligible, as in the present case (Figure 3), then the small V_h value suggests that slip boundary[26,27] conditions may be more appropriate in describing the reorientation of noninteracting rigid molecules; i.e., $V_h = \sigma V_m$. To obtain the coefficient σ, we followed ref 29 and estimated the ratio ρ by taking the ratio of the transverse dimension to the longitudinal dimension of the monomer (Figure 7). From the resulting value of $\rho = 0.25$ we found the corresponding $\sigma = 0.58$, which leads to $V_h = 209$ Å^3. Thus reasonable agreement with the experimental value of V_h is obtained using the slip hydrodynamic model and overall rotation of the monomer.

The orientation relaxation times of the 8.2 vol % pentamer ($x = 5$) and 7.5 vol % octamer ($x = 8$) solution in dioxane are listed in Table III and plotted versus η_s/T in Figure 8. The fit of eq 8 to the experimental times yields $\tau_0 = 765$ ps, $V_h = 1200 \pm 400$ Å^3, for pentamer and $\tau_0 = 685$ ps, $V_h = 2640 \pm 500$ Å^3, for octamer. The values of the intercept τ_0 are quite close in both oligomers but significantly larger than in the monomer. Despite its empirical value, τ_0 may be related to the size of the orienting unit as reflected in the moments of inertia. In the case of the two oligomers the VH spectrum is more likely to be due to the internal segmental rotation[27] rather than the overall molecular rotation observed for the monomer. This proposition is supported by the size of the segment whose length is at least twice the length of the monomer unit. This would result in a hydrodynamic volume of about 1650 Å^3, under slip boundary conditions. Moreover, an overall rotation for a rigid pentamer would lead to an extremely large hydrodynamic volume of the order of 45 000 Å^3. Thus, if the depolarized Rayleigh spectrum of pentamer and octamer indeed arise from internal rotation, then one would expect quite close values for τ_0, as was found experimentally.

At first sight the larger hydrodynamic volume for the octamer seems to be in contradiction with the assumption of internal rotations. To overcome this discrepancy, we recall that the depolarized light-scattering experiment measures a collective relaxation time, which is connected with the single segment relaxation time, τ_s, by[5]

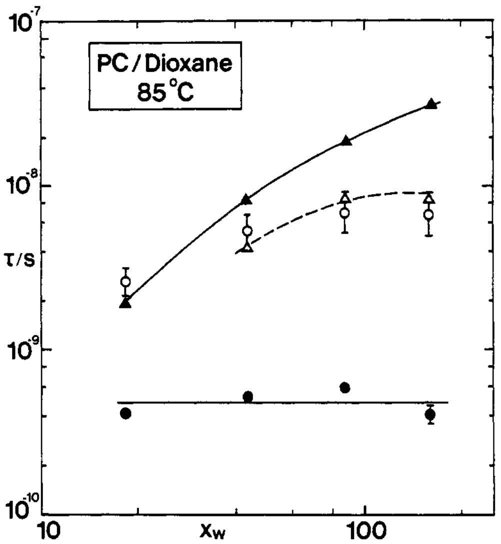

Figure 9. Relaxation times for the broad (●) and narrow (○) components of the depolarized Rayleigh spectrum of polycarbonate dilute solutions in dioxane at 85 °C. Solid triangles denote calculated relaxation times, τ_1, for the first Rouse–Zimm normal mode using eq 11 and the characteristics of the PC samples. Empty triangles are computed τ_1 times from eq 11 using number-average molecular weights.

$$\tau = (1 + F)\tau_s \qquad (9)$$

Adaptation of eq 9 implies that the V_h of the octamer is affected by intramolecular orientational correlations between different monomer units on the same chain. Consequently, the V_h of the octamer should be a factor of $1 + F = 2.1$ larger than the V_h of the pentamer, i.e., 2520 Å^3. This rough estimate is in accord with the experimental value of 2640 ± 500 Å^3 for the octamer. In conclusion, the depolarized Rayleigh spectrum of monomer is due to overall rotation under slip hydrodynamic conditions whereas those of pentamer and octamer are due to internal rotations affected by intramolecular pair correlations.

