Macromolecules **1994,** *27,* 7429–7432

Direction of the Dipole Moment in the Ester Group of Poly(ϵ-caprolactone)[†]

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Received July 28, 1994; Revised Manuscript Received September 15, 1994[®]

ABSTRACT: The low-frequency dielectric permittivity of a dioxane solution of poly(ϵ-caprolactone) was reinvestigated at a lower concentration than in earlier work. The recalculated magnitude of the dipole-moment component parallel to the virtual bond in an ester group is 0.64 D.

Introduction

The magnitudes of the dipole moments of aliphatic ester groups, determined from dielectric measurements on dilute solutions in nonpolar solvents, are quite insensitive to the chemical structure of these compounds.[1] For example, dipole moment values for methyl formate,[2] ethyl propionate,[3] and *n*-propyl propionate,[4] in benzene are reported as 1.77, 1.83, and 1.79 D, respectively. Specification of the direction of the dipole moment within an ester is a less straightforward matter. Ester groups at ordinary temperatures exist predominantly in the planar *trans* configuration. The direction of the moment in the plane of the ester group has been estimated by several different experimental methods and calculation procedures. The microwave spectra of several organic acids,[5,6] aldehydes,[6,7] and esters[7–9] in the gas phase lead to values for the barriers hindering internal rotation as well as magnitudes and directions of dipole moments. The direction of the dipole moment in the ester group has also been estimated by considering the experimental dipole moment values of a number of molecules containing two ester groups.[10] The results of these investigations[7–10] as well as estimates based on vector addition of bond dipole moments[11,12] show considerable scatter of the value of the dipole-moment angle in the plane of the ester group.

The present study extends and modifies earlier work from this laboratory[13,14] on the dielectric properties of solutions of poly(ϵ-caprolactone) (PCL), from which the magnitude and direction of the ester dipole had also been estimated. This determination is possible because the repeat units are arranged head-to-tail and each ester dipole has a component parallel to the virtual bond[12] and therefore produces a so-called[15] Type A or normal-mode relaxation process with a frequency of maximum loss that decreases rapidly with increasing molecular weight of the polymer. In dilute solution, this process is well described by the standard Zimm model[16] and is due principally to the terminal relaxation mode. For sufficiently high molecular weights, the normal-mode loss peak falls in the audio- or radio-frequency range, as in the example presented in this paper. A second loss peak (and corresponding decrease of the dielectric constant) occurs at much higher frequencies independent of molecular weight. It comes[13] at about 3 GHz for PCL in dioxane at 25 °C and is due to the ester dipole component perpendicular to the virtual bond. The posssibility of such multiple dielectric relaxation behavior was first pointed out by Van Beek and Hermans,[17] who employed the Rouse model. Their work was later generalized[18] to allow for hydrodynamic interactions as in the Zimm[16] model and for more general charge distributions along the polymer chain. A general review of normal-mode dielectric behavior has recently been given by Adachi and Kotaka,[19] and a rigorous discussion of the conformational problem is due to Mansfield.[20]

Here we present data for only a single solution of PCL in dioxane at a lower concentration than those used in the earlier work, which were all in the overlap region, $c > 1/[\eta]$, and thus required an uncertain extrapolation. We have also revised and extended the related calculations.

Since completion of our work (actually done over 5 years ago), more extensive studies of both PCL and poly(ϵ-valerolactone) in benzene have been performed by Adachi and co-workers.[21,22]

Experimental Section

1. Materials. ϵ-Caprolactone (Aldrich) was dried with calcium hydride for 3 days and then distilled over calcium hydride under argon at 0.1 mmHg pressure. The fraction of bp 64 °C was collected and stored under argon.

Benzene and dioxane were purified by refluxing over sodium under nitrogen for about 30 h and subsequently distilling under nitrogen.

2. Sample Preparation and Characterization. Poly(ϵ-caprolactone) was prepared by the method described by Morton and Wu.[23] Polymerization was carried out in a three-necked round flask. Benzene, *n*-butyllithium, and then monomer were introduced into the flask under an argon blanket. In benzene solution, concentrations of monomer and initiator were 1 and 5×10^{-3} M, respectively. Polymerization was carried out at 25 °C for a period of 6 min. The reaction was then terminated and the polymer stabilized by addition of aqueous HCl. The polymer was precipitated in methanol, filtered, and dried in a vacuum oven overnight. Conversion was 100%.

