Macromolecules 1990, 23, 1139–1144

(7) Nyström, B.; Boileau, S.; Hemery, P.; Roots, J. *Eur. Polym. J.* **1981**, *17*, 249.
(8) Layec, Y.; Layec-Raphalen, M.-N. *J. Phys., Lett.* **1983**, *44*, L-121.
(9) Kim, H.; Chang, T.; Yohanan, J. M.; Wang, L.; Yu, H. *Macromolecules* **1986**, *19*, 2737.
(10) Wheeler, L. M.; Lodge, T. P.; Hanley, B.; Tirrell, M. *Macromolecules* **1987**, *20*, 1120.
(11) Nemoto, N.; Okada, S.; Inoue, T.; Kurata, M. *Macromolecules* **1988**, *21*, 1502; 1509.
(12) Brown, W.; Zhou, P. *Macromolecules* **1989**, *22*, 4031.
(13) von Meerwall, E. D.; Amis, E. J.; Ferry, J. D. *Macromolecules* **1985**, *18*, 260.
(14) Wesson, J. A.; Noh, I.; Kitano, T.; Yu, H. *Macromolecules* **1984**, *17*, 782.
(15) Jakes, J., submitted for publication in *Czech. J. Phys.*
(16) Provencher, S. W. *Makromol. Chem.* **1979**, *180*, 201.
(17) Geissler, E.; Hecht, A.-M. *J. Phys. Lett.* **1979**, *40*, L-173.
(18) Amis, E. J.; Han, C. C. *Polymer* **1982**, *23*, 1403.
(19) Amis, E. J.; Janmey, P. A.; Ferry, J. D.; Yu, H. *Macromolecules* **1983**, *16*, 441.
(20) Amis, E. J.; Han, C. C.; Matsushita, Y. *Polymer* **1984**, *25*, 650.
(21) Kolinski, A.; Skolnick, J.; Varis, R. *J. Chem. Phys.* **1987**, *86*, 1567, 7164, 7174.
(22) Brown, W.; Stilbs, P.; Johnsen, R. M. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 1029.
(23) Phillies, G. D. J. *J. Chem. Phys.* **1974**, *60*, 983; **1983**, *79*, 2325.
(24) Pusey, P. N.; Fijnaut, H. M.; Vrij, A. *J. Chem. Phys.* **1982**, *77*, 4270.
(25) Benmouna, M.; Benoit, H.; Duval, M.; Akcasu, Z. *Macromolecules* **1987**, *20*, 1107, 1112.
(26) Hanna, S.; Hess, W.; Klein, R. *Physica A (Amsterdam)* **1982**, *111A*, 181.
(27) Altenberger, A. R.; Tirrell, M. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 909.
(28) Feed, K. F. *J. Chem. Phys.* **1983**, *79*, 6357.
(29) Ohta, T.; Oono, Y. *Phys. Lett.* **1982**, *89A*, 460.
(30) Oono, Y.; Baldwin, P. R.; Ohta, T. *Phys. Rev. Lett.* **1984**, *53*, 2149.
(31) Batchelor, G. K. *J. Fluid Mech.* **1976**, *52*, 245.
(32) Hess, W.; Klein, R. *Physica A (Amsterdam)* **1976**, *85*, 509.
(33) Wiltzius, P.; Haller, H. R.; Cannell, D. S.; Schaefer, D. W. *Phys. Rev. Lett.* **1983**, *51*, 1183.
(34) Burchard, W., in press.
(35) Štěpánek, P.; Perzynsski, R.; Delsanti, M.; Adam, M. *Macromolecules* **1984**, *17*, 2340.
(36) Brown, W.; Johnsen, R. M.; Štěpánek, P.; Jakes, J. *Macromolecules* **1988**, *21*, 2859.
(37) Deschamps, H.; Léger, L. *Macromolecules* **1986**, *19*, 2760.
(38) Zhou, P.; Brown, W. *Macromolecules* **1989**, *22*, 890.
(39) Langevin, D.; Rondelez, F. *Polymer* **1978**, *14*, 875.
(40) Cukier, R. I. *J. Chem. Phys.* **1983**, *79*, 3911.
(41) Cukier, R. I. *Macromolecules* **1984**, *17*, 252.
(42) Ogston, A. G.; Preston, B. N.; Wells, J. D. *Proc. R. Soc. London, A* **1973**, *333*, 297.
(43) Altenberger, A. R.; Tirrell, M.; Dahler, J. S. *J. Chem. Phys.* **1986**, *84*, 5122.
(44) Phillies, G. D. J.; Ullmann, G. S.; Ullmann, K. *J. Chem. Phys.* **1985**, *82*, 5242.
(45) Ullmann, G. S.; Ullmann, K.; Lindner, R. M.; Phillies, G. D. J. *J. Phys. Chem.* **1985**, *89*, 692.
(46) Brochard, F.; de Gennes, P.-G. *Macromolecules* **1977**, *10*, 1157.
(47) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: London, 1979.
(48) Pike, E. R.; Pomeroy, W. R. M.; Vaughan, J. M. *J. Chem. Phys.* **1975**, *62*, 3188.
(49) von Meerwall, E. B. *J. Magn. Reson.* **1982**, *50*, 409.
(50) Eisele, M.; Burchard, W. *Macromolecules* **1984**, *17*, 1636.
(51) Sedlak, M.; Konak, C.; Štěpánek, P.; Jakes, J. *Polymer* **1987**, *28*, 873.
(52) Brown, W.; Stepanek, P. *Macromolecules* **1988**, *21*, 1791.
(53) Ito, K.; Okumura, H.; Yoshida, H.; Ueno, Y.; Ise, N. *Phys. Rev. B* **1988**, *38* (15), 10852.
(54) Ito, K.; Nakamura, H.; Yoshida, H.; Ise, N. *J. Am. Chem. Soc.* **1988**, *110*, 6955.
(55) Antonietti, M., personal communication.
(56) Meier, G., personal communication.

