Molecular Weight Changes during Hydrochlorination. The product materials described in Table I were soluble in toluene and in many other solvents including benzene, chloroform, and tetrahydrofuran, but the completely hydrochlorinated product was not soluble in saturated hydrocarbons such as heptane and cyclohexane. As indicated in Table I, number average molecular weight measurements made on both the substrate and the completely hydrochlorinated product show that the reaction did not produce any significant chain alteration in the material. The molecular weight of the hydrochlorinated sample is only 6% higher than the value expected for a quantitative addition of hydrogen chloride. This small discrepancy can be easily explained by the limits of the experimental method. A better confirmation of the absence of any chain degradation during the present hydrochlorination of 1,4-polyisoprene can be obtained from the gel permeation chromatograms shown in Figure 5 where the curve obtained for the completely hydrochlorinated product shows a peak almost identical in both shape and half-width to that obtained for the substrate.

Physical Properties. Figure 6 shows the glass transition temperature of the samples described in Table I plotted as a function of the molar percentage of hydrochlorinated units in the polymer. A linear dependence is observed with a value of T_g for the completely hydrochlorinated polymer 103 K higher than that of the substrate. It is interesting to compare this change of T_g with that produced when saturation is achieved by catalytic hydrogenation of the same substrate. As shown in a previous paper,[13] in the later case T_g is increased by only 4 K indicating that the decrease in chain mobility produced by hydrochlorination of 1,4-polyisoprene is mainly due to the presence of the chlorine atoms along the polymer chains and not to the saturation of the double bonds.

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References and Notes

(1) C. W. Bunn and E. V. Garner, *J. Chem. Soc.*, 654 (1942).
(2) H. Staudinger and H. Staudinger, *Rubber Chem. Technol.*, **17**, 15 (1944).
(3) M. Gordon and J. S. Taylor, *J. Appl. Chem.*, **3**, 537 (1953).
(4) J. B. Pande, D. Raghunath, and C. S. Ramakrishnan, *Makromol. Chem.*, **20**, 181 (1956).
(5) M. A. Golub and J. Heller, *J. Polym. Sci., Part B*, **2**, 723 (1964).
(6) N. Grassie, "Chemistry of High Polymer Degradation Processes", Butterworth Scientific Publication, London, 1956, pp 315–319.
(7) M. A. Golub and J. Heller, *J. Polym. Sci., Part B*, **2**, 523 (1964).
(8) Y. Tanaka, H. Sato, A. Ogura, and I. Nagoya, *J. Polym. Sci., Polym. Chem. Ed.*, **14**, 73 (1976).
(9) M. W. Duch and D. M. Grant, *Macromolecules*, **3**, 165 (1970).
(10) S. Brownstein, S. Bywater, and D. J. Worsfold, *Macromolecules*, **6**, 715 (1973).
(11) E. R. Santee, V. D. Mochel, and M. Morton, *J. Polym. Sci., Part B*, **11**, 453 (1973).
(12) D. Blondin, J. Regis, and J. Prud'homme, *Macromolecules*, **7**, 187 (1974).
(13) A. Laramee, P. Goursot, and J. Prud'homme, *Makromol. Chem.*, **176**, 3079 (1975).

Possible Characterization of Homopolymer Configuration and Copolymer Sequence Distribution by Comparison of Measured and Calculated Molar Kerr Constants

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ABSTRACT: Molar Kerr constants are calculated for five homopolymers [poly(propylene) (PP), poly(vinyl chloride) (PVC), poly(styrene) (PS), poly(*p*-methylstyrene) (PPMS), and poly(*p*-chlorostyrene) (PPCS)] and three copolymers (PP–PVC, PS–PPCS, and PPMS–PPCS) as functions of their stereoregularities and sequence distributions through adoption of the rotational isomeric state model of polymer chains and the valence optical scheme for addition of bond polarizabilities. Denbigh's values of the necessary bond polarizabilities were used to construct the group polarizability tensors expressed along each of the backbone bonds. Matrix multiplication methods together with Monte Carlo polymer chain generation techniques permitted the calculation of molar Kerr constants for polymers of widely varying stereoregularities and monomer sequence distributions. Only the molar Kerr constants calculated for the polar homopolymers PVC and PPCS exhibit a marked dependence on stereoregularity, while the molar Kerr constants of each of the copolymers are very sensitive to their monomer sequence distribution. On the basis of these preliminary calculations, it appears that the molar Kerr constant may be usefully employed as a sensitive indicator of the conformation, configuration, and/or sequence distribution of polar homo- and copolymers.

