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Registry No. DDA9 (copolymer), 79062-62-7; DDA9 (repeating unit), 79079-27-9; MAA9 (copolymer), 84041-39-4; MAA9 (repeating unit), 79079-25-7; 6OAB-d_8, 84041-40-7.

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Kerr Effect and Dielectric Study of Poly(vinyl chloride) and Its Oligomers

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ABSTRACT: We present experimental results for the molar Kerr constant ${}_{\mathrm{m}}K$ and mean square dipole moment $\langle\mu^2\rangle$ for the two isomers of 2,4-dichloropentane (meso (m) and racemic (r)), the three isomers of 2,4,6-trichloroheptane (mm, mr, and rr), and poly(vinyl chloride) (PVC). We calculate configurational averages of ${}_{\mathrm{m}}K$, $\langle\mu^2\rangle$, and $\langle\gamma^2\rangle$ (mean anisotropy squared) for these molecules using the rotational isomeric state model of Williams, Pickles, and Flory. We find a strong sensitivity of ${}_{\mathrm{m}}K$ and $\langle\mu^2\rangle$ to the first-order parameter E_η, which accounts for chlorine–methine carbon interactions, and to the second-order parameter $E_{\omega''}$, which accounts for chlorine–chlorine atom interactions. We find that E_η and $E_{\omega''}$ are significantly less attractive and more repulsive, respectively, than deduced by Flory and co-workers. Deviations of bond rotational positions from 0° and ±120° are of the order of 3°. PVC stereoregularity or tacticity has a strong influence on ${}_{\mathrm{m}}K$ and $\langle\mu^2\rangle$, particularly in the highly isotactic and syndiotactic regions. We find fair agreement between the calculated and observed values of ${}_{\mathrm{m}}K$, $\langle\mu^2\rangle$, and $\langle\gamma^2\rangle$ for PVC and its oligomers.

Vinyl polymers $-\mathrm{CH_2(CHRCH_2)}_x\mathrm{CHR}-$ differ from other long-chain molecules in two important respects.[1] The substitution of an R group for an H atom at every other carbon atom in polymethylene tends to severely restrict the allowed backbone conformations about a pair of successive rotatable bonds due to steric overlap and coulombic repulsion. Also, since alternate carbons are asymmetrically substituted, the characteristics of the chain will depend sensitively on the stereochemical composition of such centers of asymmetry. This has been demonstrated experimentally and theoretically for several configurational properties of vinyl polymers, viz., end-to-end distance,[2] NMR chemical shifts,[3] dipole moments,[4] depolarized Rayleigh scattering,[5] and Kerr effect.[6–9] The chain property last mentioned, i.e., the Kerr effect, appears to be one of the most sensitive to the configurational properties of flexible polymers as demonstrated recently by calculation[6,7] and experiment.[6,8,9]

In this paper we utilize the Kerr effect and dipole moments to characterize poly(vinyl chloride) (PVC) and its oligomers 2,4-dichloropentane (DCP) and 2,4,6-trichloroheptane (TCH). We present experimental values of the molar Kerr constant ${}_{\mathrm{m}}K$ and dipole moment squared $\langle\mu^2\rangle$ and also their calculated values, based on a rotational

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Table I

${}_{\mathrm{m}}K$ ($\times 10^{-12}$ cm^7 SC^{-2} mol^{-1}), $\langle\mu^2\rangle$ ($\times 10^{-36}$ SC^2 cm^2), and $\langle\gamma^2\rangle$ ($\times 10^{-48}$ cm^6) of 2,4-Dichloropentane (DCP) (m and r), 2,4,6-Trichloroheptane (TCH) (mm, mr, and rr), and Atactic Poly(vinyl chloride) (PVC) ($p_r = 0.57$)

