Macromolecules 1982, 15, 866-869

Kerr Effect and Dielectric Study of the Copolymer Poly(styrene-*co*-*p*-halogenated-styrene)

Garo Khanarian,* Rudolf E. Cais, Janet M. Kometani, and Alan E. Tonelli

Bell Laboratories, Murray Hill, New Jersey 07974. *Received December 8, 1981*

ABSTRACT: We present experimental values of the molar Kerr constants ${}_{\mathrm{m}}K/x$ and dipole moments squared $\langle\mu^2\rangle/x$ for the copolymers poly(styrene-*co*-*p*-bromostyrene), where x is the degree of polymerization. Some results are also presented for poly(*p*-chlorostyrene) and related polymers. The rotational isomeric state model of Yoon et al. is used to calculate ${}_{\mathrm{m}}K/x$ and $\langle\mu^2\rangle/x$ values as a function of tacticity and composition. Comparison with the experimental results shows that the tacticity of these polymers is $p_{\mathrm{r}} = 0.55 \pm 0.05$, where p_{r} is the probability of racemic dyad replication.

Polystyrene and its derivatives have been widely studied; however, an important property of vinyl polymers, namely, their degree of stereoregularity or tacticity, has eluded exact determination for polystyrene. NMR, the method of choice for the determination of polymer tacticity, has not provided an unequivocal answer in the case of polystyrene.[1] Recently, Flory and co-workers have used empirical energy calculations,[2] end-to-end distance,[2] dipole moment,[3] light scattering,[4] and electric birefringence[5] methods to characterize polystyrene and related polymers. By comparing their calculated values with the experimental results, they concluded that $p_{\mathrm{r}} = 1 - p_{\mathrm{m}} \cong 0.6 \pm 0.1$, where p_{r} and p_{m} are the probabilities of racemic and meso dyad replication, respectively. However, in the case of poly(*p*-bromostyrene) they concluded that $p_{\mathrm{r}} \cong 0.8$, implying that this polymer was significantly more syndiotactic than polystyrene.

Recently, we have been using the Kerr effect to study several polymers such as the α,ω-dibromoalkanes,[6] poly(oxyethylene glycols),[7] and poly(vinyl chloride) (PVC) and its oligomers.[8,9] We have found the calculated molar Kerr constants ${}_{\mathrm{m}}K$ to be very sensitive to changes in the energetic and geometric parameters of the conformational model and to features of polymer microstructure such as the tacticity. One of us[10] has also presented calculations which show the influence of monomer compositional distribution on ${}_{\mathrm{m}}K$ of a vinyl copolymer. To date, however, there have been no experimental results reported on the Kerr effect of a copolymer.

In this paper we determine the tacticity of polystyrene by studying the Kerr effect of the series of copolymers poly(styrene-*co*-*p*-bromostyrene) over the whole composition range. The copolymers were made by the partial random bromination in the para position of the phenyl ring of the same polystyrene sample, and therefore all the copolymers had the same tacticity. We also present calculations of the molar Kerr constant ${}_{\mathrm{m}}K$ of these copolymers as functions of the degree of bromination and stereoregularity of the starting material, polystyrene, which clearly show the strong sensitivity of ${}_{\mathrm{m}}K$ to tacticity and composition of the resulting copolymer. By comparing the calculated curves of ${}_{\mathrm{m}}K$ with the experimental results, we can determine the tacticity of polystyrene. At the same time we demonstrate the usefulness of the electric birefringence technique to the study of copolymers. Analogous results are presented also for the dipole moments $\langle\mu^2\rangle$ of these copolymers and for poly(*p*-chlorostyrene).

Experimental Section

Monodisperse polystyrene ($\bar{M}_{\mathrm{w}}/\bar{M}_{\mathrm{n}} < 1.06$) with a molecular weight of 20 000 was obtained from Pressure Chemical Co. It was shown to be atactic by ^{13}C NMR. Bromination of the backbone phenyl substituents at random was achieved by addition of bromine to a nitrobenzene solution of polystyrene and stirring for 24 h in the dark at room temperature. Under these conditions only para monosubstitution takes place.[11] The extent of bromination was controlled by adjusting the bromine concentration in the reaction mixture.