Ever increasing emphasis is being placed on the tailoring of polymers to meet specific end use properties. A significant portion of this effort has led to the synthesis of copolymers with useful physical properties markedly different from the properties exhibited by either of the constitutent homopolymers.

A variety of ways exist for the construction of a copolymer from monomer units A and B, e.g., random (–A–B–B–A–B–A–A–B–A–), regularly alternating (–A–B–A–B–A–B–), and block (–A–A–A–A–A–B–B–B–B–B–). The physical properties of the copolymer, especially in the bulk solid state, are critically dependent upon the detailed arrangement of its monomer units or its sequence distribution. Whether or not a copolymer exists in a single homogeneous phase in the bulk solid, for example, is determined by its sequence distribution. Clearly then, it is necessary to develop methods for determining the sequence distributions of copolymers before their effects on copolymer physical properties can be understood and used to produce superior engineering materials.

In some copolymer systems[1–15] high resolution nuclear magnetic resonance (NMR) spectroscopy, which usually employs the C^{13} nucleus as the probe,[6–15] can be used to unravel the sequence distribution of monomer units. However, for copolymers made from asymmetric monomer units, such as the vinyls, stereoregularity effects are superimposed upon sequence distributions and often lead to complex NMR spectra[6,10] with many overlapping resonances which can preclude an unambiguous analysis of monomer sequence distribution.

Mark[16-21] has attempted to use the dimensions and dipole moments of copolymers dissolved in dilute solutions as a means to determine their monomer sequence distribution. By calculating the dimensions and dipole moments expected for copolymers of varying composition and monomer distribution and comparing these values to the dimensions and dipole moments determined experimentally for a given copolymer, he hoped to be able to determine its sequence distribution. Although the dimensions and dipole moments Mark calculated for several copolymers did depend on their sequence distribution, in some cases this dependence was either multivalued or too weak to uniquely determine the sequence distributuion.

In the spirit of Mark's search for an easily measured molecular property of a copolymer chain that is sensitive to its sequence distribution, we feel that the molar Kerr constant, as determined in an electrical birefringence experiment,[22] may hold promise as just such a molecular property for many copolymers. This belief is based on the fact that the molar Kerr constant is a molecular property whose range of values[22] for low molecular weight substances (about the size of a monomer unit) varies over four orders of magnitude and can be either positive or negative in sign. By contrast the range in dimensions and dipole moments per monomer unit observed[21,23] for randomly coiling polymer chains (homo- or copolymers) in solution seldom exceeds a factor of 5 to 10.

In addition, it appears from Monte Carlo lattice studies of Lemaire et al.[24] that the optical anisotropy of polymer chains, like their dipole moments,[25-29] may be unperturbed by excluded volume effects.[30] Since the molar Kerr constant of a polymer chain is related to its optical anisotropy, as well as to its dipole moment (see below), it may not be necessary to perform the requisite electrical birefringence measurements in a theta solvent[30] in order to obtain the molar Kerr constant of an unperturbed polymer chain, although the Kerr effect measurements of Le Fevre and co-workers[31-33] seem to argue against this hope (see Results and Discussion).

We describe here an attempt to evaluate the potential utility of the molar Kerr constant as a sensitive probe of copolymer sequence distribution. Molar Kerr constants are calculated for several homo- and copolymer systems consisting of vinyl monomer units as functions of the stereoregularity and monomer sequence distribution.