	${}_{\mathrm{m}}K$			$\langle\mu^2\rangle$			$\langle\gamma^2\rangle$		
		calcd[a]			calcd[a]			calcd[a]	
	exptl	A	B	exptl	A	B	exptl	A	B
DCP (m)	6.24	10.9, 5.53[h]	7.32, 1.86[h]	4.74	6.03	5.95	2.2[c]	1.62	1.60
DCP (r)	2.04	−9.8, 1.54[h]	−6.57, 3.65[h]	4.57	5.01	5.19	0.5[c]	0.800	1.12
TCH (mm)	−6	−32.5	−37.3		4.84	4.65		1.14	1.09
TCH (mr)	17	58.0	45.2	6.86[d]	9.30	8.87		2.17	2.08
TCH (rr)	89	142	86.5	16.6[d]	12.8	10.4		2.76	2.47
TCH (mixture)[b]	32.1	54.9	34.6	7.87	9.03	8.21		2.06	1.93
PVC[c]	−14.4	−16.9	−11.3	2.55, 2.75,[f] 2.66[g]	3.99	2.95		0.513	0.390

[a] Calculated with the following energetic parameters: $E_\tau = 500$, $E_\omega = 2000$, $E_{\omega'} = 2500$, $E_{\omega''} = 3000$ (cal mol^{-1}), and $\Delta\phi = 3°$. For A, $E_\eta = -850$ cal mol^{-1} and for B, $E_\eta = -400$ cal mol^{-1}. [b] (mm):(mr):(rr) = 0.24:0.54:0.22. [c] Values given are ${}_{\mathrm{m}}K/x$, $\langle\mu^2\rangle/x$, and $\langle\gamma^2\rangle/x$, respectively, x being the number of repeat units. [d] Shimanouchi, T., et al. *Makromol. Chem.* **1965**, *86*, 43. [e] Reference 15. [f] Reference 19. [g] Reference 20. [h] Calculated with $\Delta\phi = 0°$.

isomeric state model. We show clearly the role of the substituent Cl in restricting the conformations available to the chain and the influence of chain tacticity.

Experimental Section

The Kerr effect, dielectric apparatus, and experimental techniques have been described previously.[8] Carbon tetrachloride (Mallinckrodt) and dioxane (Matheson Coleman and Bell) were used as solvents for DCP, TCH, and PVC, respectively. Dioxane was dried over type 4A molecular sieves prior to use. DCP was obtained from Pfaltz and Bauer. TCH was synthesized according to a method to be published at a later date.[10] The mixture of the three isomers (mm, mr, and rr) was identified by ^{13}C NMR and the isomers were found to be in the ratio (mm):(mr):(rr) = 0.24:0.54:0.22. The ${}_{\mathrm{m}}K$ value of the mixture was 32.1×10^{-12} cm^7 SC^{-2} mol^{-1}. The separation of the two isomers (m and r) of DCP and the three isomers (mm, mr, and rr) of TCH was effected by a Varian P-90 gas chromatograph. The isomeric composition of the fractions of DCP and TCH was identified by ^{13}C NMR. For DCP, the isomers were found to have a purity greater than 95%. However, in the case of TCH the separation was not as complete and the three fractions had the following compositions: (1) (mm):(mr):(rr) = 0.81:0.13:0.06, (2) (mm):(mr):(rr) = 0.06:0.81:0.13, and (3) (mm):(mr):(rr) = 0.03:0.15:0.82. The ${}_{\mathrm{m}}K$ values of the mixtures were (1) 3×10^{-12}, (2) 25×10^{-12} and (3) 76×10^{-12} cm^7 SC^{-2} mol^{-1}). We can derive the ${}_{\mathrm{m}}K$ values of the individual isomers, ${}_{\mathrm{m}}K$(mm), ${}_{\mathrm{m}}K$(mr), and ${}_{\mathrm{m}}K$(rr), by assuming that they are additive. Therefore, from the ${}_{\mathrm{m}}K$ values of the mixtures 1–3, we solve three linearly independent simultaneous equations and obtain ${}_{\mathrm{m}}K(\mathrm{mm}) = -6 \times 10^{-12}$, ${}_{\mathrm{m}}K(\mathrm{mr}) = 17 \times 10^{-12}$, and ${}_{\mathrm{m}}K(\mathrm{rr}) = 89 \times 10^{-12}$ cm^7 SC^{-2} mol^{-1}. We confirm the correctness of this approach by calculating the ${}_{\mathrm{m}}K$ value of the mixture of TCH ((mm):(mr):(rr) = 0.24:0.54:0.22) and find 27×10^{-12} cm^7 SC^{-2} mol^{-1}, which compares well with the experimental result, 32×10^{-12} cm^7 SC^{-2} mol^{-1}.

