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Dielectric and Conformational Properties of Phenyl and Chlorophenyl Esters of Poly(acrylic acid)[§]

Enrique Saiz,[†] Evaristo Riande,[*,‡] Julio San Román,[‡] and Enrique L. Madruga[‡]

Departamento de Química Física, Facultad de Ciencias, Universidad de Alcalá de Henares, Alcalá de Henares, Madrid, Spain, and Instituto de Ciencia y Tecnología de Polímeros, Consejo Superior de Investigaciones Científicas, 28006 Madrid, Spain.

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ABSTRACT: Dielectric constants ϵ of benzene solutions of poly(phenyl acrylate) (PPA), poly(*o*-chlorophenyl acrylate) (POCPA), poly(*m*-chlorophenyl acrylate) (PMCPA), and poly(*p*-chlorophenyl acrylate) (PPCPA) were measured in the temperature range 30–60 °C. The values of the mean-square dipole moments $\langle \mu^2 \rangle$ of the chains, expressed in terms of the dipole moment ratio $\langle \mu^2 \rangle / x\mu_0^2$, where x is the polymerization degree and μ_0 is the dipole moment of the side group, were 0.624, 1.090, 0.574, and 0.524 for PPA, POCPA, PMCPA, and PPCPA, respectively. The dipole moments of the chains were critically interpreted by using a four-state scheme obtained by splitting each (t and g) rotational isomers into two rotational states that account for the position cis or trans of the ester group with respect to the methine hydrogen. The model gives a good account of the experimental results, assuming that the rotational angles about O–Ph bonds are $\Psi = \pm 60°$ and $\pm 120°$ for PMCPA and $\Psi = \pm 75°$ for POCPA.

Introduction

The conformation dependent properties of poly(methyl acrylate) (PMA) were studied some time ago by using a two-state rotational scheme containing four energy parameters.[1] In general, the model gives a good account of the unperturbed dimensions, stereochemical equilibrium, and NMR coupling constants. The model averages the two (cis and trans) eligible orientations of the ester group with respect to the methinic hydrogen, originated by rotation about C^α–C^* bonds (where α and $*$ identify a substituted carbon of the chain skeleton and the carbonyl carbon, respectively). Studies on the dipole moment of PMA, performed by Saiz et al.,[2] hinted the need of formulating a four-state scheme by splitting each rotational isomer into two rotational states, in which the positions (trans and cis) of the ester group with respect to the methine hydrogen were distinguished. However, further investigations[3] indicated that a two-state scheme could also reproduce the experimental dipole moments of PMA chains.

The schematic substitution of the methoxy group of the repeating unit of PMA for a phenoxy or a chlorophenoxy group leads to polymers whose polarity should be strongly dependent on the location of the halogen atom on the phenyl ring. The dipole moments should also be very sensitive to the rotational angle Ψ about O–Ph bonds in the case of those polymers in which the chlorine atom is in the ortho or meta position in the phenyl group. Earlier dielectric studies[4] performed on phenyl propionate (PP), *p*-chlorophenyl propionate (PCPP), *o*-chlorophenyl propionate (OCPP), and *m*-chlorophenyl propionate (MCPP) showed that the dipole moment of the compounds follows the trend PCPP > MCPP > OCPP > PP. Comparison of theoretical and experimental values for MCPP and OCPP suggests that the rotational angles about O–Ph bonds are $\Psi = \pm 60°$ and $\pm 120°$ for the former compound and $\Psi = \pm 75$ for the latter.[4]

In a recent work,[5] the dipole moments of model compounds of the phenyl and chlorophenyl esters of poly(acrylic acid) (i.e., phenyl, *o*-chlorophenyl, *m*-chlorophenyl, and *p*-chlorophenyl diesters of 2,4-dimethylglutaric acid) were measured and the results critically interpreted by the rotational isomeric state model. The necessity of taking into account additional rotational angles in those side chains in which the chlorine atoms are located in ortho and metha positions in the phenyl group made it advisable to use a four rotational state scheme[6] to analyze the polarity of these model compounds. This model was used in this paper to study the dielectric conformation-dependent properties of poly(phenyl acrylate) (PPA), poly(*p*-chlorophenyl acrylate) (PPCPA), poly(*o*-chlorophenyl acrylate) (POCPA), and poly(*m*-chlorophenyl acrylate) (PMCPA).

