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Conformational Characteristics of Phenyl and Chlorophenyl Esters of 2,4-Dimethylglutaric Acid

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ABSTRACT: The dipole moments of model compounds of the dyads of phenyl- and chlorophenyl-substituted acrylate polymers (phenyl, *o*-chlorophenyl, *m*-chlorophenyl, and *p*-chlorophenyl diesters of 2,4-dimethylglutaric acid) were measured in benzene solution in the temperature range 30–60 °C. The mean-square dipole moment $\langle \mu^2 \rangle$ at 30 °C ranged from 4.36 D^2 for diphenyl 2,4-dimethylglutarate to 10.30 D^2 for bis(*p*-chlorophenyl) 2,4-dimethylglutarate. Among the chlorinated compounds, bis(*o*-chlorophenyl) 2,4-dimethylglutarate exhibits the lowest polarity. All four compounds showed positive temperature coefficients (i.e., $\langle \mu^2 \rangle$ increases with increasing T). The results were interpreted in terms of the rotational isomeric states model. The four-states model previously used in the analysis of poly(methyl acrylate), after adjustment of some of the parameters, is able to reproduce the experimental values of $\langle \mu^2 \rangle$ of these model compounds.

Introduction

The schematic substitution of the methoxy group of the repeating unit of poly(methyl acrylate) (PMA) for a phenoxy or a chlorophenoxy group may considerably alter both the structural geometry and the potentials affecting the torsional rotations about the skeletal bonds of the side groups, and consequently it will have great influence on the conformational characteristics of the resulting polymers. In this case, it is expected that the conformational energies associated to the rotational states about the skeletal bonds of the main chain will be dependent on the rotational angle (ψ) about the O–Ph group, this dependence being much more important in the cases in which the substitution of the chlorine is performed on the ortho or meta positions.[1] In addition, the spatio-configurational properties will also be dependent on the rotational angle (χ) about the C^α–C^* bonds,[2-6] whose conformational energies will, of course, be affected by the location (ortho, meta, or para) of the chlorine atom on the phenoxy group.

For the reasons outlined above, the study of the statistics of poly(phenyl acrylate) (PPA) and its phenyl-halogenated derivatives requires, as a first step, studying physical properties of model compounds with structural features similar to those of the polymers indicated above and extending these studies to dimers of the polymers, in order to obtain information on the value of the conformational energies associated to the rotational states about C^α–C^* and O–Ph bonds. A physical property specially suitable for this purpose is the dipole moment. Recent dielectric studies performed on phenyl and halophenyl propionates (model compounds of the repeating unit of PPA and its halophenyl derivatives) suggest the following: (a) The effect of replacing the methoxy group in methyl propionate with a less polar phenoxy group is equivalent to introducing a small contribution, $\mu_2 = 0.3$ D, along the O–Ph bond in addition to the dipole moment, μ_1, of methyl propionate. (b) Comparison of the dipole moments of *p*-chlorophenyl and phenyl propionates indicates that the dipole moment of the former compound can be obtained by simple vectorial addition of the dipole moments of phenyl propionate and chlorobenzene. (c) The rotational angles about O–Ph bonds are $\psi = \pm 60°$ and $\pm 120°$ for *m*-chlorophenyl propionate and only $\psi = \pm 75°$ for *o*-chlorophenyl propionate.[1]

The aim of the present study is to measure the dipole moment and its temperature coefficient of phenyl and chlorophenyl diesters of 2,4-dimethylglutaric acid, specifically, diphenyl 2,4-dimethylglutarate (PDG), bis(*p*-chlorophenyl) 2,4-dimethylglutarate (PCPDG), bis(*o*-chlorophenyl) 2,4-dimethylglutarate (OCPDG), and bis(*m*-chlorophenyl) 2,4-dimethylglutarate (MCPDG), which are model compounds for the dyads of poly(phenyl acrylate) (PPA), poly(*p*-chlorophenyl acrylate) (PPCPA), poly(*o*-chlorophenyl acrylate) (POCPA), and poly(*m*-chlorophenyl acrylate) (PMCPA), respectively. Also the dielectric properties will be calculated theoretically by