Description of Calculations

Molar Kerr constants are calculated for the homopolymers poly(propylene) (PP), poly(vinyl chloride) (PVC), poly(styrene) (PS), poly(*p*-methylstyrene) (PPMS), and poly(*p*-chlorostyrene) (PPCS) and for the copolymers PVC–PP, PS–PPCS, and PPMS–PPCS. The molar Kerr constant mK of a polymer molecule is given[23,34] by

$$\mathrm{mK} = \left(\frac{2\pi N_{\mathrm{A}}}{15kT}\right)\left[\frac{\langle \mu^{\mathrm{R}}\hat{\alpha}\mu^{\mathrm{C}}\rangle_{\mathrm{o}}}{kT} + \langle \hat{\alpha}^{\mathrm{R}}\hat{\alpha}'^{\mathrm{C}}\rangle_{\mathrm{o}}\right] \qquad (1)$$

where N_{A} is Avogadro's number, μ is the dipole moment, $\hat{\alpha}$, $\hat{\alpha}'$ are the traceless optical and static polarizability tensors of the polymer chain [$\hat{\alpha} = \alpha - \frac{1}{3}(\mathrm{trace}\ \alpha)E$], and the superscripts R and C denote row and column representations of a vector or tensor. The angle brackets indicate an average over all chain conformations, and the subscript o signifies unperturbed conditions, or an absence of excluded volume effects.[30]

Table I
Bond Dipole Moments and Optical Polarizabilities

Bond	Dipole moment,[a] D	Polarizability,[b] Å^3
C–H	$\mu = 0.0$	$\alpha_{\parallel} = 0.79, \alpha_{\perp} = 0.58$
C–C	$\mu = 0.0$	$\alpha_{\parallel} = 1.88, \alpha_{\perp} = 0.02$
C–C$_6$H$_5$	$\mu = 0.4$	$\alpha_{\parallel}{}^{c} = 12.3, \alpha_{\perp}{}^{c} = 6.35$
C–Cl	$\mu = 1.9$	$\alpha_{\parallel} = 3.67, \alpha_{\perp} = 2.08$
C$_6$H$_5$–Cl	$\mu = 1.6$	$\alpha_{\parallel}{}^{d} = 3.67, \alpha_{\perp}{}^{d} = 2.08$

[a] Taken from Minkin et al.[39] [b] Taken from Denbigh.[40] [c] Approximated as the polarizability of benzene.[41] [d] Assumed to be the same as the C–Cl bond polarizability obtained[40] from the methyl chlorides.

Provided the bond dipole moments and polarizabilities of the polymer are known and are expressed in reference frames along the backbone bonds[23] it is possible to calculate the dipole moment ($\langle \mu^{\mathrm{R}}\hat{\alpha}\mu^{\mathrm{C}}\rangle$) and polarizability ($\langle \hat{\alpha}^{\mathrm{R}}\alpha'^{\mathrm{C}}\rangle$) contributions to the molar Kerr constant through utilization of the rotational isomeric state (RIS) model[23,35] of polymers, the valence optical scheme[35] of adding bond polarizabilities, and the matrix multiplication methods of Flory and co-workers.[23]

In all calculations of the molar Kerr constants of polymers prior to Nagai and Ishikawa[34] various artificial models of polymer chains were adopted. Stuart and Peterlin[36] treated a *freely jointed chain*, Dows[37] assumed a *freely rotating chain*, and Gotlib[38] treated the polymer chain whose bond rotations are hindered but remain independent of neighboring bond rotation states.

The bond dipole moments and polarizabilities used in the present calculations are presented in Table I. We realize that Denbigh's[40] polarizability values for several bonds are probably in error,[43] but until further experiments are performed to obtain the corrected polarizabilities we choose to use a consistent set like Denbigh's in these illustrative calculations.[44]

Listed below are the group polarizability tensors obtained from Denbigh's bond polarizabilities expressed in the usual reference frame along the backbone C–C bonds.[23]

$$\alpha\mathrm{CH_3\text{–}C} = \begin{bmatrix} 3.48 & 0.012 & 0 \\ 0.012 & 2.16 & 0 \\ 0 & 0 & 2.13 \end{bmatrix} \text{Å}^3$$

$$\alpha\mathrm{CH_2\text{–}H} = \begin{bmatrix} 1.99 & -0.066 & 0 \\ -0.066 & 1.82 & 0 \\ 0 & 0 & 2.01 \end{bmatrix} \text{Å}^3$$

$$\alpha\mathrm{CH_2\text{–}C} = \begin{bmatrix} 3.09 & -0.066 & 0 \\ -0.066 & 1.28 & 0 \\ 0 & 0 & 1.46 \end{bmatrix} \text{Å}^3$$

$$\alpha(\mathrm{CH_3HC\text{–}C})_{d,l} = \begin{bmatrix} 5.32 & \mp 0.114 & \pm 0.474 \\ \mp 0.114 & 2.83 & \pm 0.878 \\ \pm 0.474 & \pm 0.878 & 3.49 \end{bmatrix} \text{Å}^3$$

$$\alpha(\mathrm{ClHC\text{–}C})_{d,l} = \begin{bmatrix} 4.73 & \mp 0.283 & \pm 0.365 \\ \mp 0.283 & 3.10 & \pm 0.542 \\ \pm 0.365 & \pm 0.542 & 3.87 \end{bmatrix} \text{Å}^3$$

