Notes

Effect of a Nonpolar Spacing Group on the Type-A2 Dipole Moment of Aliphatic Polyesters

Jindong Ren and Keiichiro Adachi*

Department of Macromolecular Science,
Graduate School of Science, Osaka University,
Toyonaka, Osaka 560-0043, Japan

Received March 10, 2003
Revised Manuscript Received April 14, 2003

Introduction

Aliphatic polyesters possess the type-A dipole moment[1−3] and their dielectric behaviors have been reported by several authors.[4−8] The chemical structure is represented as $[-\mathrm{R}-\mathrm{CO}-\mathrm{O}-(\mathrm{CH}_2)_n-]_m-$ where R is either the $-\mathrm{CH(CH_3)}-$ or $-\mathrm{CH_2}-$ group. The atoms of the ester group $-\mathrm{C}-\mathrm{CO}-\mathrm{O}-\mathrm{C}-$ are on the same plane, and the group can be regarded as a virtual bond as shown in Figure 1. The virtual bond **v** possesses the type-A dipole moment $\mathbf{p}_\mathrm{A}$ parallel to the bond.[3,7] Poly(lactic acid) (PLA) ($n = 0$) does not possess the nonpolar spacing groups and PLA is classified as type-A1.[5,7] The other polyesters of $n \geq 1$ such as poly(varelolactone) (PVL) ($n = 3$) and poly(ϵ-caprolactone) (PCL) ($n = 4$) are classified as type-A2.[5,7]

In the type-A1 chains, the dipole vectors are directly linked and hence the total dipole vector $\mathbf{P}_\mathrm{A}$ of the chain is exactly proportional to the end-to-end vector **r**. On the other hand, the dipole vectors of the repeat units of the type-A2 chains are linked via nonpolar spacing groups and therefore the statistical average of $\mathbf{P}_\mathrm{A}$ is proportional to the average of **r**:

$$\langle \mathbf{P}_\mathrm{A} \cdot \mathbf{r} \rangle = \mu \langle \mathbf{r}^2 \rangle \tag{1}$$

where μ is the dipole moment per unit contour length. In this note, we report the results of dielectric measurements on poly(ω-pentadecalactone) (PPDL) ($n = 13$) focusing our attention on the effect of the long nonpolar spacing group on the dipole moment of the type-A2 polymers. We also report the calculation of the constant μ of eq 1 for the aliphatic polyesters of varying n and compare the results with the relaxation strengths for solutions of PLA, PVL, PCL, and PPDL.[6−8]

Experimental Section

Poly(ω-pentadecalactone) was synthesized by polymerization of ω-pentadecalactone as reported by Ajay et al.[9] Pentadecalactone and lipase were purchased from Aldrich (San Francisco, CA) and Wako Chemicals (Tokyo, Japan), respectively. The polymer thus synthesized was fractionated with tetrahydrofuran/n-hexane mixed solvents at 320 K. The weight-average molecular weight M_w and the polydispersity $M_\mathrm{w}/M_\mathrm{n}$ were determined to be 15 400 and 1.20, respectively. The methods of the sample characterization and dielectric measurements were described previously.[7,8]

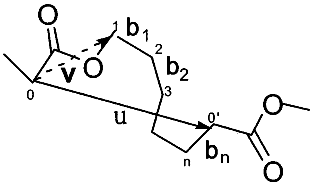

Figure 1. Structure of aliphatic polyesters and the relationship among the vectors **v**, $\mathbf{b}_i$, and **u**.

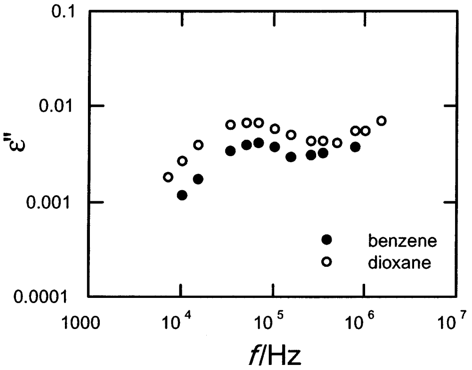

Figure 2. Frequency f dependence of dielectric loss factor ϵ'' of 20 wt % solutions of PPDL in benzene (●) and in dioxane (○).

Dielectric Relaxation in PPDL Solution

Dielectric measurements were carried out on 20 wt % solutions of PPDL in dioxane and benzene at 343 K. We did not carry out the measurements at room temperatures since PPDL does not dissolve in any solvents at room temperature due to crystallization. The ϵ'' curve is shown in Figure 2. A very weak loss peak was observed as shown in this figure. On account of the low intensity, we did not carry out measurements on solutions with C less than 20%. The increase of ϵ'' in the low-frequency region is due to the dc conduction, and that in the high-frequency region is due to local segmental motions. Using the standard methods of the analyses of dielectric data, we determined the dielectric relaxation strength $\Delta\epsilon$; i.e., $\Delta\epsilon = 0.0084$ for the benzene solution, and $\Delta\epsilon = 0.019$ for the dioxane solution. The error in this determination is ca. 10%.