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Table I
Analytical Data for Diphenyl and Bis(chlorophenyl) 2,4-Dimethylglutarates, $CH_2(CHCH_3COOR)_2$[a]

	exptl (theoretical)				
bp, °C (2 mmHg)	C	H	O	Cl	IR ν, cm^{-1}
			R = Phenyl		
185–187	81.7 (81.5)	7.0 (7.1)	11.3 (11.4)	0 (0)	C=O 1750; $C=C_{Ar}$ 1580, 1490, 1460; δ_{oop} 750, 690
			R = *o*-Chlorophenyl		
195–196	72.3 (72.5)	6.3 (6.0)	10.4 (10.2)	11.0 (11.3)	C=O 1750; $C=C_{Ar}$ 1585, 1480, 1450; δ_{oop} 755, 685
			R = *m*-Chlorophenyl		
188–190	72.4 (72.5)	6.2 (6.0)	10.0 (10.2)	11.4 (11.3)	C=O 1755; $C=C_{Ar}$ 1590, 1470, 1430; δ_{oop} 780, 675
			R = *p*-Chlorophenyl		
194–196	72.1 (72.5)	6.3 (6.0)	10.5 (10.2)	11.1 (11.3)	C=O 1750; $C=C_{Ar}$ 1590, 1485, 1460; δ_{oop} 810, 670

[a] ^1H NMR: Aliphatic protons are shown in Figure 2. Aromatic protons: (δ 7.20–7.30) complex signals characteristics of the number and position of the substituent.

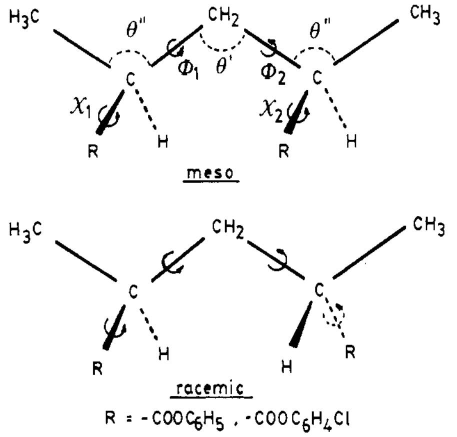

Figure 1. Schematic representation of the diesters of 2,4-dimethylglutaric acid shown in the tt conformation ($\Phi_1 = \Phi_2 = 0$).

using statistical mechanics methods, and by comparison of theory and experiments, information will be obtained concerning the rotational states around O–Ph and C^α–C^* bonds. These results will be used in a subsequent paper to study the statistics of poly(phenyl acrylate) and its halophenyl derivatives.

Experimental Section

Synthesis of the Model Compounds. Diphenyl 2,4-dimethylglutarate (PDG), bis(*p*-chlorophenyl) 2,4-dimethylglutarate (PCPDG), bis(*o*-chlorophenyl) 2,4-dimethylglutarate (OCPDG), and bis(*m*-chlorophenyl) 2,4-dimethylglutarate (MCPDG) were prepared by the condensation of 2,4-dimethylglutaric acid with the corresponding phenol derivative in a solution of dry toluene, using *p*-toluenesulfonic acid as catalyst. In a typical experiment, 0.05 mol of 2,4-dimethylglutaric acid was added to a solution of 0.1 mol of the corresponding phenol derivative and 0.1 g of *p*-toluenesulfonic acid, in 100 mL of dry toluene. The reaction mixture was refluxed in a flask equipped with a Dean-Stark separator under nitrogen atmosphere for 24 h. The crude diester was washed 3 times with diluted hydrochloric acid and then with distilled water, dried over calcium chloride, and distilled off under reduced pressure. The yield was 65–70%, and the purity of the corresponding esters was tested by GLC, exceeding 99.5%. Microanalysis data and boiling points of the compounds are listed in Table I.

Characterization. The diphenyl and bis(chlorophenyl) 2,4-dimethylglutarates obtained were characterized by IR (Perkin-Elmer 457) and ^1H NMR (Varian XL-300, 300-MHz) spectroscopies. The ^1H NMR spectra were recorded in 8% (w/v) deuteriated chloroform solutions at 40 °C, using TMS as the internal reference standard. The main characteristic signals of the IR and ^1H NMR spectra are quoted in Table I.