The composition of the poly(styrene-*co*-*p*-bromostyrene) obtained by the above procedure was determined by ^{13}C NMR. Spectra were recorded at 50.3 MHz on a Varian XL-200 spectrometer with 20% by volume polymer solutions in either dioxane-d_8 or methylene-d_2 chloride. Typically 5000 transients were accumulated with a sweep width of 10 kHz (1.6-s acquisition time) and a 3.0-s interval between 90° pulses (14-μs duration).

The backbone carbon resonances were insensitive to bromination of the monomer unit. The methine, or CH, carbon resonated at 41.25 ppm, and the methylene, or CH$_2$, carbon resonated from 42 to 47 ppm, according to its stereochemical environment. Copolymer composition was determined from the aromatic carbon resonances. For the para-brominated phenyl ring, the following assignments were made: C$_1$, 143.1; C$_2$, 129.2; C$_3$, 131.4; and C$_4$, 119.9 ppm. The carbons in the unsubstituted phenyl ring had the following chemical shifts: C$_1$, 145.4; C$_2$, 128.6; C$_3$, 128.1; and C$_4$, 126.4 ppm (C$_1$ is the quaternary carbon attached to the polymer backbone). The fraction c of brominated phenyl units was obtained from the area of C$_2$ + C$_3$ resonances in the brominated unit relative to the total C$_2$ + C$_3$ resonance area. The samples we made had c = 0.068, 0.400, 0.533, and 0.93.

Poly(*p*-bromostyrene) and poly(*p*-chlorostyrene) were obtained from Polysciences. Carbon tetrachloride (Mallinckrodt) and dioxane (Matheson Coleman and Bell) were used without further purification as solvents in the Kerr effect and dipole moment measurements. Dioxane was dried over type 4A molecular sieves prior to use. The Kerr effect, dielectric apparatus, and experimental techniques have been described previously.[6] The polymers were dissolved by continuous stirring for about 2 h. The solutions appeared optically clear and homogeneous to the naked eye. After the solution was poured in the Kerr cell and the voltage applied, the resultant birefringence was not constant but decreased with time. Also the Kerr constant of the solutions was a function of the applied voltage. After about an hour with the electric field on, the Kerr constants of the solutions reached a steady value and were sensibly independent of the applied voltage. Similar effects have been observed by us for PVC.[8] The decrease of the Kerr constant from its initial value when the electric field was first applied could not be ascribed to heating effects, since these would manifest themselves as optical inhomogeneities and as scattering and divergence of the analyzing light beam. We repeated the measurements for four different concentrations (0.5–2% (w/w)) and found a linear dependence of the Kerr constant on concentrations. No such precautions were necessary for the dielectric constant measurements. The resultant ${}_{\mathrm{m}}K$ and $\langle\mu^2\rangle$ values at 25 °C and λ = 6328 Å are given in Table I.

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

The rotational isomeric state (RIS) model and matrix multiplication methods of Flory[12] were used to calculate ${}_{\mathrm{m}}K$ and $\langle\mu^2\rangle$. To carry out the calculations we require information about the geometry of the chain, energetic parameters for the probability of the rotational states along the backbone, polarizability anisotropy and dipole mo-

0024-9297/82/2215-0866$01.25/0

Table I
Molar Kerr Constants ${}_{\mathrm{m}}K/x$ ($\times10^{-2}$ cm^7 SC^{-2} mol^{-1}) and Dipole Moments $\langle\mu^2\rangle/x$ ($\times10^{-36}$ SC^2 cm^2) per Monomer for Poly(styrene-*co*-*p*-bromostyrene) at 25 °C and λ = 6328 Å

$c^{a,b}$	${}_{\mathrm{m}}K/x$	$\langle\mu^2\rangle/x$
0 (PS) (CT)	11.2	0.22^c
0.068 (CT)	28.4	0.41^c
0.400 (CT)	78.7	1.14
0.533 (CT)	83.1	1.23
0.93 (CT)	54.1	
1.0 (PPBS) (D)	15.3	1.75
1.0 PPCS (D)	14.3	1.92,^{d} 2.55,^{e} 2.0,^{e} 1.95^f

[a] *c* is the fraction of brominated monomer units.
[b] PS = polystyrene, PPBS = poly(*p*-bromostyrene), PPCS = poly(*p*-chlorostyrene), CT = carbon tetrachloride, D = dioxane; used as solvents. [c] $\langle\mu^2\rangle/x$ calculated by the formula of Le Fèvre and Le Fèvre.[17] All other values calculated by the formula of Smith and Guggenheim.[6]
[d] Reference 18. [e] Reference 19. [f] References 3 and 20.

