the magnitude of k_{AB} and k_{BA}. k_{AB} is estimated to be 2.7 × 10^9 (±1.5 × 10^9) s^{-1} and k_{BA} 1.3 × 10^9 (±7 × 10^8) s^{-1}.

The good fits (Table I) obtained in the excimer region are understood when one takes into account the low contribution of λ_1 in eq 3 and 4 and the fact that these results are fitted with seven variables.[18]

The analysis of DNPA makes clear the importance of reversible singlet energy transfer in excimer-forming molecules. It proves the importance of intramolecular singlet energy transfer and energy migration in molecules containing two or more chromophores in solution. The process of reversible energy transfer or migration will only show up kinetically when two chromophores involved have slightly different photophysical properties.

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Notes

Kerr Effect and Dielectric Study of Poly(vinyl bromide) Oligomers

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Recently two rotational isomeric states (RIS) models have been derived to describe the conformational characteristics of poly(vinyl bromide) (PVB). Tonelli[1] estimated the conformational energies for the chain segments found in PVB and the copolymers (PEVB) of vinyl bromide (VB) with ethylene (E). RIS models for PVB and PEVB were derived from these energy estimates, where both comonomer sequence and VB stereosequence were considered. Saiz et al.[2] also performed energy estimates on PVB segments and derived an RIS model for PVB. In addition, they measured the dipole moments of atactic PVB in two solvents (*p*-dioxane and 1-methylnaphthalene).

Both conformational descriptions, RIS-T (Tonelli[1]) and RIS-S (Saiz et al.[2]), reproduce the experimentally observed[2] dipole moments of atactic PVB ($C_m = \langle \mu^2 \rangle / xm^2$ = 0.45–0.53, where x is the degree of polymerization and m is the C–Br bond dipole moment), yielding C_m = 0.41 (RIS-T) and C_m = 0.57 (RIS-S). In addition, the dimensions $C_r = \langle r^2 \rangle_0 / nl^2$, where $n = 2x$ and l is the length of a C–C bond, reported for atactic PVB by Ciferri and Lauretti[3] (C_r = 6.6) also agree with those predicted by RIS-T (5.3–5.7) and RIS-S (7.3–6.9) (see Table I).

Table I
Comparison of Calculated and Observed Dipole Moments and Dimensions for Atactic PVB

method	$C_m{}^a = \langle \mu^2 \rangle / xm^2$	$C_r{}^b = \langle r^2 \rangle_0 / nl^2$
exptl[2,3]	0.45–0.53	6.6
RIS-T[1]	0.41	5.3–5.7
RIS-S[2]	0.57	7.3–6.9

[a] For atactic[2] PVB with P_m = 0.46. [b] For atactic[1-4] PVB with P_m = 0.4–0.6.

Despite the apparent agreement between the dipole moments (C_m) and dimensions (C_r) observed for atactic PVB and the values obtained with either RIS-T or RIS-S, there are differences between the two conformational descriptions. Both RIS models find the tg and gt conformations to be preferred for meso (m) PVB diads, albiet to different degrees. Though both RIS models find the tt and gg conformers to be preferred for racemic (r) dyads, RIS-T predicts the gg conformer to be preferred over the tt conformer, while the tt conformer is preferred over the gg conformer in the RIS-S description.

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Table II
Dipole Moments $\langle \mu^2 \rangle$ (D^2) and Molar Kerr Constants ${}_{\mathrm{m}}K$ ($\times 10^{-12}$ cm^{-7} SC^{-2} mol^{-1}) for the Isomers of DBP

isomer	$\langle \mu^2 \rangle$			${}_{\mathrm{m}}K$		
m	5.29[a]	5.46[b]	5.27[c]	8.46[a]	9.22[b]	10.5[c]
r	5.00	5.64	5.52	13.6	14.9	9.3
M[d]	5.06	5.56	5.41	10.8	12.5	9.8

[a] Measured in CCl_4 at 25 °C. [b] Calculated using RIS-T.[1] [c] Calculated using RIS-S.[2] [d] 58:42 *r:m* mixture of DBP isomers.