Registry No. PEO, 25322-68-3; CH_3OH, 67-56-1; SiO_2, 7631-86-9; stearic acid, 57-11-4.

Dipole Moments and Kerr Constants of Dibenzoates of Some Diols with Different Numbers of Methylene Units as Model Compounds for Polyesters

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ABSTRACT: Dipole moments and Kerr constants of dibenzoates of several diols have been measured at 25 °C. The general structure of these compounds can be represented as $C_6H_5COO(CH_2)_mOOCC_6H_5$ with $m = 2$–6. Dipole moments were obtained from determinations of dielectric constants and refractive indices in benzene solutions. The experimental results for the mean square dipole moments were $\langle\mu^2\rangle = 7.58$, 6.71, 7.20, 7.43, and 7.74 D^2 for $m = 2$, 3, 4, 5, and 6 respectively. Kerr constants were evaluated from measurements of electric birefringence of solutions in cyclohexane (nearly isotropically polarizable solvent); experimental values obtained for $m = 2$, 3, 4, 5, and 6 were respectively ${}_mK = 29.1$, 6.9, 11.6, 9.4, and 12.3 all in 10^{-25} $m^5\ V^{-2}\ mol^{-1}$. Theoretical analysis was performed with standard method of the rotational isomeric states model. Comparison of theory with experiment indicates that $\langle\mu^2\rangle$ is almost insensitive to the conformational energies, particularly for $m > 3$; in fact, the free rotating model gives a reasonably good account for $\langle\mu^2\rangle$ for all of these molecules. Kerr constants are much more sensitive to the conformational energies. Good agreement between theoretical and experimental values of both dipole moments and Kerr constants of all these compounds is achieved by adjustment of the optical parameters and the position of the rotational isomers.

Introduction

Polyesters obtained by condensation of terephthalic acid (or any of its isomers) with different diols are an interesting kind of polymer whose repeating unit can be schematized as $C_6H_5COO(R)_mOOC$ where R represents a methylene (CH_2) group. Such repeating units combine a rigid residue coming from the acid with a flexible segment provided by the diol. The length of the flexible residue is controlled by the number m of R groups,

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and it modifies many of the macroscopic properties of the polymer.

Several properties of this kind of polymer and of some model compounds have been studied from both theoretical and experimental points of view. In some of these studies, Conformational Statistics methods were used to investigate the influence of the microstructure of the polymer on the macroscopic properties. One of the most frequently employed procedures consists of a comparison between theoretical and experimental values of some conformation-dependent properties, followed by an optimization of the parameters used in the theoretical calculations. Thus, both experimental and theoretical values of unperturbed dimensions[1,2] and dipole moments[2,3] of poly(ethylene glycol terephthalate) were reported more than 20 years ago. Many conformational properties of poly(diethylene glycol terephthalate) such as dimensions,[4] dipole moments,[4] thermoelastic behavior,[5] strain birefringence,[6] and Kerr constants[7] have also been studied. Dipole moments of poly(triethylene glycol terephthalate)[8] and of diesters obtained by condensation of isophthalic[9] and phthalic[10] acids have been reported in recent years. Recently, intramolecular excimer fluorescence of several polyesters as a function of the number of either ethylene oxide[11] or methylene[12,13] units as flexible spacers between chromophores has been studied.

However, despite the interest in this kind of polymers and the number of studies published to date, the conformational energies of the flexible residues are far from being elucidated. Flory assigned values[2,14] of $\sigma = 0.5$ and $\sigma_1 = 1.5$ to the first-order statistical weights of gauche versus trans states of $C^*O-CH_2CH_2$ and OCH_2-CH_2O bonds, respectively; thus, trans states of $C^*O-CH_2CH_2$ are about 0.4 kcal/mol lower than those of their corresponding gauche conformations (i.e., $E_\sigma = 0.4$), whereas in the case of the OCH_2-CH_2O the gauche conformations are lower in energy (i.e., $E_{\sigma_1} = -0.25$) than the trans. Furthermore, Flory postulated that E_{σ_1} should be approximately the same for either polyesters or polyoxides. Values of E_{σ_1} ranging from -0.4 to -0.2 were obtained by Abe and Mark[15] for several model compounds of polyoxides after adjustment of this energy in order to reproduce unperturbed dimensions and dipole moments of these compounds. However, completely different results with values of E_{σ_1} as high as +1 kcal/mol were obtained by Miyasaka et al.[16,17] also from the analysis of dipole moments of some model compounds of polyoxides. The pair of values $E_\sigma = 0.4$, $E_{\sigma_1} = -0.25$ kcal/mol has been used in the analysis of some polyesters.[1-4] The value of E_{σ_1} was later changed to -0.8 kcal/mol as a result of the analysis of the NMR spectra of diethylene glycol dibenzoate[18] and this has probably been the value most commonly used in studies of polyesters.[5-7,9-12] However, when the number of methylene units between the oxygen atoms increases, as happens in poly(triethylene glycol terephthalate), the value of E_{σ_1} seems to decrease in absolute value[8] to ca. 0.0 to -0.2 kcal/mol. Finally, Bahar and Mattice[13] have recently performed a conformational analysis of some model compounds of polyesters and obtained several discrepancies with the values used before.[10]

In view of the situation outlined above, we thought that it would be interesting to study the conformational energies of polyesters, performing a simultaneous analysis of two values that have proven to be very useful for this kind of study in many systems, namely, dipole moments and Kerr constants. With this purpose, five model compounds having schematic structures of $C_6H_5COO(CH_2)_mOOCC_6H_5$ were synthesized by condensation of benzoic acid with the appropriate diols. Their dipole moments and Kerr constants were experimentally determined and compared with the theoretical values obtained by standard methods of statistical mechanics. Crytical comparison between theory and experiment allowed us to reach some conclusions about the conformational energy and the position of the rotational isomers on the flexible segment of these molecules.