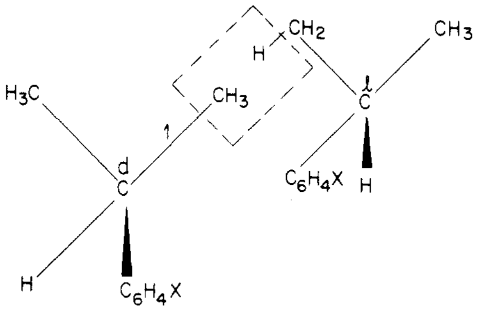

Figure 1. Portion of poly(styrene-*co*-*p*-bromostyrene), enumeration of bonds, and *d* and *l* stereochemistry indicated. X = Br, H.

ments of the repeat units, and the monomer sequence distribution in the copolymer.

The backbone bond angles were assumed to be 112° and two rotational states per bond were allowed, in accordance with the RIS model of Yoon et al.[2] Repulsions between adjoining phenyl groups may be expected to alter the position of the rotational states. Following Mark,[20] we assume that the rotational states for the two skeletal bonds leading into and out of a C$^\alpha$ atom of *d* configuration are located at $-\Delta\phi$, 120°, and $-120° + \Delta\phi$ and at $\Delta\phi$, $120° - \Delta\phi$, and 120°, respectively. The same two sets of rotational angles apply to the two skeletal bonds, respectively, out of and into a C$^\alpha$ atom of *l* configuration. The empirical energy calculations of Yoon et al.[2] reveal that $\Delta\phi \cong$ 5–30°. The statistical weight matrices were identical with those used by Saiz et al.,[3] with the following parameters: $\eta = 0.8\exp[397/RT]$, $\omega = \omega' = 1.3\exp[-(1987/RT)]$ and $\omega'' = 1.8\exp[-(2186/RT)]$, where T = 298 K is the temperature.

The polarizability tensors of these copolymers were derived in a manner similar to that used by Suter and Flory[4] for polystyrene and Saiz et al.[5] for the para-halogenated polystyrenes. The polarizability of the copolymer is assumed to be the sum of the polarizability tensors of cumene and the halogenated cumene (see Figure 1). The polarizability tensor of the aryl group in eq 1 is

$$\hat{\alpha}_{\mathrm{aryl}} = \Delta\alpha\ \mathrm{diag}\begin{bmatrix}+\frac{2}{3} & -\frac{1}{3} & \frac{1}{3}\end{bmatrix} + \Delta\alpha^{\dagger}\ \mathrm{diag}\begin{bmatrix}0 & +\frac{1}{2} & -\frac{1}{2}\end{bmatrix} \tag{1}$$

expressed in a coordinate system affixed to the phenyl ring, as shown in ref 4. Assuming that the bond angles are tetrahedral about the C$^\alpha$ carbon and adding the anisotropy of the carbon–carbon bonds along the backbone, the anisotropy $\hat{\alpha}_{l,d}$ of a monomer unit becomes

$$\hat{\alpha}_{l,d} = -\Gamma_{\mathrm{cc}}\mathbf{A}_{l,d} + \Delta\alpha\mathbf{B}_{l,d} + \Delta\alpha^{\dagger}\mathbf{C}_{l,d}$$

$$\mathbf{A}_{l,d} = \begin{bmatrix} -\frac{2}{9} & -\frac{\sqrt{2}}{9} & \pm\frac{\sqrt{6}}{9} \\ -\frac{\sqrt{2}}{9} & -\frac{1}{9} & \mp\frac{2\sqrt{3}}{9} \\ \pm\frac{\sqrt{6}}{9} & \mp\frac{2\sqrt{3}}{9} & +\frac{1}{3} \end{bmatrix}$$