Table II
Calculated Molar Kerr Constants for PP, PVC, and PVC–PP Polymers

Polymer	Stereo-regularity[a]	Sequence distribution	mK^D	mK^P	mK[b]
PP	S		0	49	49
PP	I		0	45	45
PP	A		0	39	39
PVC	S		−13 500	74	−13 426
PVC	I		287	19	306
PVC	A		45	26	71
PVC–PP	S	Reg. altn.	−611	44	−567
PVC–PP	S	50:50 random	−691	45	−646
PVC–PP	I	Reg. altn.	81	28	109
PVC–PP	I	50:50 random	79	29	108
PVC–PP	A	Reg. altn.	−416	33	−383
PVC–PP	A	10:90 random	−12	38	26
PVC–PP	A	50:50 random	−40	32	−8
PVC–PP	A	90:10 random	16	27	43

[a] S ≡ syndiotactic, I ≡ isotactic, A ≡ atactic. [b] Expressed per mole of backbone bonds in (cm^5 statvolts^{-2}) × 10^{12}.

Table III
Calculated Molated Kerr Constants for PS, PPMS, PPCS, PS–PPCS, and PPMS–PPCS Polymers

Polymers	Stereo-regularity[a]	Sequence distribution	mK^D	mK^P	mK[b]
PS	S		−18	134	116
PS	I		−4	113	107
PS	A		−1	128	127
PPMS	S		0	144	144
PPMS	I		0	138	138
PPMS	A		0	135	135
PPCS	S		−874	108	−766
PPCS	I		−164	68	−96
PPCS	A		−188	80	−108
PS-PPCS	S	Reg. altn.	449	95	544
PS-PPCS	S	50:50 random	−216	132	−84
PPMS-PPCS	S	Reg. altn.	612	118	730
PPMS-PPCS	S	50:50 random	−149	140	−9
PS-PPCS	I	Reg. altn.	−21	89	68
PS-PPCS	I	50:50 random	−34	90	56
PPMS-PPCS	I	Reg. altn.	3	97	100
PPMS-PPCS	I	50:50 random	−11	101	90
PS-PPCS	A	Reg. altn.	176	124	300
PS-PPCS	A	50:50 random	17	111	128
PPMS-PPCS	A	Reg. altn.	306	137	443
PPMS-PPCS	A	50:50 random	35	117	152

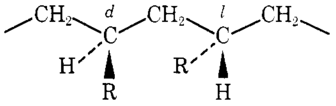
[a] S ≡ syndiotactic, I ≡ isotactic, A ≡ atactic. [b] Expressed per mole of backbone bonds in (cm^5/statvolts $^{-2}$) × 10^{12}.

$$\alpha(C_6H_5HC\text{–}C)_{d,l} = \begin{bmatrix} 10.7 & \mp 2.80 & \mp 0.06 \\ \mp 2.80 & 11.1 & \pm 0.08 \\ \mp 0.06 & \pm 0.08 & 13.1 \end{bmatrix} \text{Å}^3$$

$$\alpha(C_6H_4CH_3HC\text{–}C)_{d,l} = \begin{bmatrix} 13.5 & \mp 2.95 & \pm 0.47 \\ \mp 2.95 & 13.3 & \pm 0.88 \\ \pm 0.47 & \pm 0.88 & 15.8 \end{bmatrix} \text{Å}^3$$

$$\alpha(C_6H_4ClHC\text{–}C)_{d,l} = \begin{bmatrix} 13.0 & \mp 0.25 & \mp 0.48 \\ \mp 0.25 & 13.6 & \mp 0.38 \\ \mp 0.48 & \mp 0.38 & 16.2 \end{bmatrix} \text{Å}^3$$