The theoretical relaxation strength $\Delta\epsilon$ for a solution of concentration C (in g/cm^3) of a type-A polymer with molecular weight M is given by[2]

$$\frac{\Delta\epsilon}{C} = \frac{4\pi N_\mathrm{A} \mu^2 \langle r^2 \rangle}{3 k_\mathrm{B} T M} F \tag{2}$$

where $\langle r^2 \rangle$ is the mean square end-to-end distance, N_A

---

* Corresponding author: Telephone/Fax: +81 66850 5464. E-mail: adachi@chem.sci.osaka-u.ac.jp.

10.1021/ma034299s CCC: $25.00

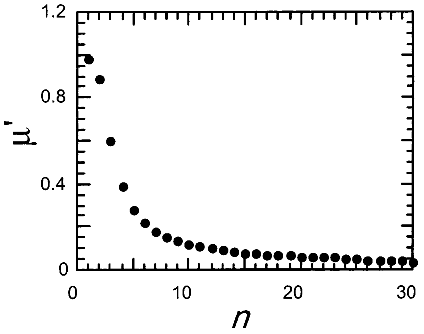

Figure 3. Dependence of the dipole moment per unit contour length μ' on the number of the carbon atoms of the nonpolar spacing group of polyester chains.

the Avogadro number, k_BT the thermal energy, and F the internal field factor. This equation indicates that $\Delta\epsilon/C$ is independent of M in the unperturbed state. In the present study, measurements were made on a 20% solution in which the excluded volume effect is almost shielded.

Previously we reported the dielectric normal mode relaxation in benzene solutions of PLA, PVL, and PCL.[5,7] Using the data at concentration C of 0.20 g/cm^3, the values of $\Delta\epsilon/C$ at 298 K for solutions of PLA, PVL, and PCL are determined to be 4.47, 1.12, and 0.74 cm^3/g, respectively, and $\Delta\epsilon/C$ at 343 K for PPDL is 0.041 cm^3/g. We see that $\Delta\epsilon/C$ decreases with increasing number of the methylene groups as expected. We note that $\Delta\epsilon/C$ of PPDL in dioxane is about two times higher than that of benzene solution indicating that the characteristic ratio C_∞ of PPDL depends strongly on the solvent. Similar behavior was observed for PLA; i.e., $\Delta\epsilon/C = 4.47$ in benzene at 20% concentration, but in the undiluted state, $\Delta\epsilon/\rho$ was only 0.67 at 372 K where ρ is the density.[8]

Dipole Moment of Type-A2 Polymers

As mentioned above, the dashed line in Figure 1 can be regarded as a virtual bond and the bond vector is defined as $\mathbf{v}$ (= 0.369 nm). The type A dipole vector $\mathbf{p}_{Aj}$ of the jth unit is parallel to $\mathbf{v}_j$:

$$\mathbf{p}_{Aj} = \mu_o \mathbf{v}_j \qquad (3)$$

where μ_o is the constant and is reported to be 1.11×10^{-11} esu.[8] The bond vectors connecting the CH$_2$ groups are defined as $\mathbf{b}_{jk}$ as shown in Figure 1. The vector $\mathbf{s}_j$ is defined by the sum of $\mathbf{b}_{jk}$: $\mathbf{s}_j = \sum \mathbf{b}_{jk}$ ($k = 1$ to n). The vector connecting C^0 and the carbon atom C$^{0'}$ of the neighboring unit is defined by $\mathbf{u}_j$ as shown in Figure 1. Then the length of the repeat unit is given by $\mathbf{u}_j = \mathbf{v}_j + \mathbf{s}_j$. The projection p_j of the dipole vector $\mathbf{p}_{Aj}$ on the vector $\mathbf{u}_j$ is given by

$$p_j = \frac{\langle \mathbf{p}_{Aj}\cdot\mathbf{u}_j\rangle}{\langle \mathbf{u}_j^{2}\rangle^{0.5}} = \frac{\mu_o\langle \mathbf{v}_j\cdot(\mathbf{v}_j + \mathbf{s}_j)\rangle}{\langle(\mathbf{v}_j + \mathbf{s}_j)^2\rangle^{0.5}} = \mu' u_j \qquad (4)$$

If this preaveraged dipole moment is used in the calculation of μ of eq 1, we obtain

$$\mu = \frac{\langle \mathbf{P}_A\cdot\mathbf{r}\rangle}{\langle \mathbf{r}^2\rangle} \simeq \frac{\langle(\mu'\sum_i \mathbf{u}_i)\cdot(\sum_j \mathbf{u}_j)\rangle}{\langle(\sum_i \mathbf{u}_i)^2\rangle} = \mu' \qquad (5)$$

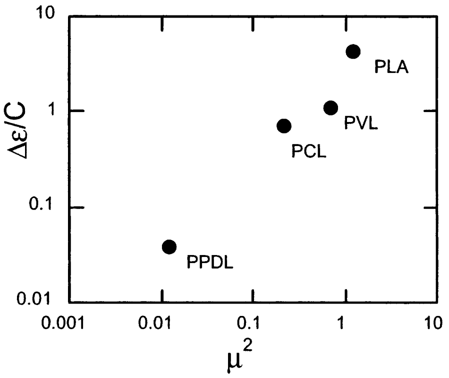

Figure 4. Plot of relaxation strength $\Delta\epsilon$ divided by concentration C against the square of dipole moment μ' for 20% solutions of PLA, PVL, PCL, and PPDL in benzene.