These differences lead to calculated dipole moments (C_m) and dimensions (C_r) for PVB which are generally larger for RIS-S compared to RIS-T, especially for the syndiotactic and isotactic chains. Because it has not been possible[4] to obtain either stereoregular form of PVB, these differences in their calculated dipole moments and dimensions cannot be checked experimentally. PVB oligomers, on the other hand, do provide an experimental means to further test both RIS models.

We have measured the dipole moments, $\langle \mu^2 \rangle$, and molar Kerr constants, ${}_{\mathrm{m}}K$, for the PVB model compounds, 2,4-dibromopentane (DBP) and 2,4,6-tribromoheptane (TBH). The molar Kerr constant of a polymer, as obtained from the electrical birefringince measured on its dilute solutions, has been demonstrated both by experiments[5-9] and by calculations[5,10] to be one of the properties most sensitive to the conformational and configurational characteristics of flexible polymers. This sensitivity to conformation prompted us to test both RIS models proposed for PVB against the Kerr effects measured for the PVB model oligomers DBP and TBH.

The m and r isomers of DBP were separated on a gas chromatograph, and the ratio of mm, mr, and rr isomers contained in our TBH sample was determined by ^{13}C NMR. Kerr effect and dipole moment measurements were performed at 25 °C in CCl_4. (See Experimental Section for details.)

A description of the methods used to calculate the molar Kerr constants are detailed in references 6, 9, and 11. The polarizability tensor and dipole moment for the C–Br bond, which are necessary to calculate ${}_{\mathrm{m}}K$ for PVB and its oligomers, are the same as derived and presented in our Kerr effect study[6] of the α,ω-dibromoalkanes. Treatment of the polarizability tensors of DBP and TBH is identical with the method used previously for 2,4-dichloropentane and 2,4,6-trichloroheptane in our study[9] of poly(vinyl chloride) and its model compounds.

Results and Discussion

The dipole moments and molar Kerr constants measured for a 58:42 r:m mixture of DBP isomers[12] and for the separated isomers are presented in Table II along with the $\langle \mu^2 \rangle$'s and ${}_{\mathrm{m}}K$'s calculated for DBP using RIS-T and RIS-S. Both RIS models predict dipole moments in close agreement with our measurements. However, RIS-S seriously underestimates the ${}_{\mathrm{m}}K$ of r-DBP, leading to a calculated ratio of ${}_{\mathrm{m}}K(\mathrm{r})/{}_{\mathrm{m}}K(\mathrm{m}) = 0.9$, while the observed ratio is 1.6, in close agreement with that calculated from RIS-T. (The agreement between the ${}_{\mathrm{m}}K$'s measured for the DBP mixture and calculated from RIS-S appears to be coincidental.)

As seen in Table III, the dipole moment measured for our TBH sample, which is a mixture of all three isomers,[12] agrees closely with the dipole moments calculated for the same mixture of TBH isomers using either RIS-T or RIS-S. While the ${}_{\mathrm{m}}K$ calculated for the TBH mixture using the RIS-T model agrees closely with the observed ${}_{\mathrm{m}}K$, the ${}_{\mathrm{m}}K$ obtained from RIS-S overestimates the observed value by 40%.

Table III
Dipole Moments $\langle \mu^2 \rangle$ (D^2) and Molar Kerr Constants ${}_{\mathrm{m}}K$ ($\times 10^{-12}$ cm^{-7} SC^{-2} mol^{-1}) for the Isomers of TBH

isomer	$\langle \mu^2 \rangle$			${}_{\mathrm{m}}K$		
mm	–[a]	4.68[b]	4.30[c]	–[a]	–82[b]	–77[c]
mr	–	6.08	8.04	–	–28	58
rr	–	12.7	12.1	–	267	245
M[d]	8.58	8.41	9.05	77.6	76.5	111

[a] Measured in CCl_4 at 25 °C. [b] Calculated using RIS-T.[1] [c] Calculated using RIS-S.[2] [d] 38:48:14 *rr:mr:mm* mixture of TCH isomers.