Backbone valence angles ∠C–C–C = 112° and ∠H–C–H = ∠H–C–R = 110° were assumed[16–21] and the phenyl groups were fixed in the conformation where they are perpendicular to the adjoining backbone bonds in the construction of these group polarizability tensors. (Oscillation of the phenyl groups up to ±30° about this position has been shown not to significantly affect other optically anisotropic properties calculated[45,46] for PS chains.) The first two polarizability tensors[23] correspond to the methyl capped end groups which were assumed to terminate each chain. The subscripts *d* and *l* derive from the stereoregularity[23] of the asymmetric centers in the vinyl chains with the upper signs of the off diagonal elements corresponding to a *d* center and the lower to an *l* center.



The RIS models for PP, PVC, and PVC–PP polymers described by Mark[18] and the RIS model of PS given by Flory et al.[23,47] which is also applicable[16,17,20,21] to PPMS, PPCS, PS–PPCS, and PPMS–PPCS are used in the present calculations. In these RIS models[48] each backbone bond is permitted to adopt the three staggered rotational states of 0° (trans), 120° (gauche$^+$), and 240° (gauche$^-$) with probabilities dependent upon the rotational states of nearest neighbor bonds. (For details of these RIS models, which correctly predict the dimensions, dipole moments, and their temperature dependence, see ref 18, 23, and 47.)

Monte Carlo chain generation techniques are used to construct those polymer chains with irregular stereo sequences and/or monomer sequence distributions. Each chain is 500 bonds in length, and 10 chains are generated and averaged over for each degree of stereoirregularity and/or monomer sequence distribution.

The matrix multiplication techniques described by Flory[23] are used to calculate the conformationally averaged and unperturbed dipole and polarizability contributions to the molar Kerr constants (see eq 1). It is assumed[49,50] throughout that the static polarizabilities are 10% greater than the experimentally obtained optical polarizabilities.

Calculated Results and Discussion

The calculated molar Kerr constants are presented in Tables II and III. Molar Kerr constants mK are presented per mole of backbone bond and are separated into dipole (mK^D) and polarizability (mK^P) contributions (see eq 1).

Among the five homopolymers studied, only the calculated molar Kerr constants of the polar polymers PVC and PPCS exhibit marked sensitivities to stereosequence. For these two polymers the sensitivity to stereosequence of the molar Kerr constants is comparable to or greater than the sensitivity exhibited by the dipole moments calculated by Mark.[16-21] In addition, the molar Kerr constant of PPCS is largest for syndiotactic chains, while Mark[16,17,20,21] finds isotactic PPCS chains to have the largest dipole moments. For PPCS both properties appear complementary and could be used together to study both ends of its stereosequence spectrum.

Alternate measures of the optical anisotropy of polymer chains, such as the depolarization of scattered light[45] and the strain birefringence,[46] have not as yet been calculated or measured for polar vinyl polymers to determine their sensitivity to stereosequence.

Le Fevre and Sundaram[33] have measured the molar Kerr constants of PVC chains dissolved in dioxane and they obtained $mK = 12.6\text{–}161.1 \times 10^{-12}$ cm^5 statvolts^{-2}/mol of backbone bonds for samples with from 1080 to 4040 backbone bonds. This may be compared with the value 71×10^{-12} calculated here for atactic PVC. The disparity is not unexpected considering the crude polarizability tensors employed in the present calculations and the possibility that excluded volume effects may cause the experimentally observed increase in mK per bond as the molecular weight increases (see below).

The molar Kerr constants calculated for each of the three copolymer systems show high sensitivities to both stereosequence and monomer sequence distribution. More important is the much greater sensitivity of the molar Kerr constants to monomer sequence distribution relative to the dipole moments calculated by Mark.[16-21] On this basis it appears that the molar Kerr constant is a molecular property of polar copolymers with a much greater sensitivity to monomer sequence distribution than is the dipole moment.