The intrinsic viscosity of resulting PCL was determined as 0.620 dL/g in dioxane at 25 °C. From the relation given by Jones, Stockmayer, and Molinari (JSM),[14]

$$[\eta] = 9.0 \times 10^{-4} M_v^{\,0.61} \qquad (1)$$

[†] Dedicated to Professor J. J. Hermans on the occasion of his 85th birthday.

[®] Abstract published in *Advance ACS Abstracts,* November 1, 1994.

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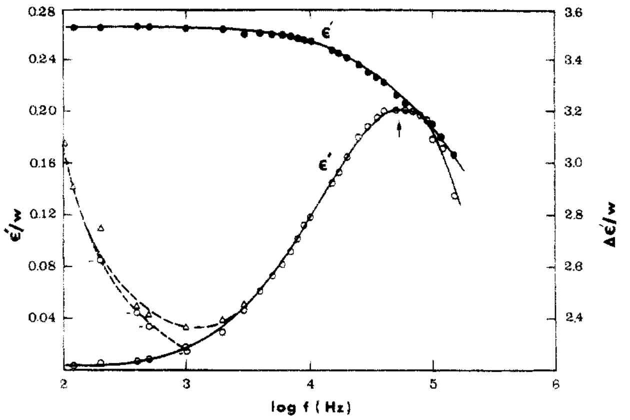

Figure 1. Dielectric constant and loss factor for a solution of poly(ε-caprolactone) in dioxane at a concentration of 1.25% w/w at 25 °C. Upper full curve and right-hand ordinate, dielectric constant; lower curve and left-hand ordinate, loss factor. The upper dashed curve is the observed loss factor; the full curve is obtained by subtraction of the hyperbolic lower dashed curve due to ionic conductance, as described in the text.

the viscosity-average molar mass is 45 × 10^3. The molar mass distribution was observed by GPC, and the polydispersity index M_w/M_n was found to be 1.27 ($M_n = 38 \times 10^3$, $M_w = 49 \times 10^3$, in THF with styrene standard). This degree of polymolecularity is greater than would be expected for conventional living polymers and is understood[23] as being due to intra- and intermolecular ester-interchange reactions between active chain ends and ester groups. The resulting chain-length distribution has been treated theoretically by Hermans.[24]

The sample just described is the same one used in a study of dielectric relaxation in the ternary system PCL/poly(4-chlorostyrene)/dioxane.[25]

3. Dielectric Measurements. The dielectric permittivities of dioxane and benzene solutions of PCL were measured over the frequency range from 100 Hz to 150 kHz with a General Radio Co. Type 1620-A capacitance and dielectric loss measuring assembly. This radio-frequency bridge was supplemented by General Radio 1330 and Hewlett Packard Type-120 oscillators to cover all frequencies in the above-mentioned range. The samples were contained in a Balsbaugh Laboratory Model 350-G three-terminal cell. The cell was introduced into a brass jacket and tightly closed with a Teflon cover. The temperature of the cell was maintained to within 0.02 °C by immersion in a water thermostat. All solutions were prepared by weighing both components. Only the dioxane results are presented here.

Results and Discussion

Figure 1 shows the dielectric permittivity of a dilute solution (1.25% w/w) of PCL in dioxane at 25 °C. In contrast to the earlier work,[14] this solution is more dilute than the overlap concentration, $c^* \cong 1/[\eta] \cong 1.6\%$ w/w, for this sample. The apparent loss factor ϵ''_{app} (dotted curve) is made up of two independent contributions and may be expressed as

$$\epsilon''_{\text{app}} = kf^{-1} + \epsilon'' \tag{2}$$

where the last term is due to inevitable ionic impurities, with k proportional to the specific ionic conductance. Since the dipole loss factor ϵ'' is proportional to f at low frequencies,[26] extrapolation of a plot of $f\epsilon''_{\text{app}}$ against f^2 leads to the value of k and thus to evaluation of ϵ'' itself (full curve), which is seen to have its maximum at 60 kHz. The low-frequency limiting value of $\Delta\epsilon'$ is about 4% smaller than that obtained by JSM[14] at 30 °C at higher concentrations and with a different cell. We have no explanation for this rather large difference.