$$\mathbf{B}_{l,d} = \begin{bmatrix} -\frac{2}{9} & -\frac{\sqrt{2}}{9} & \mp\frac{\sqrt{6}}{9} \\ -\frac{\sqrt{2}}{9} & -\frac{1}{9} & \pm\frac{2\sqrt{3}}{9} \\ \mp\frac{\sqrt{6}}{9} & \pm\frac{2\sqrt{3}}{9} & +\frac{1}{3} \end{bmatrix}$$

$$\mathbf{C}_{l,d} = \begin{bmatrix} +\frac{2}{9} & +\frac{5\sqrt{2}}{18} & \mp\frac{\sqrt{6}}{18} \\ +\frac{5\sqrt{2}}{18} & -\frac{1}{18} & \pm\frac{\sqrt{3}}{9} \\ \mp\frac{\sqrt{6}}{18} & \pm\frac{\sqrt{3}}{9} & -\frac{1}{6} \end{bmatrix} \tag{2}$$

In deriving eq 2 we have assumed that the plane of the phenyl ring is fixed and bisects the $\angle \mathrm{CH_2C^{\alpha}HCH_2}$ angle. The coordinate system used in eq 2 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 previous bond, and the *z* axis completing a right-handed coordinate system. The corresponding dipole moments are given by

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

In eq 2 and 3 the upper and lower signs refer to *l* and *d* configurations, respectively (see Figure 1). The following values[4,5,13,14] have been used for the parameters in eq 2 and 3: Γ_{cc} = 0.53, $\Delta\alpha$ = 3.85, 6.0, and 6.9, and $\Delta\alpha^{\dagger}$ = −3.0, −3.3, and −3.9 (all expressed in Å^3) for X = H, Cl, and Br, respectively; m = 0.32, 1.89, and 1.89 ($\times10^{-18}$ SC cm) (SC = statcoulomb) for X = H, Cl, and Br, respectively.

The molar Kerr constants are calculated from the equation

$${}_{\mathrm{m}}K = \frac{2\pi N_{\mathrm{A}}}{135}\left[\frac{\langle \mathrm{tr}\,(\hat{\alpha}\hat{\alpha})\rangle}{kT} + \frac{\langle \mu^{\mathrm{T}}\hat{\alpha}\mu\rangle}{k^2T^2}\right] \tag{4}$$

where $\hat{\alpha}$ and μ are the anisotropic polarizability tensor and dipole moments, respectively, of the polymer. Monte Carlo chain generation techniques were used to construct those homopolymers with irregular stereosequences. In the case of a copolymer we assumed that the placement of bromine in the para position of the phenyl ring was completely random and independent of prior placement of bromines at adjoining phenyl rings. This was also effected by a Monte Carlo approach. In the absence of strong evidence to the contrary this assumption appears to be reasonable. Each chain was 400 bonds long (200 monomers) and 15 chains were generated for each degree of stereoregularity p_r and composition c (fraction of bromination in the para position).

In order to carry out the calculation we require an accurate value of $\Delta\phi$. It was determined as follows. Extensive calculations were done of ${}_{m}K/x$ and $\langle\mu^2\rangle/x$ as a function of tacticity $p_r = 0$–1.0 and dihedral angle $\Delta\phi = 0$–$30°$, which showed that ${}_{m}K/x$ was sensitive to changes in p_r but not to $\Delta\phi$, while $\langle\mu^2\rangle/x$ was sensitive to changes in $\Delta\phi$ but not p_r. Comparison with the experimental results of poly(p-bromostyrene) revealed that $p_r = 0.47$–0.65 and $\Delta\phi = 10$–$20°$. We therefore chose the mean value of $\Delta\phi = 15°$, which is also consistent with the result obtained from empirical energy calculations.[2]

Results and Discussion

In Table I we present the molar Kerr constants and dipole moments per monomer, ${}_{m}K/x$ and $\langle\mu^2\rangle/x$, respectively, for poly(styrene-*co*-p-bromostyrene). We note that ${}_{m}K/x$ reaches a maximum value near a composition $c = 0.5$, whereas the dipole moments increase monotonically. Our ${}_{m}K/x$ value for polystyrene (11.2) agrees with those reported by Le Fèvre et al.[15] (10.6) and also by Champion et al.[16] (14.4) when their data are analyzed according to the methods of Le Fèvre and Le Fèvre.[17] Our ${}_{m}K/x$ value for poly(p-chlorostyrene) (14.3) is considerably lower than that reported by Saiz et al.[5] (101), all ${}_{m}K$ values being expressed in $\times 10^{-12}$ cm^7 SC^{-2} mol^{-1}.