Experimental Section

Synthesis of the Monomer. Phenyl acrylate and *o*-, *m*-, and *p*-chlorophenyl acrylates were prepared according to the procedure described by Patai et al.,[7] modified by the addition of 20% (v/v) dioxane to the aqueous reaction medium. In a typical experiment, a solution of the phenolic reagent (0.1 mol) in 260 mL of water/dioxane (80/20) with 5% NaOH, was placed into a three-necked flask provided with a stirrer, thermometer, and dropping funnel. The solution was cooled below 0 °C and freshly distilled acryloyl chloride (0.12 mol) was added dropwise. The crude acrylic esters were extracted 2-fold with ether, washed with distilled water, dried overnight with calcium chloride and then with calcium hydride, and finally distilled off at reduced pressure. Other experimental details are given elsewhere.[8]

Polymerization. Homopolymerization reactions were carried out in benzene solutions at 50 ± 1 °C. Monomer and initiator concentrations were 3 mol L^{-1} and 0.3 mol % of the total monomer concentration, respectively. Conversions were kept below 12%. The polymers were isolated by precipitation into cool methanol, filtered off, and exhaustively dried at vacuum until constant weight was attained.

Polymer Analysis. The tacticity of the polymers was determined from the analysis of the ^{13}C NMR spectra recorded in chloroform solutions with a Varian XL-300, at 75 MHz. TMS was used as internal reference. All the spectra were recorded with an adquisition time of 3 s and about 16 000 transients at a temperature of 40 °C. Under these conditions one might expect little difference between the relaxation times of similar carbons that differ only in their stereochemical configuration, i.e., methylene, methine, or carbonyl ester groups. The molar frac-

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[†] Universidad de Alcalá de Henares.

[‡] Consejo Superior de Investigaciones Científicas.

[§] This paper is dedicated to Professor Gonzalo M. Guzmán on the occasion of his 65th birthday.

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Table I
Conversion, Number-Average Molecular Weight, and Stereochemical Composition of Poly(phenyl acrylate) (PPA), Poly(*o*-chlorophenyl acrylate) (POCPA), Poly(*m*-chlorophenyl acrylate) (PMCPA), and Poly(*p*-chlorophenyl acrylate) (PPCPA)

polymer	wt %	$10^{-3}M_n$	*mm*	*mr* + *rm*	*rr*
PPA	11.50	240	0.04	0.33	0.62
POCPA	10.80	150	0.04	0.33	0.62
PMCPA	11.20	350	0.06	0.32	0.62
PPCPA	11.60	600	0.04	0.32	0.64

Table II
Summary of Dielectric Results for Poly(phenyl acrylate) (PPA), Poly(*o*-chlorophenyl acrylate) (POCPA), Poly(*m*-chlorophenyl acrylate) (PMCPA), and Poly(*p*-chlorophenyl acrylate) (PPCPA)

polymer	*T*, °C	$d\epsilon/dw$	$2n_1\, dn/dw$	μ_0,[a] D	$\langle\mu^2\rangle/x\mu_0^2$
PPA	30	1.416	0.181	1.669	0.624
	40	1.423	0.188	1.679	0.651
	50	1.401	0.195	1.699	0.656
	60	1.374	0.202	1.700	0.664
POCPA	30	2.200	0.174	1.800	1.090
	40	2.102	0.179	1.811	1.079
	50	2.019	0.186	1.832	1.061
	60	1.980	0.191	1.824	1.090
PMCPA	30	2.187	0.179	2.456	0.574
	40	2.142	0.184	2.463	0.588
	50	2.104	0.188	2.471	0.603
	60	2.025	0.191	2.477	0.605
PPCPA	30	2.210	0.168	2.590	0.524
	40	2.117	0.179	2.638	0.507
	50	2.050	0.190	2.648	0.510
	60	1.997	0.202	2.694	0.501

[a] Values of the dipole moment of the side groups, taken from ref 4.

tion of syndio (*rr*), hetero (*mr* + *rm*), and isotactic (*mm*) triads was determined from the analysis of the CH and C=O resonance signals.[9] The values of the corresponding sequences are given in Table I. The third column of this table shows the number-average molecular weight of the polymer samples, determined at 34 ± 1 °C in benzene solutions with a Knauer high-speed membrane osmometer.