The calculations described here seem to hold promise[51] for the molar Kerr constant as a polymeric property with enough sensitivity to stereoregularity and/or monomer sequence distribution to be of value in characterizing these aspects of polar, homo- and copolymers. It remains to demonstrate this sensitivity experimentally and to determine if the molar Kerr constant of a polymer chain measured in dilute solution is independent[24] of solvent–polymer interactions (excluded volume effects) or whether, as indicated by the measurements of Le Fevre et al.,[31-33] electrical birefringence experiments must be performed in a theta solvent.[23,30]

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References and Notes

(1) H. J. Harwood, *Angew. Chem., Int. Ed. Engl.*, **4,** 1051 (1965).
(2) U. Johnsen, *Ber. Bunsenges. Phys. Chem.*, **70,** 320 (1966).
(3) K. C. Ramey and W. S. Brey, Jr., *J. Macromol. Sci., Rev. Macromol. Chem.*, **1,** 263 (1967).
(4) H. A. Willis and M. E. A. Cudby, *Appl. Spectrosc. Rev.*, **1,** 237 (1968).
(5) J. C. Woodbrey, "The Stereochemistry of Macromolecules", Vol. 3, A. D. Ketley, Ed., Marcel Dekker, New York, N.Y., 1968.
(6) J. Schaefer, *Macromolecules*, **2,** 10, 533 (1969); **4,** 107 (1971).
(7) W. O. Crain, Jr., A. Zambelli, and J. D. Roberts, *Macromolecules*, **4,** 330 (1971).
(8) A. Zambelli, G. Gatti, O. Sacchi, W. O. Crain, Jr., and J. D. Roberts, *Macromolecules*, **4,** 475 (1971).
(9) C. J. Carman and C. E. Wilkes, *Rubber Chem. Technol.*, **44,** 871 (1971).
(10) F. A. Bovey, "High Resolution NMR of Macromolecules", Academic Press, New York, N.Y., 1972, Chapters X and XI.
(11) V. D. Mochel, *J. Macromol. Sci., Rev. Macromol. Chem.*, **6,** 289 (1972).
(12) B. Ibrahim, A. R. Katritzky, A. Smith, and D. E. Weiss, *J. Chem. Soc., Perkin Trans. 2,* 1537 (1974).
(13) A. R. Katritzky and D. E. Weiss, *J. Chem. Soc., Perkin Trans. 2,* 1542 (1974); 21, 27 (1975); *Chem. Br.*, **12,** 45 (1976).
(14) A. R. Katritzky, A. Smith, and D. E. Weiss, *J. Chem. Soc., Perkin Trans. 2,* 1547 (1974).
(15) C. J. Carman, *Macromolecules*, **7,** 789 (1974).
(16) J. E. Mark, *J. Am. Chem. Soc.*, **94,** 6645 (1972).
(17) J. E. Mark, *J. Chem. Phys.*, **56,** 451, 458 (1971); **57,** 2541 (1972).
(18) J. E. Mark, *J. Polym. Sci., Polym. Phys. Ed.*, **11,** 1375 (1973).
(19) J. E. Mark, *Polymer*, **14,** 553 (1973).
(20) J. E. Mark, "Characterization of Materials in Research", J. J. Burke, Ed., Syracuse University Press, Syracuse, N.Y., 1975, Chapter 12.
(21) J. E. Mark, *Acc. Chem. Res.*, **7,** 218 (1974).
(22) C. G. Le Fevre and R. J. W. Le Fevre, "Technique of Organic Chemistry", Vol. I, Part III, A. Weissberger, Ed., Interscience, New York, N.Y., 1960, Chapter XXXVI.
(23) P. J. Flory, "Statistical Mechanics of Chain Molecules", Interscience, New York, N.Y., 1969, Chapters II–VI and IX.
(24) B. Lemaire, G. Fourche, and E. Sanchez, *J. Polym. Sci., Polym. Phys. Ed.*, **12,** 417 (1974).
(25) J. Marchal and H. Benoit, *J. Chim. Phys. Phys.-Chim. Biol.*, **52,** 818 (1955); *J. Polym. Sci.*, **23,** 233 (1957).
(26) W. H. Stockmayer, *Pure Appl. Chem.*, **15,** 539 (1967).
(27) K. Nagai and T. Ishikawa, *Polym. J.*, **2,** 416 (1971).
(28) M. Doi, *Polym. J.*, **3,** 252 (1972).
(29) S. C. Liao and J. E. Mark, *J. Chem. Phys.*, **59,** 3825 (1973).
(30) P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, N.Y., 1953, Chapters X and XII.
(31) C. G. Le Fevre, R. J. W. Le Fevre, and G. M. Parkins, *J. Chem. Soc.*, 1468 (1958); 1814 (1960).
(32) M. Aroney, R. J. W. Le Fevre, and G. M. Parkins, *J. Chem. Soc.*, 2890 (1960).
(33) R. J. W. Le Fevre and K. M. S. Sundaram, *J. Chem. Soc.*, 1494, 4003 (1962); 1880, 3188, 3547 (1963); 3518 (1964).
(34) K. Nagai and T. Ishikawa, *J. Chem. Phys.*, **43,** 4508 (1965).
(35) M. V. Volkenstein, "Configurational Statistics of Polymeric Chains", English Translation, S. N. Timasheff and M. J. Timasheff, Ed., Interscience, New York, N.Y., 1963.
(36) H. A. Stuart and A. Peterlin, *J. Polym. Sci.*, **5,** 551 (1950).
(37) D. A. Dows, *J. Chem. Phys.*, **41,** 2656 (1964).
(38) See Chapter 7 in ref 35.
(39) V. I. Minkin, O. A. Osipov, and Y. A. Zhadanov, "Dipole Moments in Organic Chemistry", Plenum Press, New York, N.Y., 1970.
(40) K. G. Denbigh, *Trans. Faraday Soc.*, **36,** 936 (1940).
(41) H. A. Stuart, "Molekülstruktur", Julius Springer, 1934.
(42) G. D. Patterson and P. J. Flory, *Trans. Faraday Soc.*, **68,** 1098 (1972).
(43) P. Bothorel and G. Fourche, *J. Chem. Soc., Faraday Trans. 2,* **69,** 411 (1973).
(44) Professor Paul J. Flory has informed me that recent work in his laboratory by C. Carlson, U. Suter, and E. Saiz has led to improved polarizability tensors for the PVC, PS, PPMS, and PPCS chains. Utilization of these improved polarizability tensors leads to molar Kerr constants differing quantitatively from those calculated here using Denbigh's values. However, as described in the following section for Denbigh's polarizabilities, the molar Kerr constants calculated for polar vinyl homo- and copolymers also remain sensitive to stereoregularity and monomer sequence distribution when the improved set of polarizability tensors are employed.
(45) A. E. Tonelli, Y. Abe, and P. J. Flory, *Macromolecules*, **3,** 303 (1970).
(46) Y. Abe, A. E. Tonelli, and P. J. Flory, *Macromolecules*, **3,** 294 (1970).
(47) D. Y. Yoon, P. R. Sundararajan, and P. J. Flory, *Macromolecules*, **8,** 776 (1975).
(48) Though Yoon et al.[47] employed rotational states slightly displaced from perfect stagger in their PS calculations, we neglect these deviations and