^1H NMR spectra give information on the meso and racemic stereoisomers (Figure 1) of the samples studied. Figure 2 shows the expanded NMR resonance signals of the aliphatic protons of PDG. Similar spectra are obtained for the chlorophenyl-substituted derivatives. The methylene protons of the racemic isomer produce a well-defined triplet centered at 2.07 ppm from TMS, which indicates that both protons are magnetically equivalent and therefore this isomer should exist almost exclusively in the tt conformation; otherwise, the nonequivalence of these protons in gg conformation would split the signal.[7,8] In the case of the meso isomer, the nonequivalence of these protons produces two multiplets centered at 1.78 and 2.53 ppm, respectively. Similar results have been reported for other dimethylglutarates and 2,4-diphenylpentane.[7-9] A detailed examination of the fine structure of the CH_2 resonance signals of the meso isomer makes it clear that these protons can be analyzed as an ABX_2 system, with J_{AB} = 13.97 Hz, J_{AX} = 7.70 Hz, and J_{BX} = 6.90 Hz. Also the integrated intensities of these signals give the molar fraction of meso and racemic isomers in the samples prepared, all being equimolecular mixtures of both stereoisomers.

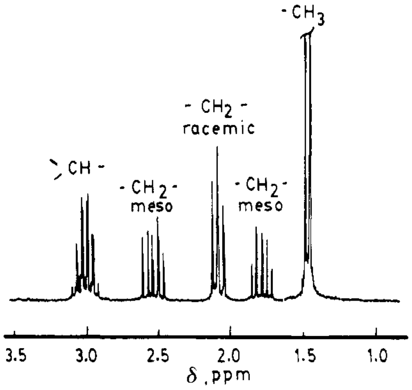

Figure 2. ^1H NMR signals of the aliphatic protons of diphenyl 2,4-dimethylglutarate. The spectrum corresponds to a equimolecular mixture of meso and racemic stereoisomers.

Dielectric Measurements. Values of ϵ, the dielectric constant of solutions of the model compounds, were obtained at 30, 40, 50, and 60 °C using a capacitance bridge with a three terminal cell[10] operating at 10 kHz. Values of the increments of the index of refraction of the solutions, n, with respect to that of the solvent, n_1, were measured at the temperatures of interest with a He–Ne KMX-16 laser differential refractometer (Cromatix Inc.) operating at 632.8 nm.

Values of the mean-square dipole moment $\langle\mu^2\rangle$ were calculated by the methods of Guggenheim[11] and Smith,[12] which results in the equation

$$\langle\mu^2\rangle = [27kTM/4\pi\rho N_A(\epsilon_1 + 2)^2][(d\epsilon/dw) - 2n_1(dn/dw)]$$

where k is the Boltzmann constant, T is the absolute temperature, ρ is the density of the solvent, and N_A is the Avogadro number. The derivatives $d\epsilon/dw$ and dn/dw were obtained, respectively, from plots of both the increments in dielectric constant ($\Delta\epsilon = \epsilon - \epsilon_1$, where ϵ_1 is the dielectric constant of the solvent) and index of refraction ($\Delta n = n - n_1$) against the weight fraction, w, of the solute. Values of the required derivatives are given in the second and third columns of Table II. This table also shows the values of $\langle\mu^2\rangle$ for PDG, OCPDG, MCPDG, and PCPDG; the uncertainty of these values was estimated to be ca. 5%.

Table II
Summary of Dielectric Results of Diphenyl and Bis(chlorophenyl) 2,4-Dimethylglutarates, $CH_2(CHCH_3COOR)_2$, in Benzene Solutions

R	T, °C	$d\epsilon/dw$	$2n_1\, dn/dw$	$\langle\mu^2\rangle$, D^2
phenyl	30	1.56_8	0.08_6	4.36
	40	1.51_9	0.09_3	4.44
	50	1.49_4	0.09_9	4.59
	60	1.44_0	0.10_7	4.61
p-chlorophenyl	30	2.94_0	0.09_5	10.30
	40	2.78_8	0.10_2	10.23
	50	2.69_6	0.10_9	10.43
	60	2.59_5	0.11_7	10.53
m-chlorophenyl	30	2.78_5	0.09_8	9.73
	40	2.67_4	0.10_5	9.82
	50	2.58_3	0.11_3	9.97
	60	2.51_2	0.12_0	10.17
o-chlorophenyl	30	1.74_5	0.09_6	6.17
	40	1.69_0	0.10_3	6.06
	50	1.67_1	0.11_0	6.30
	60	1.61_0	0.11_9	6.34

Theoretical Analysis

Conformational Model. A schematic representation of the meso and racemic diesters of 2,4-dimethylglutaric acid is shown in Figure 1. The calculations were carried out using the four-states conformational scheme employed by Yarim-Agaev et al.[5] in the analysis of oligomers of PMA which can distinguish between the two eligible orientations of the ester group generated by rotation about the C^α–C^* bond. This distinction is unnecessary for the calculation of the characteristic ratio or stereochemical equilibria, and thus it was not considered in the previous scheme;[2] however, it becomes essential for the purpose of the present calculations since the dipole moment of the repeating unit lies in the ester group.