Dilute Polycarbonate Solutions. The depolarized Rayleigh spectra of the samples with degree of polymerization 18 and higher were found to be better represented by two Lorentzians in the temperature range of 65–95 °C. We discuss the spectra at 85 °C for which good resolution was obtained using a free spectral range of 5.6 GHz. The ratio of the integrated intensities of the narrow and broad components of the $I_{VH}(\omega)$ in the temperature and molecular weight range investigated was found to be $\lambda = 0.9 \pm 0.1$. There is so far only one depolarized Rayleigh study of the relaxation processes in dilute, monodisperse PS solutions in CCl_4.[5] The $I_{VH}(\omega)$ spectra of PC were also found to exhibit a double Lorentzian feature. The molecular weight dependent width of the narrow Lorentzian has been associated with the overall rotation of the flexible coil as given by the first Rouse–Zimm time in the dilute limit[30]

$$\tau_1 = AM[\eta]\eta_0/RT \qquad (10)$$

where $[\eta]$ is the intrinsic viscosity and η_0 the shear viscosity of the solvent. The constant A is expected to take the values 0.608 and 0.422 for the free-draining and nondraining model, respectively. Experimentally, the value $A = 0.24 \pm 0.02$ was obtained[5] from the comparison of the times τ_n of the narrow components to the τ_1 of eq 10.

Figure 9 shows the variation of τ_n with the weight-average degree of polymerization, x_w, of the PC chains. In contrast to the PS results, the present τ_n times seem to exhibit a much weaker chain length dependence in disagreement with the prediction of eq 10 for monodisperse samples. However, due to the polycondensation reaction, our PC samples with $x > 18$ are quite polydisperse (Table I). This is obviously reflected by the downturn of the molecular weight dependence of τ_n in Figure 9. The presence of polydispersity will introduce a distribution of relaxation times and hence will affect both the calculation of τ_1 from eq 10 and the estimation of τ_n from the experimental spectra. If the distribution of molecular weight is known, an average τ_1 may be computed from[31]

$$\tau_1 = \frac{A[\eta]\eta_0}{RTM_w}\int M^2 f(M)\,\mathrm{d}M \qquad (11)$$

We assume that the normalized function, $f(M)$, is given by a normal distribution,[32] and the upper limit of the integral is determined from the estimation of the known moments M_n and M_w (Table I). The times τ_1 thus calculated for the characteristics of our samples and using $A = 0.24$ are shown in Figure 9. The comparison between τ_1 and τ_n is quite reasonable for the two lower molecular weight (M) PCs. For the higher M, we observe faster τ_n times as compared to the calculated τ_1 times. If there exists a distribution of relaxation times, the estimation of τ_n depends on the free spectral range used. The τ_n times of the higher M in Figure 9 more likely present the faster than the slower components of the distribution.[33] To check this possibility, we compare these τ_n times with those calculated from eq 11, substituting the integral with M_n^2. As seen in Figure 9, it appears that the experimental τ_n times for the higher M samples present fast relaxation times of the distribution.

The width of the broad Lorentzian was found to be insensitive to molecular weight variations and is therefore associated with localized segmental motions of the chain. To separate the effect of the overall molecular tumbling on the fluctuations of the optical anisotropy due only to segmental motions, we have plotted in Figure 9 the time τ after correction for the contribution of the narrow component; i.e., $\tau^{-1} = \tau_f^{-1} + \tau_n^{-1}$. This correction, however, is very small. Like the situation in PS[5] the intensities associated with the slow and fast spectral components are very close. In the framework of a rodlike model[11] the ratio of the intensity of the slow to the fast components of the $I_{VH}(\omega)$ spectrum is determined by the components of the optical polarizability tensor of the anisotropic segment. The calculations in the previous section have shown that the two phenyl rings in the repeat unit of PC contain the major part of the optical anisotropy, $\langle\gamma^2\rangle/x$, like the phenyl ring in the PS chain. However, the local structure in PS is different from that in PC as reflected in the $\langle\gamma^2\rangle/x$ values for the two polymers. The insensitivity of the ratio λ, which attains a constant value in both polymers, is therefore noticeable.

Local intramolecular motions in dissolved PC have been investigated by ^{1}H and ^{13}C NMR.[3,14-16] Several microscopic motions were assumed to describe the spin-lattice relaxation times. It is interesting to note that phenylene group rotation and segmental motion modeled with the Hall-Helfand orientation correlation function are characterized by correlation times of similar time scales.[3] This suggests that correlated cis-trans isomerizations cause also rotation of the phenyl group and hence contribute to the depolarized Rayleigh spectrum. The value of this τ_{NMR} referring to the viscosity and temperature ratio (η_s/T) of the present light-scattering experiment amounts to 0.18 ± 0.08 ns. If this motion is also probed by depolarized Rayleigh scattering, then the relaxation time, τ, of the fast component is slowing down by the positive intramolecular factor, $1 + F$. The value of $\tau_{NMR}(1 + F) = 0.4 \pm 0.1$ ns is in fair agreement with the experimental $\tau = 0.5 \pm 0.1$ ns.