retain the 0°, ±120° backbone rotational states in all calculations reported here. Rotational state statistical weights[23,47] $\eta = 0.8 \exp(200/T)$, $\tau = 0.5$, and $\omega = \omega' = \omega'' = 1.5 \exp(-1000/T)$ were used at $T = 150$ °C for the calculations performed on PS, PPMS, PPCS, PS-PPCS, and PPMS-PPCS.

(49) R. J. W. LeFevre, *Adv. Phys. Org. Chem.*, 3 (1965).

(50) T. Ishikawa and K. Nagai, *Polym. J.*, **2**, 195 (1971).

(51) Dr. E. Saiz has studied the relation between variations in the RIS model and the calculated molar Kerr constants for PPCS. He finds, as Nagai and Ishikawa[34] did, that the magnitude of the calculated molar Kerr constants for PPCS is sensitive to the details (rotational state energies, chain geometry, etc.) of the RIS model employed and cautions that Kerr constants may only be useful in the characterization of those polymers whose RIS models are firmly established.

Ternary Polymer Mixtures

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ABSTRACT: Two incompatible polymers, poly(methyl methacrylate) and poly(ethyl methacrylate), can be brought together by poly(vinylidene fluoride) to form ternary mixtures which are compatible. The melting point depression of PVF_2 in the ternary system can be calculated from Scott's equation. Mixtures containing 40 to 70% by weight of PVF_2 are amorphous when quenched from melt and each mixture consists of a single phase whose T_g is equal to the volume fraction average of the T_g of component polymers.