A sample of low molecular weight PVC ($M_w = 42\,000$, $x = 672$) was a gift of Dr. C. A. Daniels of BFGoodrich Co. From its NMR spectrum it was found to be atactic with a probability of racemic replication $p_r = 0.57 = 1 -$ BFGoodrich p_m is the probability of meso replication. The statistics of chain stereosequence were found to be Bernoullian. PVC was dissolved in dioxane by continuous stirring for about 2 h. The solutions appeared optically clear and homogeneous to the naked eye. After the solution was poured into the Kerr cell and the voltage applied, the resultant birefringence was not constant but decreased with time. Also the Kerr constant of the solution was a function of the applied voltage, which indicated the presence of aggregates.[11] After about an hour with the electric field on, the Kerr constant of the solution reached a steady value and was sensibly independent of the applied voltage. The decrease of the Kerr constant from its initial value when the electric field was applied could not be ascribed to heating effects since these would be manifest as optical inhomogeneities and result in the scattering and divergence of the analyzing laser light beam. We repeated the measurements for six different concentrations (0.5–2% (w/w)) and found a linear dependence of the Kerr constant on the concentration. No such precautions were necessary for the dielectric constant measurements. The resultant ${}_{\mathrm{m}}K$ and $\langle\mu^2\rangle$ values at 298 K and $\lambda = 633$ nm are given in Table I.

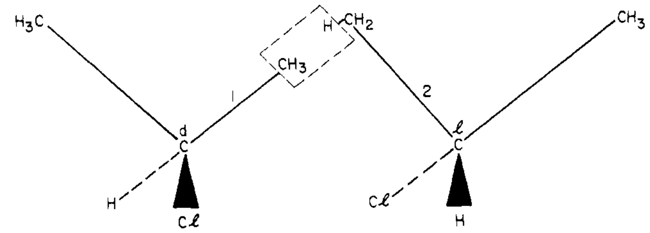

Figure 1. Generation of a PVC chain from isopropyl chloride molecules.

Calculation of ${}_{\mathrm{m}}K$ and $\langle\mu^2\rangle$

Matrix multiplication methods[1] were used to calculate ${}_{\mathrm{m}}K$ and $\langle\mu^2\rangle$. A generator matrix is assigned to each bond and is filled with information about bond angles, rotational states, dipole moments, polarizabilities, and energetic parameters for the bond rotational probabilities. The backbone bond valence angles were kept fixed at 112° and three rotational states (t and g±) were ascribed to each bond. The trans and gauche states were initially set at 0° and ±120° and we also considered alteration of the rotational minima by $\Delta\phi = 5°$ in a direction sense to minimize steric overlap as detailed by Flory.[12]

The polarizability tensors of the molecules discussed in this paper are viewed as the sum of those of isopropyl chloride. Assuming that the bond angles about the methyl carbon are tetrahedral, the elimination of a methane (see Figure 1) leaves the anisotropy of the chain unaffected. This follows from the isotropy of methane and the associated relation $\Delta\alpha_{\mathrm{CH_3}} = -\Delta\alpha_{\mathrm{CH}}$. The polarizability anisotropy tensor of isopropyl chloride is given by

$$\hat{\alpha}_{l,d} = \Gamma_{\mathrm{CC}} \begin{vmatrix} \frac{4}{9} & \frac{2\sqrt{2}}{9} & 0 \\ \frac{2\sqrt{2}}{9} & \frac{2}{9} & 0 \\ 0 & 0 & -\frac{2}{3} \end{vmatrix} + \Gamma_{\mathrm{CCl}} \begin{vmatrix} -\frac{2}{9} & -\frac{\sqrt{2}}{9} & \mp\frac{\sqrt{6}}{9} \\ -\frac{\sqrt{2}}{9} & -\frac{1}{9} & \pm\frac{2\sqrt{3}}{9} \\ \mp\frac{\sqrt{6}}{9} & \pm\frac{2\sqrt{3}}{9} & \frac{1}{3} \end{vmatrix} \quad (1)$$