The dilute solution activation energy of phenylene group motion is 13 ± 5 kJ/mol, which is to contrast with the value of 50 ± 8 kJ/mol characterizing the rather facile phenylene rotational motions in the glassy PC.[1,34] It has recently been shown that the coupling model of relaxation can explain this pertinent difference only after site heterogeneity in the glassy PC has been encountered in the model.[34] The activation energy obtained from the temperature dependence of the Lorentzian depolarized Rayleigh spectra of the oligomer PC solutions amounts to 12 ± 2 kJ/mol. This value agrees with the dilute solution activation energy derived from the NMR spin-lattice relaxation times. Theoretical quantum mechanical calculations on terephthalic acid representative of the PC monomer have recently been undertaken.[28] The energy barrier estimated for the extensive 180° flip rotation of the phenyl rings is 40 kJ/mol whereas their small-amplitude (~30°) oscillations have a low rotation barrier of about 12 kJ/mol. Similarly, local segmental motion, such as cis-trans isomerization about C-O bonds, should easily occur and can provide low-barrier mechanisms for 180° ring flips.[16,35]

Finally, we should notice the nearly twice longer relaxation time in pentamer also at 85 °C (Table III). This might suggest that the segmental motion in oligomers is different from the cooperative conformational transitions at higher M and probably with different volume requirements. In this context, it is worth mentioning that the relaxation time of the broad component in PS[5] (with the phenyl group on the side chain) correcting to our η_s (=0.6 cP) and T = 85 °C is 1.3 ± 0.3 ns. This value is nearly twice the value for the PC with the phenyl groups in the main chain. The intramolecular correlation factor, $1 + F$, is very similar in both polymers whereas the potential barrier seems to be higher in PC.[3,14]

Conclusions

The configurational average optical anisotropy, $\langle\gamma^2\rangle/x$, of polycarbonate with degree of polymerization, x, in the range x = 1-163 was obtained from the lower frequency depolarized Rayleigh spectra of dilute PC solutions in dioxane at 25 °C. The optical anisotropy, β^2, of the monomer and the mean $\langle\gamma^2\rangle/x$ of the polymer treated as constitutive property using group anisoptropies are in good agreement with the experimental values.

The depolarized Rayleigh spectra of the monomer and two oligomers were found to be well represented by a single Lorentzian line due to the overall and segmental orientation, respectively, under rather slip hydrodynamic conditions. Alternatively, a sum of two Lorentzians of roughly equal intensity produces an adequate fit of the experimental spectra of dilute polycarbonate solutions with $x \geq 18$. The width of the broad Lorentzian is insensitive to variations in molecular weight and is therefore related to local segmental motions in the chain. The corresponding relaxation time is slower than the segmental relaxation and phenylene rotation time extracted from NMR measurements, probably due to the effect of intramolecular correlations on the former. On the other hand, the relaxation time of the narrow Lorentzian component of the depolarized Rayleigh spectrum is associ-

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ated with the overall molecular tumbling characterized by the first normal-mode time, τ_1, strongly affected by polydispersity.

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Registry No. $CH_3OC_6H_4C(CH_3)_2C_6H_4OCO_2CH_3$, 124919-83-1; (Bisphenol A)(PC) (SRU), 24936-68-3; (Bisphenol A)(PC) (copolymer), 25037-45-0.

Reaction Rates in Ionomer Solutions. 2. Search for the Kinetic Excluded Volume Effect

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ABSTRACT: The rate of HCl transfer from aminostyrene copolymers of methyl methacrylate to (dimethylamino)ethyl methacrylate copolymers of methyl methacrylate was measured in toluene solution by using a stopped-flow apparatus with fluorescence detection, varying the length of the polymers carrying the interacting groups. Although theories predicted that groups attached close to the polymer chain ends would react faster, no decay of the apparent rate constant with increasing conversion was observed. For reactions between polymers of similar chain length, the rate constant decayed as the 0.6 power of the molecular weight. When the interacting groups were attached to polymers which are immiscible in bulk, the HCl transfer rate was reduced. Solvation of the aminostyrene hydrochloride residues by methanol or ethyl acetate accelerated sharply the reaction rate. There was no evidence for an effect on the reaction rate when sufficient poly(methyl methacrylate) was added to the solution of the interacting copolymers to exceed the critical chain overlap concentration.

Introduction

Recently, we embarked on a study of the kinetics of reactions involving the ion pairs in ionomer solutions. In the first investigation of this type,[1] we mixed in a stopped-flow apparatus solutions of slightly sulfonated polystyrene partially neutralized with 2-(aminomethyl)naphthalene and 9-(aminomethyl)anthracene, respectively. As long as these counterions were associated with different polymer chains, irradiation in the naphthalene absorption band led to little nonradiative energy transfer,[2] since the donor and acceptor fluorophores were too distant from one another. However, increasing counterion interchange led to an increasing association of both counterions with the same chain molecule, and the increasing efficiency of energy transfer (i.e., emission from the

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