Values of $\theta'' = 112°$ and $\theta' = 114°$ were used for the valence angles. Two rotational states (t,g) were allowed for the skeletal Φ angles. Calculations were performed with three different sets of values of the Φ angles. In set I, the rotational states were located at the average torsions $\langle\Phi\rangle$ deduced from the conformational energy calculations on oligomers of PMA (Scheme I in ref 5); namely, $\langle\Phi_1,\Phi_2\rangle_{tt} = 16°,16°$, $\langle\Phi_1,\Phi_2\rangle_{tg} = 3°,114°$, and $\langle\Phi_1,\Phi_2\rangle_{gt} = 114°,3°$ were used for the meso dyad, while $\langle\Phi_1,\Phi_2\rangle_{tt} = 3°,3°$ were used for racemic dyad with omission of all the other states whose statistical weights are negligibly small.[5] In set II, all the trans states were located at $\langle\Phi\rangle_t = 10°$, while $\langle\Phi\rangle_g = 110°$ was used for any gauche state. Finally, in set III, the perfectly staggered positions $\langle\Phi\rangle_t = 0$ and $\langle\Phi\rangle_g = 120°$ were used.

Each rotational isomer of the skeleton was splitted into two states in order to take into account the two possible orientations of the side group defined by the rotation $\chi = 0$ and $\chi = \pi$, representing, respectively, the orientations in which the carbonyl oxygen is synperiplanar and antiperiplanar with the methine hydrogen. The appropriate statistical weight matrices, with the states in the order $(t,\chi=0)$, (t,π), $(g,0)$, and (g,π), are[5]

$$U' = \begin{bmatrix} 1 & 0 & 1 & 0 \\ 0 & \rho & 0 & \rho \\ 1 & 0 & 0 & 0 \\ 0 & \rho & 0 & 0 \end{bmatrix}$$

for the CH_2–C^α–CH_2 bond pair, and

$$U_r'' = \begin{bmatrix} 1 & \gamma_1 & 0 & 0 \\ \gamma_1 & \gamma_2 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \qquad U_m'' = A \times \begin{bmatrix} 1 & \gamma & \beta & \beta \\ \gamma & 1 & \beta & \beta \\ \beta & \beta & 0 & 0 \\ \beta & \beta & 0 & 0 \end{bmatrix}$$

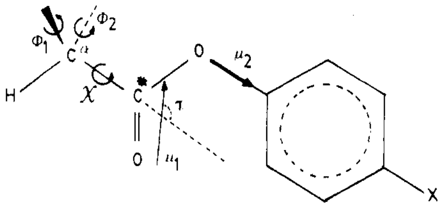

Figure 3. Side groups of phenyl (X = H) and *p*-chlorophenyl (X = Cl) diesters of the 2,4-dimethylglutaric acid shown in the $\chi = 0$ conformation.

for racemic and meso configurations of the C^α–CH_2–C^α bond pair. The statistical weight of $\chi = \pi$ relative to $\chi = 0$ orientations is denoted by ρ. The factors γ_1 and γ_2 arise from the differences in Coulombic interactions of $t0,t\pi$ (or $t\pi,t0$) and $t\pi,t\pi$ relative to $t0,t0$ in the racemic dyad. In the meso dyad, γ comes from the difference in Coulombic interactions between $t0,t\pi$ (or $t\pi,t0$) and $t0,t0$ (or $t\pi,t\pi$); A and β are combinations of statistical weights defined as $A = \omega''\delta_m/\delta_r$ and $\beta = 1/\eta\delta_m\omega''$ with ω'' representing the weight for the second-order interaction between two ester groups juxstaposed as in the meso tt state, η is the first-order statistical weight for trans versus gauche, and δ_m and δ_r represent Boltzmann factors of the Coulombic interactions in t0,t0 orientations of m and r dyads, respectively.