$\Gamma_{\mathrm{CC}} = \gamma_{\mathrm{CC}} - 2\gamma_{\mathrm{CH}}$ and $\Gamma_{\mathrm{CCl}} = \gamma_{\mathrm{CCl}} - \gamma_{\mathrm{CH}}$. γ_{CC}, γ_{CH}, and γ_{CCl} are the anisotropies of the C–C, C–H, and C–Cl bonds,

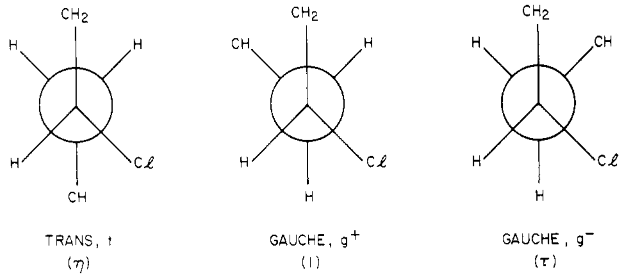

Figure 2. Newman projections of the three rotational states about PVC skeletal bonds and the corresponding statistical weight factors for the *d* and *l* isomers.

respectively. The upper and lower signs refer to *l* and *d* configurations, respectively, at the methine carbons in PVC (see Figure 1). The signs are obviously relevant only in the context of a chain molecule. The coordinate system used in eq 1 follows Flory's convention, being affixed to bond 1 (see Figure 1), with the x axis along the C–C bond, the y axis in the plane of bond 1 and the previous bond and subtending an acute angle with the positive x axis of the previous bond, and the z axis completes a right-handed coordinate system. The dipole moment is assumed to be along the C–Cl bond. Thus

$$\mu_{l,d} = m \begin{vmatrix} -\dfrac{1}{3} \\ \dfrac{\sqrt{2}}{3} \\ \pm\dfrac{\sqrt{6}}{3} \end{vmatrix} \tag{2}$$

Chen and Le Fèvre[13] have reported that $10^{12}{}_{\mathrm{m}}K = 70.23$ cm^7 SC^{-2} mol^{-1} (SC = statcoulomb) and $10^{18}m = 2.05$ SC cm. An additional quantity we require[14] is $10^{24}\Gamma_{\mathrm{CC}} = 0.54$ cm^3. Since

$${}_{\mathrm{m}}K = \frac{2\pi N_{\mathrm{A}}}{135}\left(\frac{2\gamma^2}{3kT} + \frac{\mu^{\mathrm{T}}\hat{\alpha}\mu}{k^2T^2}\right) \tag{3}$$

and

$$\gamma^2 = {}^3\!/_2 \operatorname{tr}(\hat{\alpha}\hat{\alpha}) \tag{4}$$

it follows from eq 1–4 and the relevant constants that $10^{24}\Gamma_{\mathrm{CCl}} = 1.81$ cm^3. This agrees well with the values deduced by Chen and Le Fèvre[13] (1.96) and Carlson and Flory[15] (1.8) (in units 10^{-24} cm^3). In this calculation we have assumed the equality of static and optical polarizabilities.

The rotational isomeric state model is the same as that derived by Williams, Pickles, and Flory[16,17] and used by Mark.[18] There are first-order interaction parameters η and τ, which yield rotational state probabilities about single bonds, as indicated in Figure 2. There are also second-order interaction parameters ω, ω', and ω'', which depend on the rotational states of a pair of adjacent bonds. ω accounts for interactions between two carbon atoms, ω' for interactions between CH$_2$ groups and Cl atoms, and finally ω'' for interactions between a pair of Cl atoms, each pair of atoms or groups being separated by four bonds. On the basis of epimerization studies of DCP and TCH, Flory and co-workers[16,17] have assigned $\eta = 4.2$ at 25 °C to the trans (t) state, corresponding to an energy difference $E_\eta = -850$ cal mol^{-1} relative to the g$^+$ state. The values of the other parameters are less certain. Flory and Cantera et al.[19] have estimated $\tau = 0.42$, which corresponds to an energy difference of $E_\tau = 500$ cal mol^{-1} relative to the g$^+$ state. Our calculated ${}_{\mathrm{m}}K$ and $\langle\mu^2\rangle$ are insensitive to the value assigned to E_τ. E_ω is set at 2000 cal mol^{-1}, corresponding to the second-order interaction energy between a pair of CH$_2$ groups in polymethylene.[1] Our calculated ${}_{\mathrm{m}}K$ and $\langle\mu^2\rangle$ are also insensitive to the value chosen for this parameter. $E_{\omega''}$ plays a crucial role since it reflects the probability of conformations when two C–Cl bonds are approximately parallel, resulting in huge ${}_{\mathrm{m}}K$ and $\langle\mu^2\rangle$ values. The large values of ${}_{\mathrm{m}}K$ and $\langle\mu^2\rangle$ belonging to these conformations more than compensate the low statistical weight assigned to them. Finally, $E_{\omega'}$, which accounts for interaction between Cl and CH$_2$ groups, has been chosen to equal the average of E_ω and $E_{\omega''}$.