In Table I we have also presented $\langle\mu^2\rangle/x$ values of poly(p-chlorostyrene) by Kotera et al.,[18] Baysal et al.,[19] Saiz et al.,[3] and Mark.[20] For the homopolymers containing chlorine and bromine only, we expect their dipole moments to be comparable since the dipole moments of the model compounds p-chlorotoluene and p-bromotoluene are the same and also because the probabilities of the rotational states along the backbone would be expected to be independent of the substituent in the para position of the phenyl ring. This is borne out by the experimental results.

In Figure 2 we present the calculated curves of ${}_{m}K/x$ as a function of the fraction c of brominated monomer units in the copolymer for a given tacticity of the polystyrene initially used to make the copolymer. We note the extraordinary sensitivity of ${}_{m}K/x$ to both composition and tacticity, which covers a range of 3 orders of magnitude and also changes sign. This is particularly true when the polar component of the copolymer increases. The sensitivity of ${}_{m}K/x$ to the degree of stereoregularity has been noted before by us[8-10] and also by Saiz et al.[5] Here we also show the strong sensitivity of ${}_{m}K/x$ to the fraction of polar component in an otherwise only slightly polar polymer. This fact would appear to recommend the Kerr effect as a means to study the composition of copolymers made up of polar and nonpolar monomers. In Figure 2 we have also shown the experimental results obtained by us for these copolymers. A comparison with the calculated curves clearly shows that the tacticity of these copolymers is $p_r = 0.55 \pm 0.05$, which is a refinement of the range of p_r values previously obtained from the comparison of the ${}_{m}K/x$ values calculated and observed for poly(p-bromostyrene) ($c = 1.0$). It should be noted that poly(p-bromostyrene) was not made by brominating polystyrene but was a commercial sample, presumably made by free radical polymerization. The ${}_{m}K/x$ value of this homopolymer could also be explained by assuming that $p_r = 0.55 \pm 0.05$. It would appear that the tacticity of the halogenerated polystyrenes is similar to that of polystyrene, in contrast to the results of Saiz et al.,[5] who obtained $p_r \cong 0.8$. Additional evidence supporting this conclusion is provided by a comparison of the experimental and calculated ${}_{m}K/x$ values of poly(p-chlorostyrene). As in the case of poly(p-bromostyrene), the value of ${}_{m}K/x$ changes sign from a large negative to a large positive value around $p_r = 0.5$. The slightly positive value observed experimentally indicates that poly(p-chlorostyrene) is slightly syndiotactic, with $p_r = 0.55 \pm 0.05$.