Experimental Section

Synthesis and Characterization of the Diesters. 1,2-Ethanediol dibenzoate ($m = 2$), 1,3-propanediol dibenzoate ($m = 3$), 1,4-butanediol dibenzoate ($m = 4$), 1,5-pentanediol dibenzoate ($m = 5$), and 1,6-hexanediol dibenzoate ($m = 6$) were prepared by reaction of benzoyl chloride with the corresponding diol in a solution of chloroform in the presence of triethylamine, at room temperature. The reaction product was washed successively with water, aqueous sodium bicarbonate, and more water and dried and the solvent distilled off under reduced pressure. All the crude diesters, but 1,5-pentanediol dibenzoate, were purified by several crystallizations. 1,5-Pentanediol ester was previously purified by column chromatography in deactivated alluminium oxide using *n*-hexane as solvent and then recrystallized. The purity of the diesters was checked by HPLC. Melting points of the compounds were 72–72.5, 56–59, 77–81, 79–81, and 55–56 °C for $m = 2, 3, 4, 5$, and 6, respectively.

The main characteristic signals of the IR spectra, in reciprocal centimeters, were the following. Diester $m = 2$: 1719 (C=O); 1582, 1491 (C=C); 1452 (CH_2—O—C scissoring); 1259, 1120 (C—O stretching); 705, 680. Diester $m = 3$: 1719; 1583, 1491; 1450; 1276, 1108; 709, 686. Diester $m = 4$: 1710; 1582, 1482; 1445; 1275, 1112; 705, 680. Diester $m = 5$: 1709; 1580, 1475; 1448; 1272, 1124; 708, 685. Diester $m = 6$: 1719; 1601, 1582; 1452; 1277, 1108; 710. The ^1H NMR spectra were recorded in deuterated chloroform using TMS as reference standard. The signals for aromatic protons (δ 7.45–7.96), $CH_2OCOC_6H_5$ (δ 4.38), $CH_2COCOC_6H_5$ (δ 1.94), and $CH_2CCOCOC_6H_5$ (δ 1.55) were according to the number of protons of each compound.

Cyclohexane (Merck, RPE grade) and benzene (Carlo Erba, RPE grade), stored over 4 A molecular sieves, were used without further purification as solvents for our measurements.

Dipole Moments. Dielectric measurements were performed at 25 ± 0.05 °C with a WTW dipolmeter Model DM-01 at a fixed frequency of 2.0 MHz. The cell was calibrated at 25 °C with substances of known dielectric constant (i.e., benzene, carbon tetrachloride, and cyclohexane). Increments in the refractive indices were determined in a Brice-Phoenix 2000-V differential refractometer. Values of the dipole moment were calculated from the equation of Guggenheim and Smith:[20,21]

$$\langle \mu^2 \rangle = \frac{27kTM}{4\pi N(\epsilon_1 + 2)^2 d_1} \left\{ \left(\frac{d\epsilon}{d\omega} \right) - \left(\frac{dn^2}{d\omega} \right) \right\}$$

where k is the Boltzmann constant, N is the Avogadro number, T is the absolute temperature, M is the molecular weight of the solute, ϵ_1 and d_1 are respectively the dielectric constant and density of the solvent, and ω is the solute weight fraction.

Values of $d\epsilon/d\omega$ and $dn^2/d\omega$ were obtained as the slope from plots of the increments of the dielectric constant ($\Delta\epsilon = \epsilon - \epsilon_1$) and the index of refraction ($\Delta n = n - n_1$) against ω, by a least-squares linear fit. An illustrative plot of this kind is shown, as an example, in Figure 1. The results obtained are shown in Table I. The uncertainty in the values of $\langle \mu^2 \rangle$ was estimated to be ca. ±5%.

Kerr constants were obtained from electrical birefringence measurements. Details of a similar apparatus are given elsewhere.[22] In brief, a 5-mW He-Ne laser (Spectra-Physics, 120 S, $\lambda = 632.8$ nm) was used as the light source; the polarizer and analyzer were Glan-Thompsom prisms (Oriel); the electric field was applied by means of a continuous power supply (Universal Voltronics Corp., BAP-22); the compensator contains a quarter wave plate (Newport Corp.) and a Faraday coil (Leybold-Heraeus); finally a photomultiplier (Pacific Precision Inst.) with

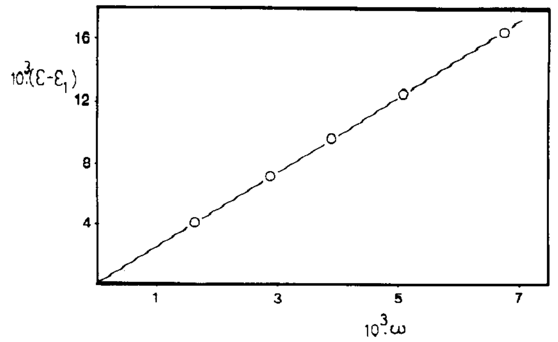

Figure 1. Concentration dependence of the increments in the dielectric constant for $C_6H_5COO(CH_2)_mOOCC_6H_5$ (m = 3).

Table I
Experimental Values of the Mean Square Dipole Moment $\langle\mu^2\rangle$ (Measured in Benzene Solutions) and the Kerr Constant (Measured in Cyclohexane Solutions) $_mK$ of Five Diesters $C_6H_5COO(CH_2)_mOOCC_6H_5$

m	$\langle\mu^2\rangle$, D^2	$_mK$, 10^{-25} m^5 V^{-2} mol^{-1}
2	7.58	29.1 ± 1.6
3	6.71	6.9 ± 3.9
4	7.20	11.6 ± 1.5
5	7.43	9.4 ± 2.4
6	7.74	12.3 ± 2.7

a lock-in amplifier (Princeton Applied Res., 128A) equipped with a mechanical chopper working at 93 Hz was used as the detector. An original thermostatic system[22] keeps the temperature at 25 °C to within ±0.2 °C.