Monte Carlo chain generation techniques were used to construct those polymer chains with irregular stereosequences. Each chain was 400 bonds long (200 repeat units) and 15 chains were generated for each degree of stereoirregularity p_{r}. Both terms of eq 3 and 4 were evaluated under the assumption that the static and dynamic polarizabilities were equal.

Results and Discussion

Le Fèvre and Sundaram[20] and Cantera et al.[19] have reported $\langle\mu^2\rangle/x$ values for PVC in the range (2.6–2.8) × 10^{-36} SC^2 cm^2), which are in good agreement with our results. However, our ${}_{\mathrm{m}}K/x$ value for PVC differs considerably from that reported by Le Fèvre and Sundaram.[20] They report a range of values (2.7–35.7) × 10^{-12} cm^7 SC^{-2} mol^{-1} for samples in the molecular weight range 3.3 × 10^4 to 1.2 × 10^5 (x = 538–2022). Our value is −14.4 × 10^{-12} cm^7 SC^{-2} mol^{-1}. While we may not infer anything from our measurements concerning the molecular weight dependence of ${}_{\mathrm{m}}K/x$ for PVC, studies by us on other polar and nonpolar polymers[9,21] show ${}_{\mathrm{m}}K/x$ to be independent of molecular weight. Therefore we have reservations about the validity of Le Fèvre and Sundaram's measurements. We also note that we had to wait a considerable amount of time before the birefringence of the solutions attained their equilibrium values. If instead we had taken the initial reading alone, then we also would have obtained positive ${}_{\mathrm{m}}K$ values. This might explain the discrepancy between our measurements and those of Le Fèvre and Sundaram.

We now turn to the calculation of ${}_{\mathrm{m}}K$ and $\langle\mu^2\rangle$. At the outset we varied the three parameters that we expected would have the greatest influence on the calculations, namely, $E_{\omega''}$, E_η, and $\Delta\phi$. To narrow the range of values of these parameters, we sought first of all those quantities (${}_{\mathrm{m}}K$ or $\langle\mu^2\rangle$) that were mostly sensitive to changes in one parameter only. Thus, the dipole moment $\langle\mu^2\rangle/x$ of PVC was mostly sensitive to E_η and the experimental results dictated that $E_\eta \cong -400$ cal mol^{-1}. Also, the ${}_{\mathrm{m}}K/x$ value of PVC was mostly sensitive to $\Delta\phi$ and we found that $\Delta\phi \cong 3°$. Next, we found the ${}_{\mathrm{m}}K$ values of the m and mm DCP and TCH isomers were very sensitive to changes in $E_{\omega''}$. (See Figure 3.) To obtain agreement with the experimental results, we find that $E_{\omega''}$ = 2000–3000 cal mol^{-1}. Having derived a reasonable approximate set of energetic and geometrical parameters, we set out varying $E_{\omega''}$, E_η, and $\Delta\phi$ to obtain the best fit to all the experimental data. We found that the parameters $E_\eta = -400$, $E_\tau = 500$, $E_\omega = 2000$, $E_{\omega'} = 2500$, $E_{\omega''} = 3000$ (all in cal mol^{-1}), and $\Delta\phi = 3°$ gave the best overall agreement. (See Table I.)