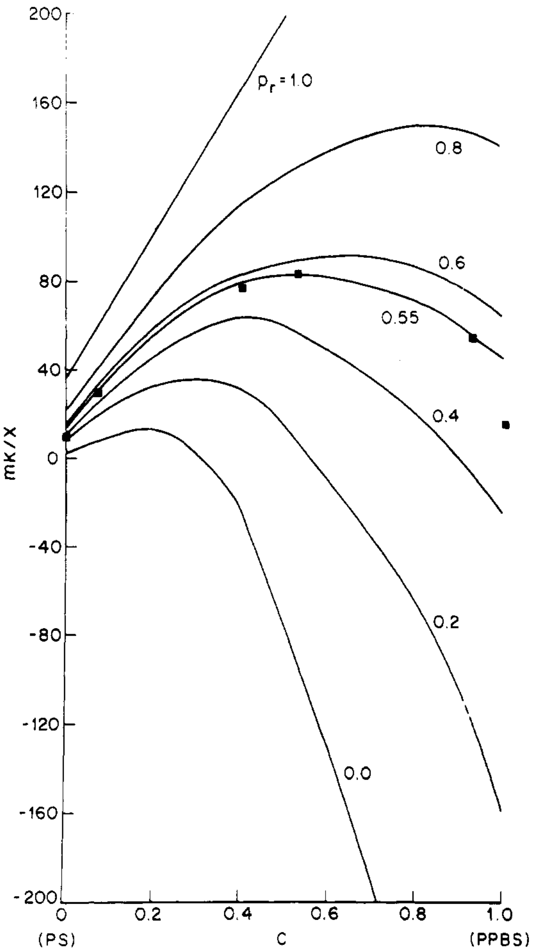

Figure 2. ${}_{m}K/x$ ($\times 10^{-12}$ cm^7 SC^{-2} mol^{-1}) of the copolymer as a function of composition c and tacticity p_r. Black squares are experimental results.

We also calculated the dipole moments $\langle\mu^2\rangle/x$ of these copolymers as a function of composition, as shown in Figure 3. The calculations are presented only for a single degree of stereoregularity $p_r = 0.55$, since we did not find $\langle\mu^2\rangle/x$ to be strongly dependent on tacticity. In addition to our experimental results for poly(styrene-*co*-p-bromostyrene), we have also given the experimental results of Kotera et al.[18] and others[3,19,20] for poly(styrene-*co*-p-chlorostyrene). As discussed earlier we would expect the two halogenated copolymers to have the same dipole moment dependence on composition and tacticity. The agreement between the calculated curve and the experimental results is reasonably good, although there are some small discrepancies remaining for the halogenated homopolymer. It should be emphasized that dipole moment studies could not have been used to accurately determine the tacticity of polystyrene and its derivatives because of the insensitivity to tacticity of the calculated dipole moment curves. However, dipole moments are useful[21] to study the fraction of the polar component in an otherwise nonpolar copolymer.

Conclusions

To calculate ${}_{m}K/x$ and $\langle\mu^2\rangle/x$ for a copolymer it was necessary to make a number of assumptions concerning

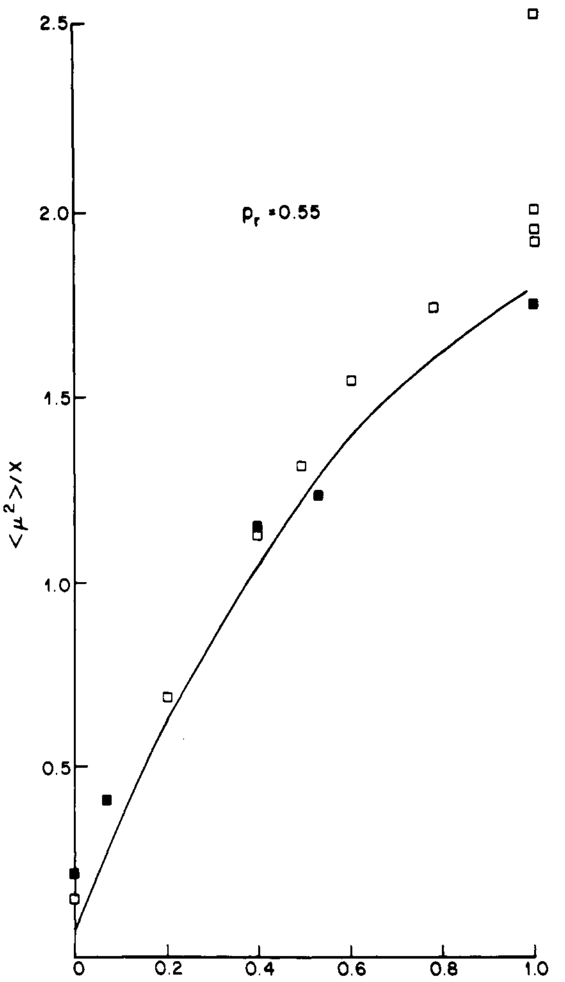

Figure 3. $\langle\mu^2\rangle/x$ ($\times 10^{-36}$ SC^{-2} cm^2) of the copolymer as a function of composition c for $p_r = 0.55$. Black squares, X = Br this work; white squares, X = Cl ref 3 and 18–20.