Dielectric Measurements. Values of the dielectric constant ϵ of solutions of phenyl and chlorophenyl esters of poly(acrylic acid) were obtained with a capacitance bridge (General Radio, type 1620 A) operating with a three-terminal cell at 10 kHz.[10] Values of the increments of the index of refraction of the solutions with respect to that of the solvent, n_1, were measured with a He-Ne KMX-16 laser differential refractometer (Chromatix Inc.) operating at 632.8 nm.

Results

Values of the derivatives $d\epsilon/dw$ were obtained from the slopes of the plots of the increments ($\Delta\epsilon = \epsilon - \epsilon_1$) of the dielectric constant ϵ of the solutions with respect to that of the solvent ϵ_1, against the weight fraction w of the polymer in the limit $w \rightarrow 0$. The results obtained at 30, 40, 50, and 60 °C are shown in the third column of Table II. The derivatives dn/dw were also obtained from the plots of the increments ($\Delta n = n - n_1$) of refractive indices of the solutions versus w, and the values obtained are given in the fourth column of Table II. The values of the mean-square dipole moments $\langle\mu^2\rangle$ were determined by means of the equation of Guggenheim[11] and Smith[12]

$$\langle\mu^2\rangle = \frac{27\kappa TM}{4\pi\rho N_a(\epsilon_1 + 2)^2}\left(\frac{d\epsilon}{dw} - 2n_1\frac{dn}{dw}\right)$$

where κ is the Boltzmann constant, T is the absolute temperature, N_a is Avogadro's number, and ρ is the density of the solvent.

The values of the mean-square dipole moment were expressed in terms of the dipole moment ratio $\langle\mu^2\rangle/x\mu_0^2$, where $x\mu_0^2$ is the mean-square dipole moment of the chain with x repeating units, each of them associated with a dipole moment μ_0. The values of μ_0 of the side groups are indicated in the fifth column of Table II. The magnitude of the dipole moment ratio corresponding to each polymer is given in the sixth column of the table; the uncertainty of these values was estimated to be ±3%.

Theoretical Analysis

The model used for the present work has been previously employed for the analysis of oligomers of PMA[6] and phenyl and chlorophenyl diesters of 2,4-dimethylglutaric acid[5] (dimers of the polymers studied here). A four-state conformational scheme was used in order to distinguish between the two orientations of the ester group generated by rotation about the C^α–C^* bond and represented by the rotational angle χ whose two allowed states are $\chi = 0, \pi$ (when the carbonyl oxygen is synperiplanar, antiperiplanar with the methine hydrogen). The statistical weight matrices for this scheme are[5,6]

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

for the CH_2–C^α–CH_2 pair and

$$U''_r = \begin{pmatrix} 1 & \gamma_1 & 0 & 0 \\ \gamma_1 & \gamma_2 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

$$U''_m = A \times \begin{pmatrix} 1 & \gamma & \beta & \beta \\ \gamma & 1 & \beta & \beta \\ \beta & \beta & 0 & 0 \\ \beta & \beta & 0 & 0 \end{pmatrix}$$

for the racemic and meso configurations of the C^α–CH_2–C^α bond pair, the rotational isomers appearing in the order (t,χ=0), (t,π), (g,0), (g,π). A brief explanation of the statistical parameters follows.[5,6] γ_1 and γ_2 come 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 diad, whereas γ arises from the difference in electrostatic interactions between $t0,t\pi$ (or $t\pi,t0$) and $t0,t0$ (or $t\pi,t\pi$) in the meso diad. The statistical weight of $\chi = \pi$ relative to $\chi = 0$ orientations is denoted by ρ. $A = \omega''\delta_m/\delta_r$ and $\beta = 1/\eta\delta_m\omega''$, where ω'' represents the second-order statistical weight for the two ester groups juxtaposed as in the meso *tt* state, η is the first-order Boltzmann factor for trans versus gauche, and δ_m and δ_r are Boltzmann factors of the Coulombic interactions in $t0,t0$ orientations of *m* and *r* diads, respectively. Table III summarizes the values of the statistical weights taken from ref 5 and referred to as the "main set".