Birefringences δ produced by electric fields E up to 3×10^6 V/m were measured and the Kerr constant B was evaluated as

$$B = \delta/2\pi l E^2$$

where l is the effective length of the cell. The values of B were converted into molar Kerr constant by means of the equation[23]

$$_mK = 54\lambda n_1(\lim_{c\to 0}(\Delta B/c) + vB)(n_1^2 + 2)^{-2}(\epsilon_1 + 2)^{-2}$$

where λ is the wavelength of radiation used in the measurements, v is the solute molar volume, and c is the concentration in moles per liter. The contribution of the solute to the Kerr constants ΔB is evaluated as the difference of the B values for the different solutions and cyclohexane used as solvent for these measurements due to its nearly isotropical polarizability. Limits are obtained as the intercepts of the plots depicted in Figure 2. Experimental values for $_mK$ are summarized in Table I.

Theoretical Calculations

Standard methods of the matrix multiplication scheme[2,24] were used to compute the conformational averages of $\langle\mu^2\rangle$, $\beta = \langle\mu\hat{\alpha}\mu^T\rangle$, and $\gamma^2 = (3/2)\langle\mathrm{tr}\,\hat{\alpha}\hat{\alpha}\rangle$ where the traceless $\hat{\alpha}$ tensor represents the anisotropic part of the polarizability of the molecule, μ is the dipole moment written as a row vector, and μ^T is the transposed of μ. The magnitudes β and γ^2 were used to calculate Kerr constants according to[25,26]

$$_mK = \frac{2\pi N_A}{15kT}\left\{\frac{\beta}{kT} + \frac{2}{3}\gamma^2\right\}$$

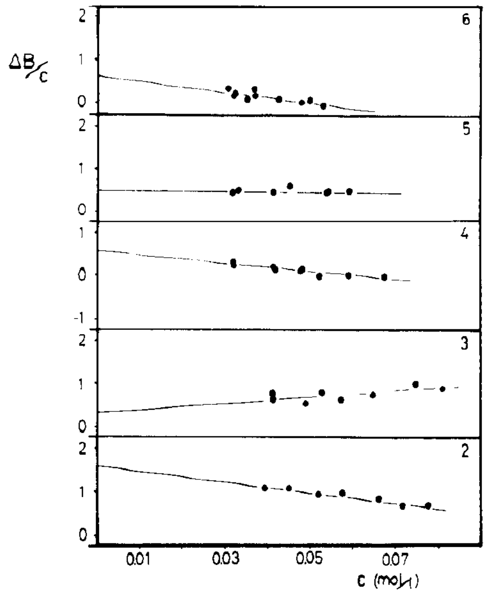

Figure 2. Ratios of the difference $\Delta B = B - B_1$ to the molarity (mol/L) plotted againsts c for five diesters $C_6H_5COO(CH_2)_mOOCC_6H_5$.

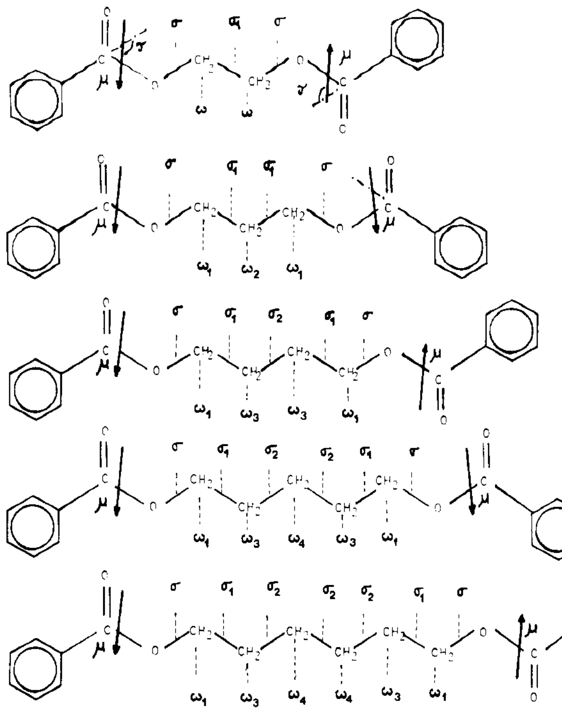

Figure 3. Structures of the five diesters shown in their all-trans conformation. The positive direction of the dipole moments is represented by an arrow whose orientation is determined by the angle τ. First/second-order statistical weights are indicated above/below the skeleton of the molecules.

Bond angles were taken from earlier publications on polyesters.[1-13] Rotational isomers were located at three symmetrical positions defined as $\phi = 0, \pm\phi_g$, with ϕ_g ranging from 100° to 140° (i.e., keeping the symmetry of the chain and allowing displacements of ±20° from the perfectly staggered positions of the gauche states[15]). Three first-order statistical weights are required for these molecules; they will be written as σ, σ_1, and σ_2 representing the stability of gauche versus trans states on bonds $O\text{-}CH_2$, $OCH_2\text{-}CH_2CH_2$, and $CH_2CH_2\text{-}CH_2CH_2$, respectively. Similarly, second-order factors ω, ω_1, ω_2, ω_3, and ω_4 representing interactions $C^*\cdots O$, $C^*\cdots CH_2$, $O\cdots O$, $O\cdots CH_2$, and $CH_2\cdots CH_2$ are used. Figure 3 shows a schematic representation of the five molecules; first/second-order factors required for each of them are indicated above/below the skeleton of the molecules.