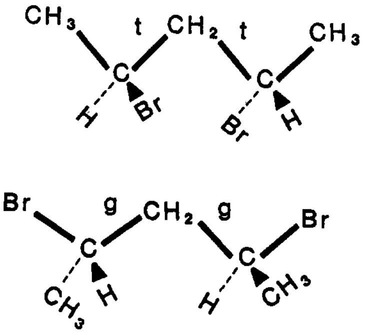

Figure 1. Schematic representation of r-DBP in the tt and gg conformations.

It is apparent that both RIS models account for the dipole moments observed in atactic PVB and the PVB oligomers DBP and TBH. However, of the two only the RIS-T model accurately predicts the molar Kerr constants observed for DBP and TBH. The reason for this behavior can be understood by considering the tt and gg conformations for r-DBP, which were found to be energetically preferred by both RIS models. As can be seen in Figure 1, the net dipole moment in the gg conformer lies in the plane of the backbone, which is the plane of maximum polarizability due to the presence of both highly anisotropic C–Br bonds also in this plane. In the tt conformer the C–Br bonds, as well as their net dipole moment, are nearly perpendicular to the backbone. Thus, in the tt conformer anisotropic C–Br bonds are not in the plane of the backbone and the overall anisotropy of the polarizability tensor is less than in the gg conformer.

The tt and gg conformers have nearly identical dipole moments ($\mu^2 \sim 6$ D^2). But because the molar Kerr constant[11] is proportional to the vector product of the dipole moment and the direction of maximum polarizability, the gg conformer has ${}_{\mathrm{m}}K = 20$, while ${}_{\mathrm{m}}K = 2$ for the tt conformer.

In the RIS-S model the tt conformer is preferred over the gg conformer, while the opposite conformational preference is predicted by the RIS-T model. This explains why ${}_{\mathrm{m}}K = 9.3$ and 14.9 for r-DBP when calculated with the RIS-S and RIS-T models, respectively. Since $\mu^2 \sim 6$ D^2 for both preferred conformers, both RIS models yield $\langle \mu^2 \rangle = 5.5$–5.6 D^2 for r-DBP.

This comparison of PVB RIS models with the molar Kerr constants observed for PVB oligomers illustrates once again the sensitivity of ${}_{\mathrm{m}}K$ to the conformational and configurational characteristics of flexible polymer chains. When the conformational characteristics of polymers are studied, the Kerr effect and the concomitant dielectric measurements required[6] to obtain ${}_{\mathrm{m}}K$ are clearly preferred over just the dielectric measurements, from which only the dipole moment can be derived.

Experimental Section

The DBP and TBH samples employed here have been discussed previously.[4,13] DBP was separated on a Varian P-90 gas-phase chromatograph using the same conditions employed previously[9] to isolate the isomers of 2,4-dichloropentane. The Kerr effect and dielectric apparatus along with the experimental techniques have been previously described.[6] Carbon tetrachloride at 25 °C was employed as the solvent for all measurements reported here.

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Effect of Hydrogen Bonding on the Lower Critical Solution Temperature of a Polymer Mixture

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The free energy of mixing of two polymers, according to recent theories,[1,2] can be analyzed in terms of three contributions: combinational entropy of mixing, an interactional energy term, and a "free volume" term. To achieve miscibility of two polymers of high molecular weight, a negative interaction energy is required. Phase separation takes place on raising the temperature to the lower critical solution temperature (LCST) because the free volume term becomes more positive and the interactional energy term less negative at elevated temperatures. A simplified version of the Prigogine–Flory theory has been given by Patterson and Robard[3,4] in an approximate equation that describes the essential features of the theory

$$\frac{\chi^{12}}{V_1^*} = \frac{P_1^*}{RT_1^*}\left[\frac{\tilde{V}_1^{1/3}}{\tilde{V}_1^{1/3}-1}\left(\frac{X_{12}}{P_1^*}\right) + \frac{\tilde{V}_1^{1/3}}{2(4/3-\tilde{V}_1^{1/3})}\tau^2\right] \qquad (1)$$