We said above that the dipole moment of PVC dictated that $E_\eta = -400$ cal mol^{-1}. Additional evidence for this value is also given by the ${}_{\mathrm{m}}K$ value of the rr isomer of TCH. (See Table I.) The small positive ${}_{\mathrm{m}}K$ value of the m DCP isomer dictates that $E_{\omega''} = 3000$ cal mol^{-1}. (See Figure 3.) The reason for the sensitivity of ${}_{\mathrm{m}}K$ to $E_{\omega''}$ is easy to see. DCP (m) has two conformations, tt and g$^-$g$^+$, that have

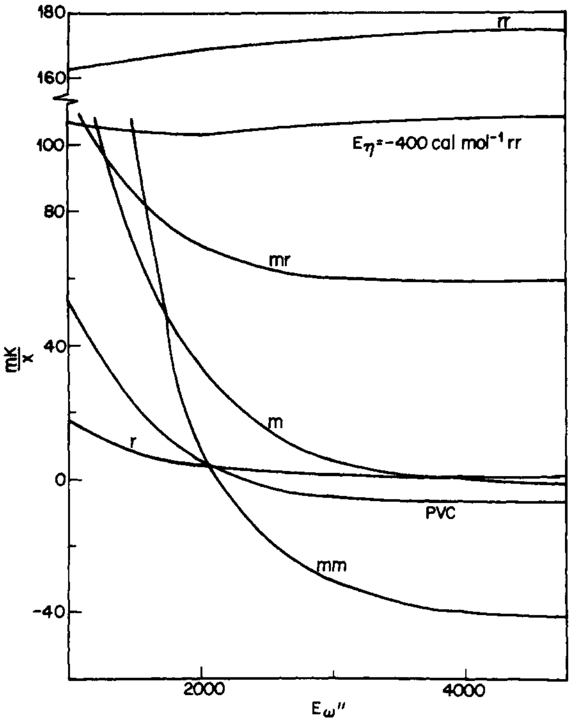

Figure 3. $_mK$ ($\times10^{-12}$ cm^7 SC^{-2} mol^{-1}) vs. $E_{\omega''}$ (cal mol^{-1}) for DCP (m and r), TCH (mm, mr, and rr), and PVC ($p_r = 0.57$). $_mK/x$ calculated with $E_\eta = -850$, $E_\tau = 500$, $E_\omega = 2000$, $E_{\omega'} = (E_\omega + E_{\omega''})/2.0$(cal mol^{-1}), and $\Delta\phi = 0°$ unless otherwise stated.

very large μ^2 and $_mK$ values relative to other conformations since the C–Cl bonds are parallel to each other. Even though the tt and g^-g^+ conformations have low statistical weights $\eta^2\omega''$ and $2\tau\omega''$, respectively, they contribute significantly to $\langle\mu^2\rangle$ and $_mK$. Because of the sensitive interplay between the $_mK$ values of the different conformers, we have presented in Table I other sets of geometric and energetic parameters that are also plausible.

There remain two discrepancies, namely, the $_mK$ values of the mm and mr isomers of TCH. We predict large negative and positive values, respectively, for these two isomers, whereas we find experimentally smaller negative and positive values. It is clear from Figure 3 that with $E_{\omega''} = 2000$ cal mol^{-1} instead of 3000 cal mol^{-1}, the agreement will be better for the $_mK$ value of the mm isomer of TCH, but then the $_mK$ value of the m isomer of DCP will be very large and positive. We were unable to resolve this discrepancy. Also we could obtain better agreement for the $_mK$ value of the mr isomer of TCH with $E_\eta = -100$ cal mol^{-1} instead of -400 cal mol^{-1}, but then the dipole moment of PVC and the $_mK$ value of the rr isomer of TCH would be discordant with the experimental results. With the set of parameters given in Table I (set B) we are able to account for most of the Kerr effect results. We are also able to predict the sign of the $_mK$ values of mm and mr isomers of TCH. It is clear from Table I that we can also account for the dipole moments and mean square anisotropies of the oligomers of PVC, although they appear to be less sensitive to isomerism than the Kerr effect.