The dielectric increment $\Delta\epsilon'$ (excess of dielectric constant over that of the pure solvent) has two contributions corresponding to the longitudinal and transverse components of the ester dipole, respectively. The mean square longitudinal dipole moment of a polymer chain containing x repeat units (ester linkages) is given by[20]

$$\langle \mu_{\text{p}}^2 \rangle = \langle \mu \cdot \mathbf{r} \rangle^2 / \langle r^2 \rangle = x D_\infty m_{\text{p}}^2 \alpha_r^2 \tag{3}$$

where μ is the instantaneous total dipole moment vector and $\mathbf{r}$ is the end-to-end vector. In the second relation, D_∞ is the dipole-moment ratio[12] of the unperturbed chain, m_{p} is the magnitude of the longitudinal component (parallel to the virtual bond) of ester-group dipole, and α_r^2 is the expansion factor for the mean square end-to-end distance.

For the transverse contribution, we have

$$\langle \mu_{\text{s}}^2 \rangle = x D_\infty m_{\text{s}}^2 \tag{4}$$

where m_{s} is the magnitude of the ester dipole perpendicular to the virtual bond. It is observed that the transverse moment has no expansion factor. Equations 3 and 4 are consistent with Mansfield's[20] theory.

Taking polydispersity into account, we may now formulate the two contributions to the dielectric increment $\Delta\epsilon'$ (excess of dielectric constant over that of pure solvent) as follows, where $\Delta\epsilon'_0$ is the limiting low-frequency value of $\Delta\epsilon'$ and $\Delta\epsilon'_{\text{u}}$ is the plateau value (end of the normal-mode region):

$$(\Delta\epsilon'_0 - \Delta\epsilon'_{\text{u}})/w = 4\pi N_{\text{A}} d_1 (\epsilon_1 + 2)^2 D_\infty m_{\text{p}}^2 \alpha_r^2 / 27 k_{\text{B}} T M_0 \tag{5}$$

$$(\Delta\epsilon'_{\text{u}}/w)(\epsilon_1 + 2)^{-2} - 2n_1(\Delta n/w)(n_1^2 + 2)^{-2} = 4\pi N_{\text{A}} d_1 D_\infty m_{\text{s}}^2 / 27 k_{\text{B}} T M_0 \tag{6}$$

These relations are appropriate to c.g.s. units and correspond to the treatment of Guggenheim[27] and Smith[28] with neglect of a possible small contribution due to vibrational polarization. The symbol M_0 stands for the molar mass (= 114 g mol^{-1}) of a repeat unit; N_{A} is Avogadro's number; $k_{\text{B}}T$ has its usual meaning; n is refractive index for visible light (here 546 nm); d_1 is solvent density; ϵ_1 and n_1 are solvent static dielectric constant and refractive index; w is weight fraction of solute; and α_r^2 is a weight-average value.

From Figure 1 we obtain $(\Delta\epsilon'_0/w) = 3.53$. The quantity $(\Delta\epsilon'_{\text{u}}/w)$ represents the plateau between the low- and high-frequency processes, but the data in Figure 1 do not extend to sufficiently high frequencies to afford a reliable direct extrapolation. We have two alternate routes that yield identical results: (1) interpolation to 25 °C of the earlier[13] data for 15, 30, and 55 °C; or (2) assumption of a descent of $(\Delta\epsilon'/w)$ centered about the value 3.24 at the inflection point corresponding to the maximum loss factor at 60 kHz. Both routes give $(\Delta\epsilon'_{\text{u}}/w) = 2.95$. We also take[14] $(\Delta n/w) = 0.0505$.

From the intrinsic viscosities[14] in dioxane and in a Θ solvent and using an appropriate Schulz–Zimm distribution, we calculate

$$\alpha_r^2 = \Sigma W_i \alpha_{ri}^2 = 1.33$$

for the present sample. Further, we rely on a calculation by Flory and Williams,[29] who obtained $D_\infty = 0.98$