the RIS model, the monomer unit dipole moments and polarizabilities, and the comonomer sequence distribution. Since we obtain good agreement between the calculations and a large number of experimental values, it follows that our assumptions must be essentially correct. Thus the RIS model of Yoon et al.[2,3] is correct for the energetic parameters of the bond rotational probabilities and the rotational angles. Additional evidence for this model is given by the calculated characteristic ratio C_∞ of the dimensions of atactic ($p_r = 0.55$) polystyrene. We calculate $C_\infty = 8.3$ and the experimental value[2] is ~10. Also the monomer unit dipole moments and polarizabilities deduced by Suter and Flory[4] and Saiz et al.[5] from model compounds appear to be correct. Finally our assumption that the para position of the phenyl ring is randomly brominated is also supported as evidenced by the close agreement between the calculated and experimental results.

The most fundamentally important unknown factor at the beginning of this study was the tacticity of polystyrene and its derivatives. It is clear from the results of Figure 1 that only by assuming $p_r = 0.55$ are we able to explain all the experimental data presented here. The Kerr effect results are particularly persuasive in this regard and would appear to hold great promise for further studies of polymers and copolymers.

Acknowledgment. We thank Dr. G. D. Patterson for the loan of optical components used in the Kerr effect apparatus.

References and Notes

(1) Bovey, F. A. "High Resolution NMR of Macromolecules"; Academic Press: New York, 1972; p 118.
(2) Yoon, D. Y.; Sundararajan, P. R.; Flory, P. J. *Macromolecules* **1975**, *8*, 776.
(3) Saiz, E.; Mark, J. E.; Flory, P. J. *Macromolecules* **1977**, *10*, 967.
(4) Suter, U. W.; Flory, P. J. *J. Chem. Soc., Faraday Trans. 2* **1977**, *73*, 1521.
(5) Saiz, E.; Suter, U. W.; Flory, P. J. *J. Chem. Soc., Faraday Trans. 2* **1977**, *73*, 1538.
(6) Khanarian, G.; Tonelli, A. E. *J. Chem. Phys.* **1981**, *75*, 5031.
(7) Khanarian, G.; Tonelli, A. E. *Macromolecules* **1982**, *15*, 145.
(8) Khanarian, G.; Schilling, F. C.; Cais, R. E.; Tonelli, A. E., submitted to *Macromolecules*.
(9) Khanarian, G.; Tonelli, A. E. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1981**, *22*, 409.
(10) Tonelli, A. E. *Macromolecules* **1977**, *10*, 153.
(11) Kambour, R. P.; Bopp, R. C. *Bull. Am. Phys. Soc.* **1981**, *26*, 431.
(12) Flory, P. J. "Statistical Mechanics of Chain Molecules"; Interscience: New York, 1969; Chapters III–VI and IX.
(13) Aroney, M. J.; Calderbank, K. E.; Le Fèvre, R. J. W.; Pierens, R. K. *J. Chem. Soc. B* **1970**, 1120.
(14) Aroney, M. J.; Calderbank, K. E.; Le Fèvre, R. J. W.; Pierens, R. K. *J. Chem. Soc. B* **1969**, 159.
(15) Le Fèvre, C. G.; Le Fèvre, R. J. W.; Parkins, G. M. *J. Chem. Soc.* **1958**, 1468.
(16) Champion, J. V.; Meeten, G. H.; Southwell, G. W. *Polymer* **1976**, *17*, 651.
(17) Le Fèvre, C. G.; Le Fèvre, R. J. W. In "Techniques of Chemistry"; Weissberger, A., Ed.; Wiley-Interscience: New York, 1972; Vol. 1, Part IIIc, Chapter VI.
(18) Kotera, A.; Suzuki, K.; Matsumura, K.; Shima, M.; Joko, E. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 750.
(19) Baysal, B.; Lowry, B. A.; Yu, H.; Stockmayer, W. H. In "Dielectric Properties of Polymers"; Karasz, F. E., Ed.; Plenum Press: New York, 1972; p 329.
(20) Mark, J. E. *J. Chem. Phys.* **1971**, *56*, 458.
(21) Mark, J. E. *J. Am. Chem. Soc.* **1972**, *94*, 6645.