Calculations

Diphenyl 2,4-Dimethylglutarate (PDG) and Bis(*p*-chlorophenyl) 2,4-Dimethylglutarate (PCPDG). The ester groups of these two molecules are shown in Figure 3. The dipole moment of each ester group was represented by the sum of two contributions: μ_1 and μ_2 (see Figure 3) assigned as to reproduce the dipole moments of phenyl and *p*-chlorophenyl propionates in benzene solutions.[1] Thus, μ_1 represents the contribution of a methyl ester for which a modulus[13,14] of 1.757 D and a orientation[15] defined by the angle $\tau = 123°$ were used. The component μ_2 represents the effect of replacing a methyl by either a phenyl or a *p*-chlorophenyl group; values of $\mu_2 = 0.3$ and -1.3 D (i.e., the actual direction of this vector is the opposite of that shown in Figure 3) were used, respectively, for PDG and PCPDG molecules.[1]

Standard methods[16,17] were used to transform the μ_1 and μ_2 vectors into the coordinates system affixed to skeletal bond C^α–CH_2 for $\chi = 0$ and $\chi = \pi$ orientations of both ester groups. The dipole moments of the two groups were then added for every allowed combination of rotational states over Φ_1 and Φ_2 angles for both meso and racemic configurations of the molecules. The squares of the dipole moments of the conformations thus generated were averaged to obtain $\langle\mu^2\rangle$ of both configurations.

Bis(*o*-chlorophenyl) 2,4-Dimethylglutarate (OCPDG). Figure 4 represents the ester group of the OCPDG molecule whose dipole moment was obtained by addition of three contributions chosen as to reproduce the dipole moment of *o*-chlorophenyl propionate (OCPP) in benzene solutions,[1] namely $\mu_1 = 1.757$ D with $\tau = 123°$, $\mu_2 = 0.3$, and $\mu_3 = 1.6$ D. The value of μ for the ester group depends upon the rotational angle, ψ, governing the rotation over the O–Ph bond; according to calculations of conformational energies[1,18] confirmed by analysis of the dipole moment of OCPP,[1] the allowed positions of this angle are $\psi \approx \pm 75°$.

The values of $\langle\mu^2\rangle$ of the OCPDG molecule were calculated as explained above for PDG and PCPDG, with the only difference being that the existence of the ψ rotations on OCPDG increases the number of conformations to be

Table III
"Best Set" of Conformational Parameters and Theoretical Values of Mean-Square Dipole Moments

compd	$\langle\Phi\rangle$[a]	ρ	β	γ_1	γ_2	γ	$\langle\mu^2\rangle_m$	$\langle\mu^2\rangle_r$	av
PMA[b]	set I	1.1	1.8	2.0	1.3	4.0	5.4	5.1	5.25
PDG[c]	set I	1.1	1.8	1.4	2.5	4.5	4.43	4.28	4.36
	set II	1.1	1.8	1.6	2.5	4.5	4.47	4.24	4.36
	set III	1.1	1.8	1.6	2.5	4.5	4.39	4.32	4.36
PCPDG[c]	set I	1.1	5.0	1.4	2.3	0.2	11.95	8.67	10.31
	set II	1.1	5.0	1.6	1.6	0.2	12.67	7.93	10.30
	set III	1.1	5.0	1.4	2.3	0.2	11.14	9.47	10.31
OCPDG[c]	set I	1.1	0.3	2.0	0.2	2.3	5.97	6.36	6.17
	set II	1.1	0.6	1.8	0.3	2.1	6.24	6.11	6.17
	set III	1.1	0.2	2.0	0.2	2.4	5.83	6.52	6.17
MCPDG[c]	set I	1.1	2.4	0.2	3.1	0.2	11.87	7.59	9.73
	set II	1.1	2.7	0.2	3.5	0.2	12.08	7.39	9.73
	set III	1.1	2.2	0.2	2.9	0.2	11.63	7.80	9.72

[a] Average location of rotational angles in degrees. Set I: $\langle\Phi_1,\Phi_2\rangle_{tt}$ = 3°,3° for racemic; $\langle\Phi_1,\Phi_2\rangle_{tt}$ = 16°,16°, $\langle\Phi_1,\Phi_2\rangle_{tg}$ = 3°,114°, $\langle\Phi_1,\Phi_2\rangle_{gt}$ = 114°,3° for meso. Set II: $\langle\Phi\rangle_t$ = 10°, $\langle\Phi\rangle_g$ = 110°. Set III: $\langle\Phi\rangle_t$ = 0, $\langle\Phi\rangle_g$ = 120°. [b] Dimers of PMA. Taken from ref 5. T = 20 °C. [c] Present work. T = 30 °C.