Two different sets of conformational energies, namely, those reported by Mendicuti et al.,[11] which will be referred to as set I, and those of Bahar and Mattice,[13] which we shall name as set II, were used as the starting point for the analysis presented below. According to our nomenclature, and using in units of kilocalories per mole, set I can be summarized as $E_\sigma = 0.4$; $E_{\sigma_1} = -0.8, -0.4, -0.2,$

Table II
Set II of Conformational Energies (kcal/mol) Tabulated with Respect to the tt State (Taken from Ref 13)

bond pair	isomeric states			
	tg$^{\pm}$	g$^{\pm}$t	g$^{\pm}$g$^{\pm}$	g$^{\pm}$g$^{\mp}$
CO*–CH$_2$–CH$_2$OC*	0	0.7	0.6	1.6
C*O–CH$_2$–CH$_2$CH$_2$O	−0.4	0.6	0.2	3.4
OCH$_2$–CH$_2$–CH$_2$OC*	−0.4	−0.4	−0.8	−0.5
C*O–CH$_2$–CH$_2$CH$_2$C	−0.2	0.4	0.2	11.0
OCH$_2$–CH$_2$–CH$_2$CH$_2$O	0.5	−0.2	0.3	0.85
CH$_2$CH$_2$–CH$_2$–CH$_2$CH$_2$O	0.5	0.5	1.0	3.0

Table III
Theoretical Values of the Kerr Constant ${}_{\mathrm{m}}K$ (10^{-25} m^5 V^{-2} mol^{-1}) and the Mean Square Dipole Moment $\langle\mu^2\rangle$ (D^2) Calculated at 25 °C for Five Diesters $C_6H_5COO(CH_2)_mOOCC_6H_5$[a]

	free rot		set I[b]		set II[c]	
m	$\langle\mu^2\rangle$	${}_{\mathrm{m}}K$	$\langle\mu^2\rangle$	${}_{\mathrm{m}}K$	$\langle\mu^2\rangle$	${}_{\mathrm{m}}K$
2	6.91	14.2	9.03	33.5	7.36	22.4
3	7.06	16.0	6.55	18.3	5.81	17.5
4	7.11	16.7	6.89	18.2	6.56	17.5
5	7.13	16.9	7.07	19.2	6.88	19.7
6	7.14	17.1	7.01	18.1	6.74	17.6

[a] All the calculations performed with $\Delta\alpha_{MB} = 5.3$; $\Delta\alpha_{MB}{}^{+} = 4.0$ Å^3, and $\phi_g = 120°$ (i.e., rotational isomers placed at 0, ±120°). [b] Set I, conformational energies taken from ref 11. [c] Set II, conformational energies of ref 13.

−0.2, and −0.2 respectively for $m = 2, 3, 4, 5$, and 6; $E_{\sigma_2} = 0.5$; $E_\omega = 2.0$; $E_{\omega_1} = \infty$; $E_{\omega_2} = 0.4$; $E_{\omega_3} = 0.6$; and $E_{\omega_4} = 2.0$. We have adjusted slightly the values of E_σ and E_{σ_1}, leaving all the other values unchanged; in the case of the second-order parameters (i.e., E_ω's), their effect on the results is small and therefore an accurate assignation is not required, while σ_2 represent interactions very similar to those occurring in a polyethylene chain for which a value[27] $\sigma_2 = 0.4$ (i.e., $E_{\sigma_2} = 0.5$) is customarily used. Set II of conformational energies[13,19] is summarized in Table II; we have not performed any kind of modification on these parameters.

The dipole moment of each molecule was computed by adding two contributions, one for each ester group. These contributions were identified with the experimental dipole moment of methyl benzoate molecules for which a modulus of 1.89 D and an orientation defined by $\tau = 121°$ (see Figure 3) was found.[26,28]

Each of the five diesters can be formally obtained by condensation of two molecules of methyl benzoate, MB, with the appropriate number of molecules of ethane, ET, through elimination of methane for which $\hat{\alpha}_{Me} = 0$ due to its spherical symmetry. Consequently, the $\hat{\alpha}$ tensors for these molecules can be computed by adding two kind of contributions, namely, $\hat{\alpha}_{MB}$ and $\hat{\alpha}_{Et}$. The $\hat{\alpha}_{MB}$ tensor is not exactly diagonal; however, its off-diagonal terms are very small and their contribution to any magnitude is negligible.[26,29] Omission of the off-diagonal terms of $\hat{\alpha}_{MB}$ allows these contributions to be written as

$$\hat{\alpha}_{MB} = \Delta\alpha_{MB}J + \Delta\alpha_{MB}{}^{+}K$$

$$\hat{\alpha}_{Et} = \Delta\alpha_{Et}J = \Gamma_{cc}J$$

with $J = \mathrm{diag}\ (2/3, -1/3, -1/3)$ and $K = \mathrm{diag}\ (0, 1/2, -1/2)$. The values of $\Delta\alpha_{MB}$ and $\Delta\alpha_{MB}{}^{+}$ for methyl benzoate can be obtained by addition of the corresponding parameters for benzene[25] and methyl acetate[23] molecules; the result of this addition gives $\Delta\alpha_{MB} = 5.33$, $\Delta\alpha_{MB}{}^{+} = 4.0$ Å^3. Flory and co-workers[26,29] used a value of $\Delta\alpha_{MB} = 6.93$ in the analysis of Kerr constants of methyl benzoate and explained the increment of this parameter as a consequence of inductive effects between the polarizabilities of benzene and ester residues; however, the analysis of diethylene glycol terephthalates[7] seems to indicate that there are no inductive effects on that kind of molecules. We have used these two anisotropies as adjustable parameters while a value of $\Gamma_{cc} = 0.53$ Å^3 was used throughout all the present analysis since this parameter has been well established for several molecules,[30] and, moreover, it has little effect on the results for the compounds that we are studying.