The valence angles were taken as $\theta' = 114°$ and $\theta'' = 112°$. All the results shown below were computed with the rotational isomers of the skeleton located at the average torsions $\langle\Phi\rangle$ deduced from the conformational energy calculations on oligomers of PMA (set I in ref 5 and 6), namely, $\langle\Phi_1,\Phi_2\rangle_{tt} = 16,16°$, $\langle\Phi_1,\Phi_2\rangle_{tg} = 3,114°$, and

Table III
Main Set of Statistical Weights at 30 °C (Taken from Reference 5) and Values of the Dipole Moment Ratio D_x[a]

polymer	ρ	β	γ_1	γ_2	γ	D_x
PPA	1.1	1.8	1.4	2.5	4.5	0.630
POCPA	1.1	0.3	2.0	0.2	2.3	1.015
PMCPA	1.1	2.4	0.2	3.1	0.2	0.523
PPCPA	1.1	5.0	1.4	2.3	0.2	0.942

[a] Calculated with these weights for polymers of x = 200 repeating units and w_m = 0.30.

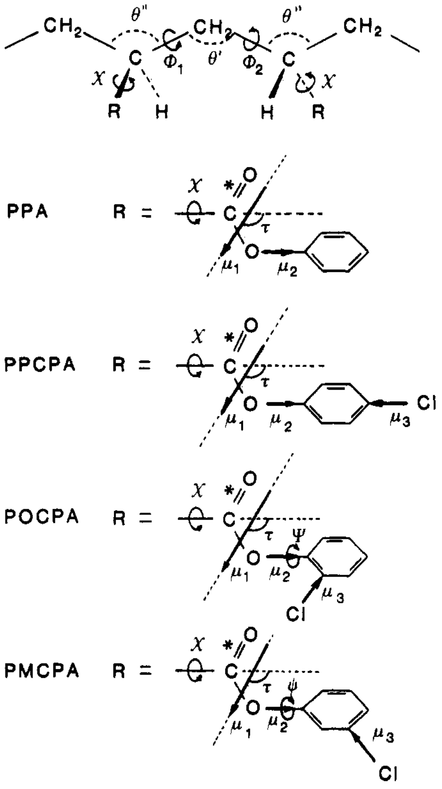

Figure 1. Schematic representation of a segment of the syndiotactic chain shown in the all-trans ($\Phi_1 = \Phi_2 = 0$) conformation. The side groups R of the four polymers studied in the present work are depicted in order to show the internal rotations (χ and Ψ) and the contributions to the dipole moment of each group. The orientation $\Psi = 0$ is shown in both POCPA and PMCPA.

$\langle \Phi_1,\Phi_2 \rangle_{gt}$ = 114,3° for the meso diad and $\langle \Phi_1,\Phi_2 \rangle_t$ = 3,3° for the racemic, with omission of all other states whose statistical weights are negligibly small.[5,6] Exploratory calculations carried out with other values of $\langle \Phi \rangle$ (Schemes II and III in ref 2) proved that in the region of $w_m \approx 0.3$, the dipole moments of these polymers are almost insensitive to small changes in the value of Φ.

Figure 1 shows a schematic representation of the chain skeleton, together with the structure of the side group R, for the four polymers studied here. The dipole moment of each side group was represented by the sum of two or three contributions, assigned to reproduce the experimental dipole moments of phenyl and chlorophenyl propionates measured in benzene solution.[4] Thus μ_1 represents the contribution of a methyl ester for which a modulus[13,14] of 1.75 D and an orientation[15] defined by the angle τ = 123° were used. The contribution μ_2 represents the effect of replacing a methyl by a phenyl group and its value[4] is 0.3 D. Finally, μ_3 represents the dipole moment of the chloro-phenyl bond and the value 1.6 D, taken from chlorobenzene,[4,13] was assigned to this contribution. In the cases of POCPA and PMCPA, the dipole moment of the side groups depends on the rotation of the O–Ph bond, represented by the angle Ψ, the orientation Ψ = 0° being indicated in Figure 1. Two orientations, defined as Ψ = ±75°, were used for POCPA while in the case of PMCPA the allowed positions were[4,5,16] Ψ = ±60,±120°.