The first term on the right-hand side of eq 1 is the interactional contribution and the second, the free volume contribution. In eq 1, χ is the Flory–Huggins interaction parameter, $\tilde{V}$ is the reduced volume, the starred symbols are calculated from equation-of-state properties, and X_{12} is the exchange (or contact) interaction parameter. The interaction and free volume terms are characterized by molecular parameters X_{12}/P^* and τ^2, respectively, where $\tau = 1 - T_1^*/T_2^*$. Equation 1 was used successfully by Patterson and Robard to describe the various features of polystyrene–poly(vinyl methyl ether) blends.[3,4]

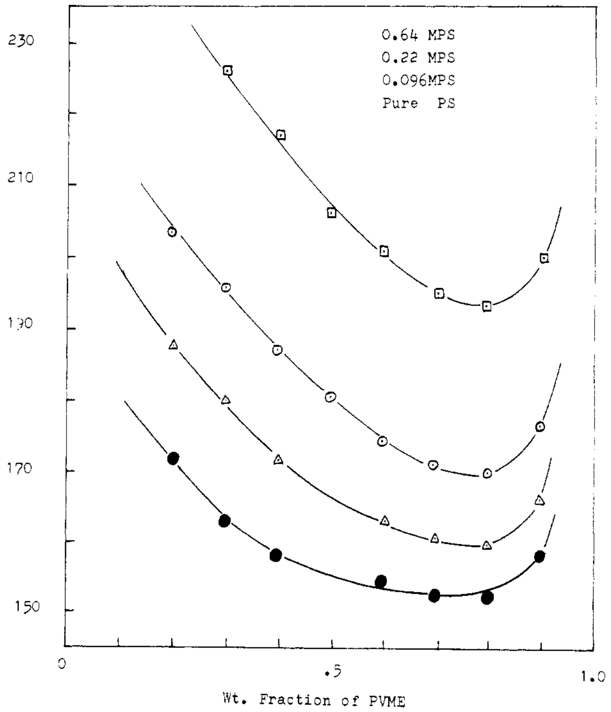

Figure 1. LCST phenomena of the various modified PS's and PVME systems at the heating rate of 2 °C min^{-1}: (□) 0.64MPS; (○) 0.22MPS; (△) 0.096MPS; (●) pure PS.

An increase in the strength of interaction (more negative) leads to a higher temperature for phase separation. This was verified experimentally when polystyrene was modified to contain a small amount of vinylphenylbis(trifluoromethyl)carbinol as comonomer units.[5] The bis(trifluoromethyl)carbinol group, a strong hydrogen bond donor, interacts with the ether group of PVME and, as a result, the LCST is raised. The purpose of the present note is to demonstrate that the increase in interaction due to hydrogen bonding indeed balances the increase in the free volume term when phase separation takes place at a higher temperature for the blend containing modified polystyrene (MPS) and PVME.

The relevant LCST data are shown in Figure 1. Note that the nomimal concentration of the $C_6H_4C(CF_3)_2OH$ group in the modified polystyrenes reported as 0.1, 0.2, and 0.4% in ref 5 should be amended to become 0.096, 0.22 (both calculated from reactivity ratios), and 0.64% (from fluorine analysis). The LCST values for mixtures containing 80% by weight of PVME are 425 K for PS and 433, 442, and 446 K respectively for the three modified polystyrenes. At each LCST, the free volume term can be calculated from equation-of-state properties, with the approximation that the parameters for PS can be used for MPS because the degree of modification is very small. Since $\chi = 0$ at LCST for high molecular weight polymers, X_{12} can be calculated from the free volume term. If the change in the dispersion forces in the temperature range of interest is ignored, the *increase* in X_{12} upon the incorporation of the $C_6H_4C(CF_3)_2OH$ group in MPS is then a direct measure of the number of hydrogen bonds, C_b, remaining at the phase separation temperature because the enthalpy of hydrogen bonding can be estimated independently for this system. The fraction of hydrogen bonds remaining at LCST calculated by this procedure should be consistent with a reasonable value of the equilibrium constant of hydrogen bonding at room temperature and the Arrhenius temperature dependence of hydrogen bonding (from ΔH).

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