We summarize our results by saying that $E_{\omega''} \geq 3000$ cal mol^{-1}, $E_\eta = -850$ to -400 cal mol^{-1} (corresponding to $\eta = 4.2$–2.0), and $\Delta\phi = 0$–$5°$, in order to achieve agreement with the measured values. In Table I we present $_mK$ and $\langle\mu^2\rangle$ values calculated with the preferred set of parameters $E_\eta = -850$ or -400, $E_\tau = 500$, $E_\omega = 2000$, $E_{\omega'} = 2500$, $E_{\omega''} = 3000$ (all in cal mol^{-1}), and $\Delta\phi = 3°$. We also present results for γ^2 (anisotropy squared). As noted previously, we get better agreement with $E_\eta = -400$ cal mol^{-1} than -850 cal mol^{-1}, particularly for the $_mK$ value of the rr isomer of TCH and $\langle\mu^2\rangle/x$ of PVC. The value of $E_\eta = -850$ cal mol^{-1} was accurately determined by Flory[16,17] and co-workers from the epimerization of DCP and TCH. Cantera et al.[19] also concluded that $E_\eta = -850$ cal mol^{-1} from empirical energy calculations, although they found that their calculated values of $\langle\mu^2\rangle/x$ for PVC disagreed with experiment. Boyd and Kessner[22] also performed empirical energy calculations and concluded that $E_\eta = -300$ to -400 cal mol^{-1} and found good agreement between the calculated and experimental dipole moments of PVC. Our $_mK$ and $\langle\mu^2\rangle$ results in Table I favor the lower value of $E_\eta = -400$ cal mol^{-1}.

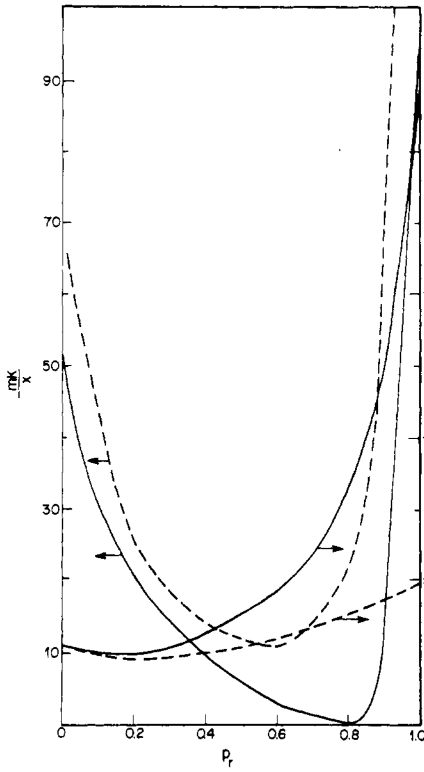

Figure 4. $_mK/x$ ($\times10^{-12}$ cm^7 SC^{-2} mol^{-1}) and $\langle\mu^2\rangle/x$($\times10^{-36}$ SC^{-2} cm^2) vs. tacticity p_r for a PVC chain. Full line, $E_\eta = -850$, $E_\tau = 500$, $E_\omega = 2000$, $E_{\omega'} = 2500$, $E_{\omega''} = 3000$ (cal mol^{-1}), and $\Delta\phi = 0°$. Broken line, $E_\eta = -400$, $E_\tau = 500$, $E_\omega = 2000$, $E_{\omega'} = 2500$, $E_{\omega''} = 3000$ (cal mol^{-1}), and $\Delta\phi = 3°$.

From intrinsic viscosity–molecular weight measurements[23] performed on PVC fractions in benzyl alcohol at the Θ temperature (155.4 °C), Mark[18] used the Flory–Fox equation[24] to deduce the unperturbed dimensions ($\langle r^2\rangle_0$) of PVC. Expressed as the characteristic ratio $C_\infty = (\langle r^2\rangle_0/nl^2)_{n\to\infty}$, where n and l are the number and length of the C–C bonds, he found $C_\infty = 9.75$ when the hydrodynamic constant[24] Φ_0 was set to 2.5×10^{21}. Kurata[25] used $\Phi_0 = 2.7 \times 10^{21}$ and derived $C_\infty = 8.65$ from the same viscosity data.