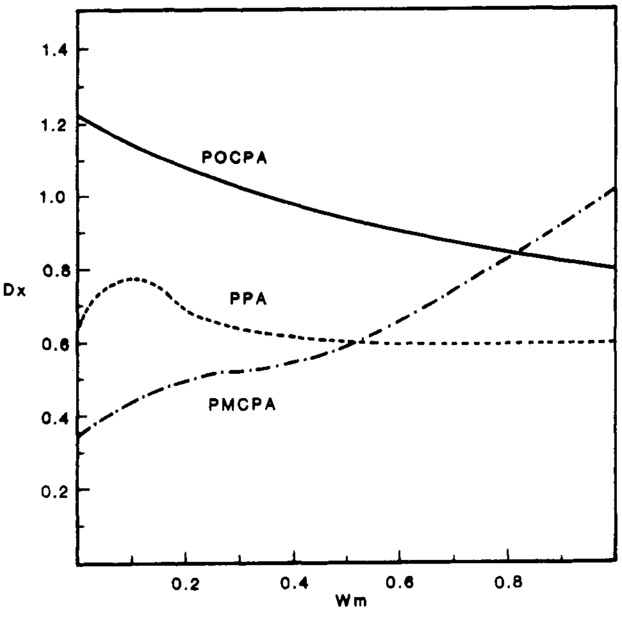

Figure 2. Variation of the dipole moment ratio $D_x = \langle \mu^2 \rangle / x\mu_0^2$ with the fraction of meso diads w_m. Calculations were performed at 30 °C with x = 200 repeating units.

The dipole moments of the side groups were transformed[17] into the coordinates system affixed to the skeletal bond C^α–CH_2 for each possible orientation (i.e., for each allowed combination of values of χ and Φ angles). The matrix multiplication scheme[18,19] was then used to generate chains of the desired degree of polymerization x with predetermined values w_m of the fraction of meso diads and Bernoullian placement of meso and racemic units. The mean-square dipole moments of these chains were computed and transformed into the dimensionless dipole ratio D_x. As was indicated above, dipole moments of phenyl and chlorophenyl propionates[4] were used as the value of μ_0 for the repeating units.

In the cases of PPA and PPCPA, the only conformational freedom of the side group is the χ angle, which is already taken into account in the model. Consequently, the standard procedure was used for the calculation and all the results shown below for heterotactic chains (i.e., $0 < w_m < 1$) are averages over 20 independently generated chains. However, in the cases of POCPA and PMCPA, the incorporation of the Ψ rotation into the statistical weight matrices would require schemes with 8 × 8 or 16 × 16 states, which would be too cumbersome to use. On the other hand, a Monte Carlo simulation would require too much computation time. For these reasons a combination of both methods was used. Thus a 4 × 4 scheme was employed with the incorporation of a random routine to decide which of the allowed orientations of Ψ should be used for each unit. The number of generated chains was increased to 40, in the case of POCPA, and 80 for PMCPA (even for pure isotactic and syndiotactic chains), and it was seen that, on the average, each orientation of Ψ amounted to (50.0 ± 0.5)% and (25.0 ± 0.5)% for POCPA and PMCPA. Several tests of the program showed that the results were reproducible and that the procedure is easier and faster than either splitting the scheme or performing a Monte Carlo simulation.