A first calculation was carried out allowing for free rotation of all the bonds (i.e., all statistical weights set equal to unity). The results of this calculation are summarized in columns two and three of Table III. They indicate that the free rotation is not a good approximation for the calculation of Kerr constants; however, it is not too bad for dipole moments since the differences between the values thus obtained and the experimental results (see Table I) are smaller than 9% in all the cases.

Results obtained with the more realistic models described by sets I and II are collected in columns four to seven of Table III. As these results indicate, theoretical values of ${}_{\mathrm{m}}K$ computed with any of the two sets are larger than experimental results for all five compounds.

One possible way of lowering the theoretical results of ${}_{\mathrm{m}}K$ could be to modify the conformational energies. However, some exploratory calculations proved that agreement between theory and experience is only achieved by using $E_\sigma < 0$ and $E_{\sigma_1} > 0$ in contrast with the requirements of all the other conformational properties studied to date. Another possibility would be to change the modulus μ and orientation τ of the dipole moment of the benzoate group; however, besides the facts that these two parameters are well established and that a significant variation will drastically change the values of $\langle\mu^2\rangle$, no conceivable combination of μ and τ could reproduce ${}_{\mathrm{m}}K$ for the five compounds simultaneously; thus, while the results for $m = 2$ can be reproduced with $\mu \approx 1.8$ D that of $m = 3$ would required to use $\mu \approx 0.5$ D.

The value of ${}_{\mathrm{m}}K$ is also sensitive to the optical parameters $\Delta\alpha_{MB}$ and specially to $\Delta\alpha_{MB}{}^{+}$ while Γ_{cc} has a much smaller effect on ${}_{\mathrm{m}}K$. The values summarized on Table III are roughly reduced by 5% if $\Delta\alpha_{MB}$ decreases 1 Å^3, while the same variation in $\Delta\alpha_{MB}{}^{+}$ reduces the values of ${}_{\mathrm{m}}K$ by ca. 25%. Agreement between theoretical and experimental values of ${}_{\mathrm{m}}K$ can be achieved with set I of conformational parameters using $\Delta\alpha_{MB}{}^{+} = 3.5, 1.0, 2.5, 1.8$, and 2.8 respectively for $m = 2, 3, 4, 5$, and 6. Since it seems quite unlikely that these optical parameters could depend on the number m of CH$_2$ groups, we have selected the values $\Delta\alpha_{MB} = 5.0$ and $\Delta\alpha_{MB}{}^{+} = 3.0$ Å^3 for the analysis presented below.

Both $\langle\mu^2\rangle$ and ${}_{\mathrm{m}}K$ depend strongly on the location of the rotational isomers. In order to test this dependence we have performed some calculations allowing for three rotational isomers located at the symmetrical positions defined by $\phi = 0, \phi_g, -\phi_g$. The largest effect is obtained with modification of ϕ_g for the OCH$_2$–CH$_2$ bonds while the value of ϕ_g for CH$_2$CH$_2$–CH$_2$CH$_2$ bonds has a negligible effect on the results. Figures 4 and 5 represent respectively the values of $\langle\mu^2\rangle$ and ${}_{\mathrm{m}}K$ calculated with set I of conformational energies as a function of ϕ_g for the OCH$_2$–CH$_2$ bonds. The main features of these figures are quite easy to explain. Thus, taking $\phi_g = 0$ amounts to keeping these bonds in the trans conformation, which favors cancellation/reinforcement of the dipole moments of the two ester groups for m even/odd; consequently, $\langle\mu^2\rangle$ increases/decreases as ϕ_g departs from zero for m

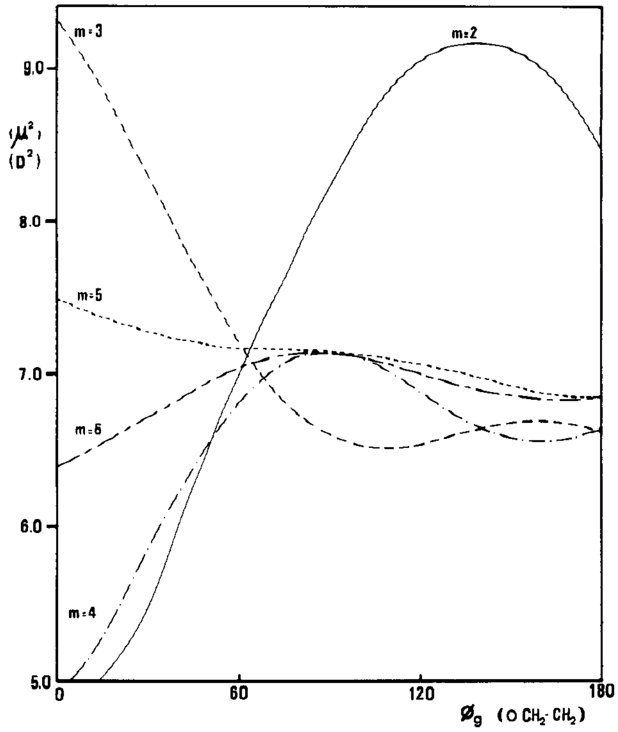

Figure 4. Values of $\langle \mu^2 \rangle$ obtained with set I of conformational energies as a function of ϕ_g, the location of gauche states of bonds OCH_2–CH_2. Calculations were performed at 25 °C keeping ϕ_g = 120° for O–CH_2 and CH_2CH_2–CH_2CH_2 bonds.