These equations allow us to calculate μ without calculating the vector sum of the dipole moment allover the chain.

Numerical calculation of μ' was performed on the basis of the RIS approximation.[10] Generally the coordinates of the main chain atoms of a chain can be represented in terms of the bond angle θ_j, the angle of internal rotation ϕ_j, and the bond length b_j:

$$\mathbf{x}_{j-1} = \mathbf{T}_j\mathbf{x}_j + \mathbf{b}_j \qquad (6)$$

$$\mathbf{T}_j = \begin{pmatrix} -\cos\theta_j & -\sin\theta_j & 0 \\ \sin\theta_j\cos\phi_j & -\cos\theta_j\cos\phi_j & -\sin\phi_j \\ \sin\theta_j\sin\phi_j & -\cos\theta_j\sin\phi_j & \cos\phi_j \end{pmatrix} \qquad (7)$$

$$\mathbf{x}_j = \begin{pmatrix} x_j \\ y_j \\ z_j \end{pmatrix}, \quad \mathbf{b}_j = \begin{pmatrix} b_j \\ 0 \\ 0 \end{pmatrix} \qquad (8)$$

where $\mathbf{x}_j$ is the coordinate of the jth atom. ϕ_j is defined so that $\phi_j = 180°$ for the trans state and $\theta_j = 109°$. b_j is the bond vector between the atoms $j - 1$ and j. The calculation was performed as follows. First the set of $\{\phi_j\}$ was generated by using random numbers so that the probabilities of the occurrence of trans (t), gauche$^+$ (g$^+$), and gauche$^-$ (g$^-$) are proportional to the Boltzmann factor for the corresponding isomeric states. Here the energy difference between the trans and gauche states of polymethylene was taken to be 2.1 kJ/mol (=500 cal/mol) as reported by Flory.[10] The energy difference between the trans and gauche states of the bond $\mathbf{b}_1$ is estimated by Flory to be 430 ±70 cal/mol for polyoxyethylene.[10] We assumed that the energy is the same as that for polymethylene since the difference is small. The conformations of g$^+$g$^-$ or g$^-$g$^+$ were avoided due to the so-called pentane effect. Second the calculation of eq 6 was performed and the vector $\mathbf{u}$ was determined. Then the scalar product $\mathbf{u}\cdot\mathbf{p}_A$ was determined. This procedure was repeated and the average of $\langle\mathbf{u}\cdot\mathbf{p}_A\rangle$ was determined. The sampling number of 1000 gave almost the constant value of $\langle\mathbf{u}\cdot\mathbf{p}_A\rangle$ but we repeated the calculation 5000 times to make sure. Thus, the calculated μ' is plotted against n in Figure 3. We see that μ' decreases steeply around $n = 4$ but decays very gradually in the range of n above 10.

Figure 4 shows the double logarithmic plot of $\Delta\epsilon/C$ of PLA, PVL, PSL, and PPDL against μ'^2. It is seen that the plot conforms approximately to a line of slope 1, indicating that the value of $\langle r^2\rangle/M$ is almost independent of the number of the methylene groups. The small deviation from the straight line is due to the approximation of eq 5 and due to the dependence of C_∞ on the chemical structure of the polyesters. For further studies, we need the data for the chain dimensions of these polyesters.

References and Notes

(1) Stockmayer, W. H. *Pure Appl. Chem.* **1967**, *15*, 539.
(2) Adachi, K.; Kotaka, T. *Prog. Polym. Sci.* **1993**, *18*, 585.
(3) Adachi, K. In *Dielectric Spectroscopy of Polymeric Materials*; Runt, J. P., Fitzgerald, J. J., Eds.; American Chemical Society: Washington, DC, 1997; Chapter 9.
(4) Jones, A. A.; Stockmayer, W. H.; Molinari, R. J. *J. Polym. Sci., Polym. Symp.* **1976**, *54*, 227.
(5) Urakawa, O.; Adachi, K.; Kotaka, T.; Takemoto, Y.; Yasuda, H. *Macromolecules* **1994**, *27*, 7410.
(6) Baysal, B. M.; Stockmayer, W. H. *Macromolecules* **1994**, *27*, 7429.
(7) Ren, J.; Urakawa, O.; Adachi, K. *Polymer* **2003**, *44*, 847.
(8) Ren, J.; Urakawa, O.; Adachi, K. *Macromolecules* **2003**, *36*, 210.
(9) Kumar, A.; Kalra, B.; Dekhterman, A.; Gross, R. A. *Macromolecules* **2000**, *33*, 6303.
(10) Flory, P. J. *Statistical Mechanics of Chain Molecules*; Wiley: New York, 1971.

MA034299S