The dimensions calculated for PVC ($p_r = 0.57$) with $E_\tau = 500$, $E_\omega = 2000$, $E_{\omega'} = 2500$, $E_{\omega''} = 3000$ (all in cal mol^{-1}), and $\Delta\phi = 0°$ are 7.5 with $E_\eta = -400$ cal mol^{-1} and 9.8 with $E_\eta = -850$ cal mol^{-1}. Temperature coefficients of the dimensions (d ln $\langle r^2\rangle_0/\mathrm{d}T$) calculated with $E_\eta = -400$ and -850 cal mol^{-1} are -1.7×10^{-3} and -1.6×10^{-3}, respectively. Mark[18] deduced d ln $\langle r^2\rangle_0/\mathrm{d}T = -1.5 \times 10^{-3}$ from intrinsic viscosity–temperature measurements[26] made on PVC in a good solvent[24] ($T \neq \Theta$).

It appears that comparison of observed and calculated dimensions and their temperature coefficient for atactic PVC does not permit us to choose between the values of -400 or -850 cal mol^{-1} for the first-order interaction energy E_η.

Finally, we discuss the influence of tacticity on $\langle \mu^2 \rangle / x$ and ${}_{\mathrm{m}}K/x$. In Figure 4 we present calculations for the two sets of parameters indicated. The curves for $\langle \mu^2 \rangle / x$ agree with those presented by Cantera et al.[19] and Boyd and Kessner.[22] ${}_{\mathrm{m}}K$ shows a remarkable sensitivity to tacticity, particularly for highly isotactic and syndiotactic PVC chains, which makes this quantity particularly important for characterizing the microstructure of vinyl polymers.

Conclusions

The rotational isomeric state model of Williams, Pickles, and Flory as modified and presented here accounts fairly well for a large number of configurational-dependent properties of PVC and its oligomers. We have shown clearly the importance of second-order interactions, particularly between adjoining Cl atoms in determining the averages of various properties. Cl–Cl repulsive interactions appear to be stronger[27] than previously assumed by Flory and co-workers.[16,17] Also, the first-order interaction parameter E_η, which yields calculated ${}_{\mathrm{m}}K$ and $\langle \mu^2 \rangle$ values in closest agreement with the observed values, is considerably less attractive than the value obtained from epimerization studies. ${}_{\mathrm{m}}K$ appears to be remarkably sensitive to second-order interactions and the tacticity of PVC oligomers and polymers.

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Synthesis and Hydrolysis of Poly(vinyl acetals) Derived from Poly(vinyl alcohol) and 2,6-Dichlorobenzaldehyde[1]

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ABSTRACT: We describe the synthesis and hydrolysis of poly(vinyl acetals) derived from poly(vinyl alcohol) and the pesticide 2,6-dichlorobenzaldehyde. The acetalization reaction under a variety of conditions gave at best a polymer with 68% acetalization. The structure of the polymer, i.e., the ratio of acetal units derived from meso and racemic dyads of poly(vinyl alcohol), was determined by ^{1}H NMR. The acid-catalyzed hydrolysis of this poly(vinyl acetal) in aqueous dioxane at 60 °C was studied in detail. The rate constant for the hydrolysis of the meso and racemic acetal units and the equilibrium constant for meso–racemic intramolecular acetal exchange were determined from these measurements.

Introduction

As part of a general program dealing with controlled-release pesticides, we have prepared a poly(vinyl acetal) from poly(vinyl alcohol) and 2,6-dichlorobenzaldehyde. This aldehyde has been reported[2] to have strong herbicidal and moderate fungicidal activity. In this paper we report the preparation and characterization of the polymer and a detailed study of the kinetics of hydrolysis.

Results and Discussion

Synthesis and Characterization. The acetalization of poly(vinyl alcohol) (PVA) has been studied for a variety of aldehydes.[3] The reaction leads to (1) intramolecular acetalization of primarily 1,3-diol groups, (2) intramolecular acetalization of the occasional 1,2-diol groups, and (3) intermolecular acetalization. Intermolecular acetalization is more a function of reaction conditions and can lead to branched and eventually cross-linked polymer. The latter is easily removed in the purification process. The number of 1,2-diol units in commercial PVA is generally 1–2% and

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