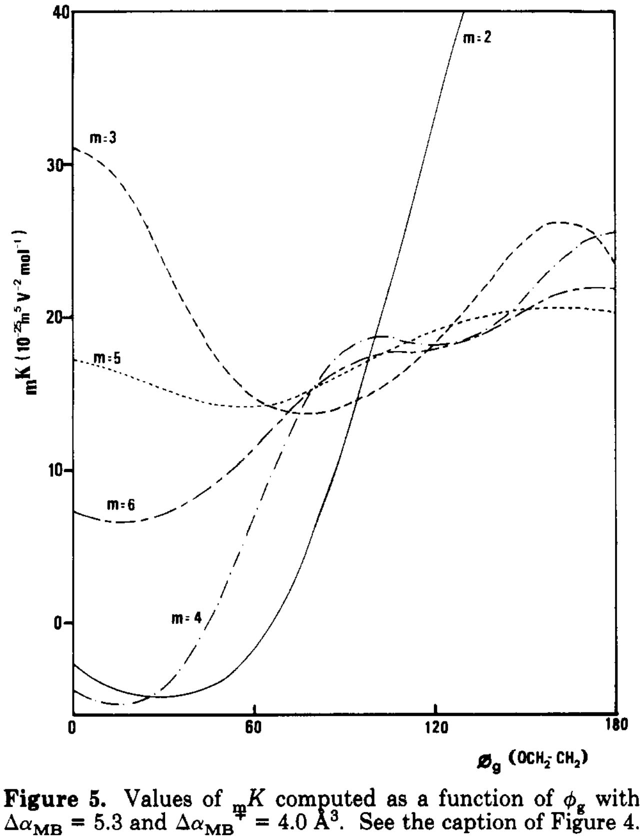

Figure 5. Values of $_mK$ computed as a function of ϕ_g with $\Delta\alpha_{MB}$ = 5.3 and $\Delta\alpha_{MB}{}^+$ = 4.0 Å^3. See the caption of Figure 4.

even/odd. The effect becomes smaller as m increases due to the increment of the separation between the two polar groups. In the case of $_mK$, the largest contribution comes from the term $\beta = \langle \mu \hat{\alpha} \mu^T \rangle$ in which the dipole moment plays a very important role and therefore the lines of Figure 5 have a shape quite similar to those of Figure 4.

Table IV
Theoretical Values of the Kerr Constant $_mK$ (10^{-25} m^5 V^{-2} mol^{-1}) and the Mean Square Dipole Moment $\langle \mu^2 \rangle$ (D^2)[a]

	compound				
	m = 2	m = 3	m = 4	m = 5	m = 6
		Set I[b]			
ϕ_g(O–CH_2)	100	140	140	140	140
ϕ_g(OCH_2–CH_2)	120	100	120	100	100
$\langle \mu^2 \rangle$	8.11	6.78	6.93	7.11	7.11
$_mK$	27.9	9.6	14.3	12.3	13.6
		Set II			
ϕ_g(O–CH_2)	100	140	140	140	140
ϕ_g(OCH_2–CH_2)	140	100	120	100	100
$\langle \mu^2 \rangle$	7.40	6.29	6.80	7.12	7.10
$_mK$	28.9	9.2	13.3	11.5	14.9

[a] Calculated with sets I and II of conformational parameters after adjustment of rotational angles ϕ_g and values of E_σ, $E_{\sigma 1}$ of set I. All the calculations were performed at 25 °C with $\Delta\alpha_{MB}$ = 5.0, $\Delta\alpha_{MB}{}^+$ = 3.0 Å^3. [b] All the conformational energies as in ref 11 with the exceptions of E_σ = 0.7 and $E_{\sigma 1}$ = −0.6 and −0.2 respectively for m = 2 and m > 2.

By use of the optimized values $\Delta\alpha_{MB}$ = 5.0 and $\Delta\alpha_{MB}{}^+$ = 3.0 Å^3 and ϕ_g adjusted for bonds O–CH_2 and OCH_2–CH_2 to within ±20° of the staggered positions, set II of conformational parameters is able to give a reasonable account of both $\langle \mu^2 \rangle$ and $_mK$ of the five diesters. The results are given in Table IV.

In the case of set I the results are improved if the values of E_σ and E_{σ_1} are also adjusted. The best combination is presented in Table IV, which shows that both sets of energies give almost identical results.

The analysis presented above seems to lead to the following conclusions: (1) The dipole moment is not a good property for testing the conformational energies of this kind of compounds since they have only two polar groups separated by several nonpolar bonds; as the number of nonpolar bonds increases, the correlation between the dipoles decreases and $\langle \mu^2 \rangle$ tends to reach the value of freely jointed dipoles (7.14 D^2 in this case). But, even in the cases in which the number of bonds is not too large (i.e., m = 2, 3), a freely rotating model gives a good account of the experimental results of $\langle \mu^2 \rangle$. (2) The Kerr constant is more sensitive to these energies probably due to the fact that the CH_2 groups connecting the two esters have a nonnegligible contribution. (3) Values of the optical parameters $\Delta\alpha_{MB}$ and $\Delta\alpha_{MB}{}^+$ smaller than those obtained by addition of contributions of phenyl and ester residues are required to reproduce experimental values of $_mK$ for these molecules. (4) The most recent set of conformational energies reported by Bahar and Mattice[13] (set II) is able to reproduce both $\langle \mu^2 \rangle$ and $_mK$ of the five compounds, provided that gauche states are allowed to move ±20° from the staggered positions. Comparison between theory and experiment suggests an adjustment of E_σ and E_{σ_1} parameters of the set previously used (set I), which brings both sets of energies into practical coincidence.

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Registry No. $C_6H_5CO_2(CH_2)_2OCOC_6H_5$, 94-49-5; $C_6H_5CO_2(CH_2)_3OCOC_6H_5$, 2451-86-7; $C_6H_5CO_2(CH_2)_4OCOC_6H_5$, 19224-27-2; $C_6H_5CO_2(CH_2)_5OCOC_6H_5$, 6624-73-3; $C_6H_5CO_2(CH_2)_6OCOC_6H_5$, 22915-73-7.