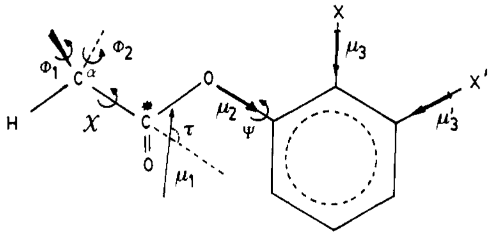

Figure 4. Side groups of the *o*-chlorophenyl (X = Cl, X′ = H, μ_3 = 1.6, μ_3' = 0) and *m*-chlorophenyl (X = H, X′ = Cl, μ_3 = 0, μ_3' = 1.6) esters of the 2,4-dimethylglutaric acid shown in the ψ = 0, χ = 0 conformation.

considered for each configuration of this molecule.

Bis(*m*-chlorophenyl) 2,4-Dimethylglutarate (MCPDG). The values of $\langle\mu^2\rangle$ for this molecule were calculated as explained above for OCPDG, with the only difference being that in the case of MCPDG there are four rotational isomers over the O–Ph bond defined[1,18] as $\pm\psi$ and $\pm(180 - \psi)$ with $\psi \approx 60°$ (see Figure 4).

Results and Discussion

Table III summarizes the theoretical values of the mean square dipole moments of the four compounds studied here. The second line of this table shows the results calculated by Yarim-Agaev et al.[5] for the dymer of PMA; this line was included with the purpose of comparison. Some exploratory calculations were also performed allowing for the existence of gg conformations on the racemic isomer. Using statistical weights up to 0.4 for gg conformations relative to t0,t0 produces variations of $\langle\mu^2\rangle_m$ that range from 1.5% in OCPDG to 10% in MCPDG.

It is impossible to reproduce the experimental results of all five compounds using the same set of conformational parameters. The second column of Table III indicates the set of rotational angles $\langle\Phi\rangle$ used in the calculation. Columns three through seven of Table III collect the "best set", i.e., the set of values of these parameters which gives the best fit for each of the five molecules. Columns eight and nine contain the theoretical values of $\langle\mu^2\rangle$ calculated, respectively, for meso and racemic dyads; the last column shows the average between those two values, which is the result that can be compared with our experimental values obtained for equimolecular mixtures of both stereoisomers.

The third column of Table III shows that the value of ρ is the same for all of these compounds. This result indicates that the rotation over the C^α–C* bond depends only on the carboxylic COO group, with the R residue attached to the oxygen having very little importance. That residue, however, plays a important role in determining the values of the other conformational parameters.

Table IV
Variation of the Mean-Square Dipole Moment Computed with Set I of Rotational Angles and Written as 10^3[d(ln $\langle\mu^2\rangle$)/d(parameter)] of Equimolecular Mixtures of Meso and Racemic Stereoisomers with the Conformational Parameters Used in the Calculation

	compound			
parameter	PDG	PCPDG	OCPDG	MCPDG
T	0.8	0.7	0.4	0.7
ρ	-199.6	-294.2	11.9	-275.3
β	28.7	-7.3	63.5	-16.4
γ_1	5.7	36.4	-4.5	63.7
γ_2	-40.2	-67.9	33.9	-43.8
γ	-22.9	19.4	-40.0	1.4
ψ			21.0	0.0

The effect of the position of $\langle\Phi\rangle$ on the dipole moments of the four molecules studied here is not large and can be compensated for by small modifications of the energetic parameters.

The conformational parameters needed to reproduce $\langle\mu^2\rangle$ of PDG are not too different from those of PMA. However, the substitution of one hydrogen by a chlorine atom requires a substantial modification of these parameters which become sensitive to the position of the chlorine. Thus, para and meta substitutions increase the stability of racemic tg versus tt (i.e., they increase the value of β), while in ortho substitutions tt is preferred over tg. The three kinds of substitutions decrease the value of γ (i.e., racemic t0,tπ becomes more unstable), although the effect is much stronger in the cases of para and meta than in ortho. The ortho substitution has almost no effect on γ_1, while it strongly decreases γ_2; on the contrary, para and meta decrease γ_1 and increase γ_2. Unfortunately, these molecules have too many rotational freedoms to perform an accurate computation of conformational energies which may rationalize these modifications.