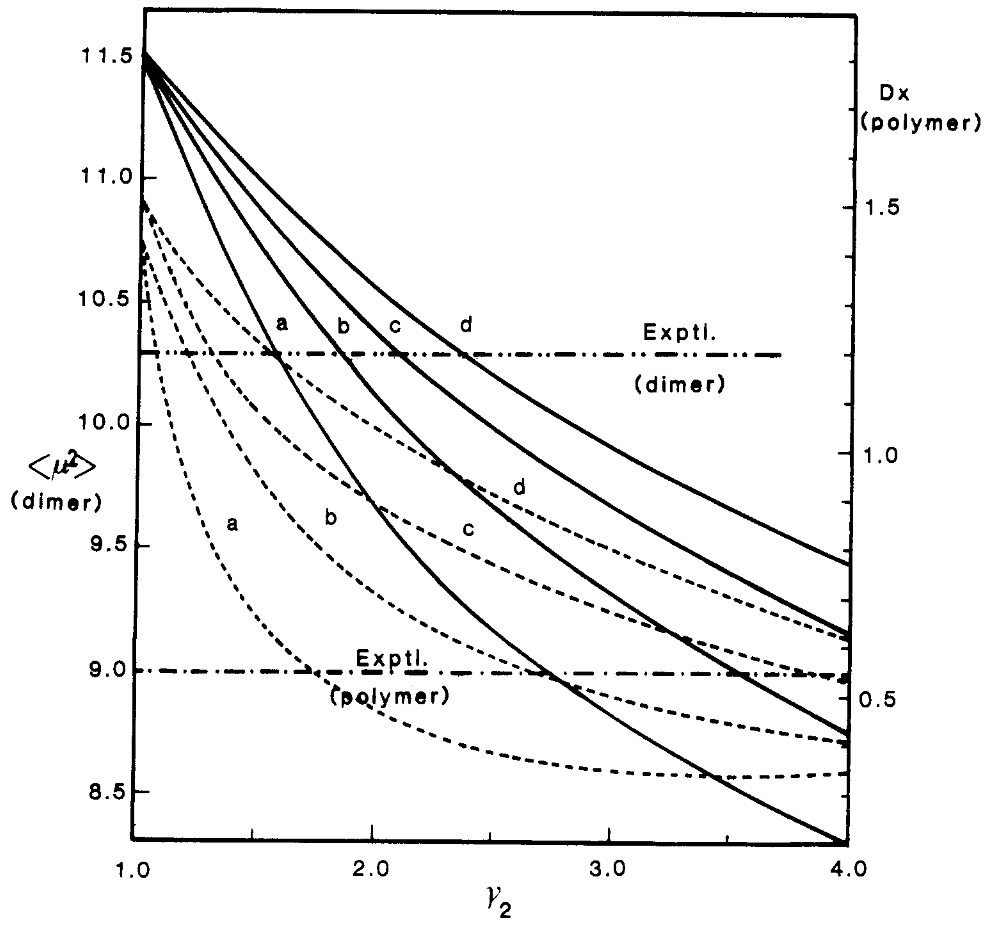

Figure 3. Dipole ratio D_x of PPCPA (broken lines) and $\langle \mu^2 \rangle$ of the dimer (solid lines) as functions of γ_2 for the values of γ_1 = 0.0, 0.5, 1.0, and 1.5 (lines a, b, c, and d, respectively). Calculations were performed at 30 °C with ρ = 1.1, β = 5.0, and γ = 0.2. The results corresponding to the polymer were obtained for x = 200 and w_m = 0.3, whereas those for the dimer correspond to a equimolecular mixture of meso and racemic stereoisomers.

Table IV
Variation of the Dipole Moment at 30 °C for Chains with x = 200 and w_m = 0.30[a]

	$10^3\ d(\ln \langle \mu^2 \rangle)/d(\text{param})$			
param	PPA	PPCPA	POCPA	PMCPA
T	1.8	3.0	-0.2	2.3
θ'	-3.0	-55.8	-5.3	-7.0
θ''	4.5	40.2	8.6	3.8
ρ	-785.4	-1520.1	54.1	-459.2
β	47.9	-17.6	73.8	-14.9
γ_1	45.8	733.8	25.8	275.0
γ_2	-126.0	-647.6	-136.7	-81.7
γ	-35.5	144.3	-34.6	-26.2
τ	-12.8	29.6	-13.7	-18.4
Ψ			19.7	0.3

[a] For PPA, POCPA, and PMCPA the main set of statistical weight parameters was used in the calculations. For PPCPA the calculations were performed with ρ = 1.1, β = 5.0, γ_1 = 0.1, γ_2 = 1.8, and γ = 0.2.

Some preliminary calculations were carried out in order to check the dependence of D_x on the degree of polymerization x. They proved that the dipole moment ratio increases as x increases and reaches asymptotic limits at $x \approx$ 150–200. All the results shown below were obtained with x = 200 for which the differences between D_x and the extrapolated value D_∞ are ca. 1–2% in the heterotactic composition region.

Results and Discussion

The last column of Table III summarizes the values of D_x, calculated at 30 °C with the main set of parameters, for polymers having w_m = 0.3. Comparison of these values with the experimental results shown in Table II indicates a good agreement in three of the four polymers, namely, in the cases of PPA, POCPA, and PMCPA, while in the case of PPCPA the calculated value is roughly twice the experimental result.

The variation of D_x with the fraction of meso diads w_m for PPA, POCPA, and PMCPA is shown in Figure 2, where the standard errors of the averages are roughly represented by the thickness of the lines. This variation is consistent with the differences between the values of $\langle \mu^2 \rangle$ for meso and racemic configurations of the dimers.[5] Thus, in the case of PPA both dimers have roughly the same dipole moment and D_x of the polymer is almost insensitive to the tacticity, with the exception of a small maximum obtained for predominantly syndiotactic chains that still have a few isotactic units to interrupt the all-trans syndiotactic sequences. The value of D_x increases and decreases with w_m for PMCPA and POCPA, respectively; the same kind of variation is observed for their respective dimers.