References and Notes

(1) Wallach, M. L. *Makromol. Chem.* **1967**, *103*, 19.

(2) Flory, P. J. *Statistical Mechanics of Chain Molecules*; Interscience: New York, 1969.
(3) Williams, A. D.; Flory, P. J. *J. Polymer Sci., A-2* **1967**, *5*, 417.
(4) Riande, E. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 1397.
(5) Riande, E.; Guzman, J.; Tarazona, M. P.; Saiz, E. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 917.
(6) Riande, E.; Guzman, J.; Llorente, M. A. *Macromolecules* **1982**, *15*, 298.
(7) Mendicuti, F.; Saiz, E. *Polym. Bull.* **1984**, *11*, 533; *Makromol. Chem.* **1986**, *187*, 2483.
(8) Riande, E.; Guzman, J. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 1235.
(9) Riande, E.; Guzman, J.; de Abajo, J. *Makromol. Chem.* **1984**, *185*, 1943.
(10) Riande, E.; de la Campa, J. G.; Schlereth, D. D.; de Abajo, J.; Guzman, J. *Macromolecules* **1987**, *20*, 1641.
(11) Mendicuti, F.; Viswanadhan, V. N.; Mattice, W. L. *Polymer* **1988**, *29*, 875.
(12) Mendicuti, F.; Patel, B.; Viswanadhan, V. N.; Mattice, W. L. *Polymer* **1988**, *29*, 1669.
(13) Bahar, I.; Mattice, W. L. *J. Chem. Phys.* **1989**, *90*, 6783.
(14) Actually, Flory, and many other authors after him, represent these two factors by σ_{x} and σ_{η}. We have tried to simplify the nomenclature (see below) and used σ, σ_1, and σ_2 for the three first-order parameters in the analysis of these molecules.
(15) Abe, A.; Mark, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 6468.
(16) Miyasaka, T.; Kinai, Y.; Imamura, Y. *Makromol. Chem.* 1981, *182*, 3533.
(17) Miyasaka, T.; Yoshida, T.; Imamura, Y. *Makromol. Chem.* **1983**, *184*, 1285.
(18) San Roman, J.; Guzman, J.; Riande, E.; Santoro, J.; Rico, M. *Macromolecules* **1982**, *15*, 609.
(19) Bahar and Mattice (ref 13) obtain the energies of given conformations for pairs of bonds without separating the contributions E_σ, E_{σ_1}, etc. Consequently, these authors do not assign values to these parameters.
(20) Guggenheim, E. A. *Trans. Faraday Soc.* **1949**, *45*, 714; **1951**, *47*, 573.
(21) Smith, J. W. *Trans. Faraday Soc.* **1950**, *46*, 394.
(22) Mendicuti, F. *Rev. Sci. Instrum.* **1988**, *59* (5), 728.
(23) Saiz, E.; Suter, U. W.; Flory, P. J. *J. Chem. Soc., Faraday Trans. 2* **1977**, *73*, 1538.
(24) Flory, P. J. *Macromolecules* **1974**, *7*, 381.
(25) Suter, U. W.; Flory, P. J. *J. Chem. Soc., Faraday Trans. 2* **1977**, *73*, 1521.
(26) Irvine, P. A.; Erman, B.; Flory, P. J. *J. Phys. Chem.* **1983**, *87*, 2929.
(27) Abe, A.; Jernigan, R. L.; Flory, P. J. *J. Am. Chem. Soc.* **1966**, *88*, 631.
(28) Saiz, E.; Hummel, J. P.; Flory, P. J.; Plavsic, M. *J. Phys. Chem.* **1981**, *85*, 3211.
(29) Flory, P. J.; Saiz, E.; Erman, B.; Irvine, J. P.; Hummel, J. P. *J. Phys. Chem.* **1981**, *85*, 3215.
(30) Patterson, G. D.; Flory, P. J. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 1098.

Radical Trapping and Termination in Free-Radical Polymerization of MMA

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ABSTRACT: Post-effect measurements of radical concentrations for bulk free-radical polymerization of methyl methacrylate (MMA) at 25 °C with 5.0 wt % 2,2′-azobis(2-methylpropionitrile) (AIBN) initiated by an ultraviolet light (UV) were made by using an on-line ESR spectrometer. Number-average termination rate constants were therefrom directly measured by using radical decay rates. It was found that these termination rate constants decrease dramatically in the post-effect period at high conversions. These observations are in disagreement with the concept of termination by propagation–diffusion that was expected to be the dominant mode of termination at these high conversion levels. It was also found that a fraction of the radicals are trapped during the course of polymerization. In other words, there exist two radical populations in the reacting mass: free radicals and trapped radicals. The former is in the liquid state (as indicated by 13-line ESR spectra) while the latter are in solid state (9-line spectra). These two radical populations have very different reactivities in both propagation and termination reactions. Our data show that there is no minimum value of the termination rate constant for the long-lived trapped radicals. The trapped radical fractions measured directly herein suggest that heterogeneity in the polymerization medium can have a significant effect and must be properly accounted for when an analysis of the kinetics of polymerization is made.

Introduction

Although the termination reaction has been a matter of study for over 3 decades,[1] the molecular processes involved are not well understood, particularly at high conversions. The reasons for this lack of understanding are 2-fold. Firstly, the process itself is very complex, generally consisting of three definable steps. These include the following: two radical molecules migrate together via translational diffusion; the radical centers reorient by segmental diffusion; they overcome the chemical activation barrier and react. The activation energy for free radical reactions is quite small. The termination reaction is, therefore, likely to be diffusion-controlled, either segmental diffusion-controlled (usually at low polymer concentrations) or translational diffusion-controlled (at intermediate and high polymer concentrations). As polymer concentration increases, the macromolecular chains become

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