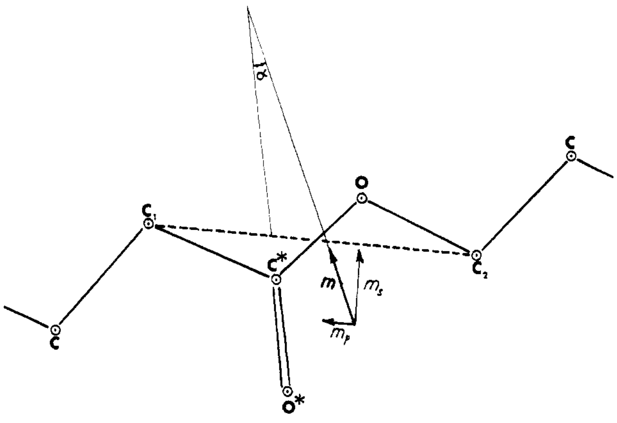

Figure 2. Monomer unit of poly(ϵ-caprolactone) with the virtual bond (- - -) spanning the rigid ester group. The geometry is described by the following bond lengths (in Å) and bond angles: $C_1C^* = 1.51$, $C^*O^* = 1.22$, $C^*O = 1.33$, $OC_2 = 1.44$; $\angle C_1C^*O^* = 120°$, $\angle O^*C^*O = 124°$, $\angle C^*OC_2 = 113°$. Calculated length of virtual bond $C_1C_2 = 3.66$ Å. The longitudinal and transverse group moments m_p and m_s and the net moment m are shown by arrows pointing in the positive direction. Also shown is the angle α between m and C*O*. In the earlier calculation of JSM[14] the other direction was taken for m_p.

for poly(ϵ-caproamide) and opined that the same figure would serve for the polylactone. The numerical results obtained from eqs 3–6 are

$$m_p = 0.64 \text{ D} \qquad (7)$$

$$m_s = 1.60 \text{ D} \qquad (8)$$

The value of m_s is almost the same as that reported by JSM,[14] for the new figure for m_p is considerably smaller, partly because the new value of $(\Delta\epsilon'_0/w) = 3.53$ is lower but also because the earlier value implicitly included the expansion factor and thus really corresponds to $\alpha_r m_p$. If we take this circumstance into account, the JSM results correspond to about $m_p = 0.74$ D.

Equations 7 and 8 yield a total ester dipole moment, $m = (m_p^2 + m_s^2)^{1/2} = 1.72$ D, which is visibly smaller than the typical values quoted earlier for simple aliphatic esters. We therefore also consider the alternative treatment by Adachi and Kotaka,[19,29] who consider that the internal field factor $(\epsilon_1 + 2)/3$ is applicable to a sequence of connected longitudinal dipoles producing a low-frequency "normal-mode" relaxation process. Thus, in place of eq 5, they would write

$$(\Delta\epsilon'_0 - \Delta\epsilon'_u)/w = 4\pi N_A d_1 D_\infty m_p^2 \alpha_r^2 / 3k_B T M_0 \qquad (5')$$

which with our data gives $m_p = 0.90$ D. Since the transverse component is not affected by this maneuver, their method yields a total ester group moment $m = 1.84$ D, possibly a preferable result. However, we are not theoretically convinced that eq 5′ is better than eq 5; and indeed an intermediate situation might obtain, depending on the separation of the adjacent dipoles and the local structure.[31]

To find the direction of the ester-group dipole, we refer to Figure 2, which shows a repeat unit of PCL with the virtual bond spanning the rigid planar *trans* ester group. The bond lengths and bond angles given in the figure caption were taken from tables of interatomic distances and angles.[8,32] The length of the virtual bond is $C_1C_2 = 0.366$ nm. The resulting angle between the dipole-moment vector and the carbonyl C*O* bond is α = 9° if m_p is taken from eq 5 and 17° if eq 5′ is used. If alternatively one adopts the ester-group geometry based on the β-tricaprin or β-triacetin structure,[33,34] only a minor change in α ensues (8 or 16°). Thus our result by either method of calculation is in substantial agreement with the conclusion of Saiz, Hummel, Flory, and Plavsic[10] that α is small.[35] A small value of α is also indicated by recent molecular-mechanics calculations by Smith and Boyd.[35]

An ambiguity remains, however: the *direction* of the vector m_s along the virtual bond is not uniquely determined by the dielectric data, and our choice was made in order to secure a small value of α. If we choose the direction opposite to that shown in Figure 2 as in the earlier study from this laboratory[14] and as suggested by microwave results[2] for methyl formate, we obtain the much larger figure α ≅ 35°. The Osaka group[21] appear to favor such a large value. It has to be concluded that the magnitude of α remains uncertain. A possible effect that has not been considered is the effect of electrostatic dipole–dipole interaction among the ester groups of the chain, which could alter the value of D_∞.

Acknowledgment. The experimental work described here was performed at Dartmouth College and supported by the National Science Foundation, Division of Materials Research, Polymers Program, under Grant DMR-86-08633.

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