As can be seen in Table III, the dipole ratio of PPCPA cannot be reproduced by using the set of parameters selected from the analysis of bis(p-chlorophenyl) 2,4-dimethylglutarate (PCPDG), which can be considered a dimer of PPCPA. Some exploratory calculations were performed to optimize the parameters in order to reproduce simultaneously the dipole moments of both the dimer and the polymer. They proved that the best optimization is obtained by decreasing both γ_1 and γ_2, at the same time. Figure 3 shows the dependence of $\langle \mu^2 \rangle$ (for equimolecular mixtures of meso and racemic configurations) for the dimer, and D_x of PPCPA ($w_m = 0.3$ and $x = 200$), upon γ_2, for several values of γ_1, keeping all the other parameters as in the main set. The best choice is $\gamma_1 = 0.1$, $\gamma_2 = 1.8$, which gives $\langle \mu^2 \rangle = 10.05$ D^2 and $D_x = 0.540$, in good agreement with the experimental values of 10.30 D^2 for the dimer[5] and 0.524 for the polymer (see Table II).

The variation of D_x with the parameters used in the calculations is summarized in Table IV. The temperature coefficient (first row in the table) is positive in three of the polymers and roughly zero in POCPA. As can be seen, the comparison with the experimental results is satisfactory in three of the cases and poor for PPCPA. Thus PPA and PMCPA show an increase in $\langle \mu^2 \rangle$ with increasing temperature, whereas the dipole moment of POCPA is roughly independent of temperature. However, the experimental measurements seem to indicate a negative temperature coefficient for PPCPA, in contrast with the positive value obtained by the calculations.

The variation of the dipole moment ratio with all the other parameters is quite similar to that exhibited by the dimers.[5] Thus in three of the cases, namely, PPA, PPCPA, and PMCPA, D_x sharply decreases as ρ increases owing to the fact that racemic $t0,t0$ has a much higher dipole moment than any of the other three allowed conformations. In contrast, $t\pi,t\pi$ is the conformation of highest dipole moment in the racemic diad of POCPA, with the other three allowed conformations having roughly the same polarity; the stability of $t\pi,t\pi$ depends on ρ^2, whereas the stability of $t0,t\pi$ and $t\pi,t0$ depends on ρ. Therefore to modify ρ means to change simultaneously, and in the same direction, the incidence of both high and low polarity conformations and, as result, D_x is less sensitive to ρ than in the other polymers.

The four polymers are quite sensitive to the angle τ governing the orientation of the dipole moment of the ester group μ_1. In the case of PPCPA, D_x increases with increasing τ; the reason is that μ_3 is much larger than μ_2 and therefore the resultant of these two vectors points from Ph to O. As τ increases, μ_1 comes closer to that direction and the total dipole moment of the whole group increases. In contrast, in PPA μ_2 is the only dipole moment of the alcoholic residue and it points from O to Ph, so that the net dipole moment of the group decreases with increasing τ. As in the case of the dimers,[5] the value of Ψ modifies substantially the dipole moment of POCPA, whereas it is almost irrelevant for PMCPA. The reason is that there are two symmetrical values of χ allowed for POCPA and, in both orientations, the partial cancellation between μ_1 and μ_3 becomes smaller as Φ increases; consequently, D_x increases with Φ. However, in PMCPA the number of positions allowed for Φ is four and when the cancellation between μ_1 and μ_3 increases for two of the orientations, it decreases for the other two and the net effect is negligible.

Finally, we conclude that the four-state scheme developed for oligomers of PMA[6] gives a good account of the statistical properties of phenyl and chlorophenyl esters of polyacrylic acid and their dimers.[5] In three of the compounds studied in the present work the set of parameters chosen in an earlier work[5] for the dimers can be used without any modification for the polymers; however, in the case of PPCPA it was necessary to optimize two of the statistical weights in order to reproduce simultaneously the results of both dimer and polymer.

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Registry No. PPA, 28133-04-2; POCPA, 28156-39-0; PMCPA, 50828-87-0; PPCPA, 28156-40-3.