The variation of the mean-square dipole moment of equimolecular mixtures of meso and racemic stereoisomers (i.e., the average between $\langle\mu^2\rangle_m$ and $\langle\mu^2\rangle_r$) with the parameters used in the calculations, computed with set I of rotational angles in the vicinities of the "best set" and written as 10^3d(ln $\langle\mu^2\rangle$)/dT are collected in Table IV. The first line of this table contains the temperature coefficients which in all the cases are positive and small, in good agreement with experimental results that show a increase of $\langle\mu^2\rangle$ with increasing temperature, although the variation is too close to the experimental error to allow for the computation of an accurate value.

Three of the compounds, namely PDG, PCPDG, and MCPDG, show a great sensitivity to ρ; their value of $\langle \mu^2 \rangle$ decreases with increasing ρ. This effect comes mainly from the racemic dyad which in the t0,t0 conformation exhibits a value of μ^2 much larger than any of the other three allowed conformations; as ρ increases, the incidence of t0,t0 grows smaller and consequently $\langle \mu^2 \rangle$ shows a sharp decrease. In racemic OCPDG, however, μ^2 is largest for $t\pi,t\pi$, while the other three conformations have roughly the same value. To increase ρ means then to raise the stability of $t\pi,t\pi$ which depends on ρ^2, but it also stabilizes $t0,t\pi$ and $t\pi,t0$ that depend on ρ. The net effect is a small increase of $\langle \mu^2 \rangle$ with increasing ρ.

The value of OCPDG is also very sensitive to the rotation, ψ, over the O–Ph bond with $\langle \mu^2 \rangle$ increasing as ψ increases. The explanation is straightforward: when $\psi = 0$ (as shown in Figure 4), the μ_1 and μ_3 components of the dipole moment of the ester have almost opposite directions and, therefore, there is a strong cancellation between them. This cancellation becomes smaller as ψ departs from 0, and consequently $\langle \mu^2 \rangle$ for the dymer increases with increasing ψ. However, in the case of MCPDG, $\langle \mu^2 \rangle$ is practically independent of ψ. The reason is that in this molecule the allowed positions for that rotation are ψ and $180-\psi$ (besides their symmetrical $-\psi$ and $180+\psi$). With $\psi \approx 60°$, there is a partial cancellation between μ_1 and μ_3', but there is also a reinforcement between these two components when the rotation is $180-\psi$. To modify the value of ψ changes both the cancellation and the reinforcement in practically the same way, and, therefore, $\langle \mu^2 \rangle$ remains almost unchanged.

We conclude by saying that the four-states scheme developed by Yarim-Agaev et al.[5] for oligomers of PMA can also be applied to phenyl and chlorophenyl esters. Among the five conformational parameters used in the calculation, ρ is independent of the kind of ester, while the other four depend strongly on the chemical structure of the alcoholic residue of the ester.

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Registry No. PDG, 117341-06-7; PCPDG, 117341-07-8; OCPDG, 117341-09-0; MCPDG, 117341-08-9.

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Infrared Dichroism Measurements of Molecular Relaxation in Binary Blend Melt Rheology

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ABSTRACT: A new rheooptical technique to measure dynamic infrared dichroism was used with deuterium labeling to observe the relaxation of each molecular weight component in a bidisperse entangled polymer melt. The bulk relaxation is measured simultaneously by using birefringence. The relaxation dynamics of the bulk and of each component depend upon the two polymer relaxation times and the blend ratio. Nearly monodisperse pairs of hydrogenated and deuteriated polyisoprenes of molecular weights 53 000 and 370 000, both several times the entanglement molecular weight, were used. Results for the linear viscoelastic step shear strain relaxation of each component and of the bulk for blends containing 10, 20, 30, 50, and 75 vol % long chains are presented. The component dynamics are qualitatively predicted by current molecular theories of polymer melt rheology; however, some important differences are observed. In particular, it was found that polydispersity can strongly retard the orientational relaxation of the low molecular weight component and decrease the longest relaxation time of the high molecular weight component.

I. Introduction

The rheology of entangled polymer melts has been the subject of a large number of experimental studies and theoretical investigations. Industrial polymer melts typically have a broad distribution of molecular weights which strongly affects their viscoelastic properties. The complexity of these effects in an arbitrary molecular weight distribution has motivated researchers to study model polydisperse systems. Binary blends of well-characterized, nearly monodisperse, linear polymers of different molecular weights have proven to be simple, well-defined systems for investigation. Traditionally the goal of research on binary blends has been to determine appropriate blending

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