In previous studies[2,3] of mixtures of poly(vinylidene fluoride) (PVF_2) with poly(methyl methacrylate) (PMMA) or poly(ethyl methacrylate) (PEMA), binary interaction parameters obtained from melting point depression of PVF_2 were found to be negative, indicative of compatibility in the molten state. When quenched from the melt, blends of PVF_2 with PMMA were amorphous and exhibited a single glass transition for each composition.[2,4,5] Quenched mixtures containing 60% or more PEMA were also amorphous and showed single glass transitions. When the PEMA content is low, crystallization of PVF_2 was observed even at high quenching rates (≥320 °C/min) and the crystalline regions coexisted with two conjugated amorphous phases which contained ~100 and ~45 wt % PVF_2.[3]

Although both PMMA and PEMA are compatible with PVF_2 and the binary interaction parameters are similar in magnitude, the two methacrylate polymers are incompatible with each other.[6] Therefore we wish to explore the possibility of rendering these two polymers compatible using PVF_2 as a common solvent. The notion of bringing together two incompatible polymers by a third material is practiced with low molecular weight polymers in coating formulations but, to our knowledge, has not been demonstrated with high molecular weight vinyl polymers.

The principal tool of our investigation is calorimetry. The melting temperatures of PVF_2 in the as-cast films of ternary mixtures and the glass transition temperatures of quenched specimens were determined. Electron microscope studies of PMMA–PEMA blends were also undertaken to verify the results of calorimetric investigations.

Experimental Section

Materials. Poly(vinylidene fluoride), Kynar 821, from Pennwalt Corp., poly(methacrylate), Acrylite H-12, from American Cyanamid Co., and poly(ethyl methacrylate) from Haven Chemicals Inc. were the same materials as used in earlier studies.[13] Films were cast from 3% dimethylformamide (DMF) solution and maintained at 90 °C in a forced-air oven for 3 days. To ensure complete removal of DMF from films containing high percentages of PMMA, all films were given additional drying at 130 °C in a vacuum oven overnight. The compositions of mixtures are recorded in weight percentages unless otherwise stated.

Calorimetry. Calorimetric studies were conducted using a Du Pont Thermal Analyzer, Model 990, with a DSC cell. Melting point measurements were carried out at a heating rate of 10 °C/min. In the determination of glass transitions, the specimens were quenched from the melt at 50 °C/min to −120 °C and then heated at 20 °C/min. The endothermic response associated with glass transition was often broad and weak in ternary mixtures and triplicate runs were made in most cases to ascertain T_g. The uncertainty in T_g measurement is ±2 °C.

Electron Microscopy. Kato's technique of OsO_4 staining[7] was applied to PMMA–PEMA mixtures. Ultrathin sections of stained specimens were examined with transmission electron microscopy.

Results and Discussions

(1) PMMA–PEMA Mixtures. Although PMMA and PEMA are chemical homologues, phase separation has been reported to take place in chloroform solution.[6] Because the refractive index difference between the two polymers is insignificant, the transparency of films cast from DMF cannot be taken as an indication of homogeneous mixing. Rather, evidence for the two-phase nature of these films is seen in calorimetric results. The thermograms of PEMA, PMMA, and four mixtures containing 85, 60, 40, and 15% PEMA, respectively, are shown in Figure 1. Each of the four mixtures exhibits two glass transitions at 68 and 104 °C, nearly identical with the T_g values for the pure polymers, namely, 67 °C for PEMA and 102 °C for PMMA. The magnitudes of ΔC_p associated with the two transitions in curves B to E agree well with the predictions based on the ΔC_p values of the component polymers and the compositions of the mixtures (Figure 2). These results suggest very strongly that PMMA–PEMA mixtures undergo phase separation into nearly pure components.

Further evidence for the two-phase nature of the blends was obtained from electron microscopy. Although we did not anticipate preferential absorption of osmium tetraoxide in either polymer, the staining technique revealed vividly the presence of microscopic domains. Typical photomicrographs are shown in Figures 3A and 3B. Judging both from the cutting mark left by the diamond knife on the hard phase and from phase volume, we believe that the spherical domains consist of PMMA.

(2) Melting Point Depression of PVF_2 in Ternary Systems. The melting temperatures of PVF_2 in ternary mixtures are listed in Table I. The value of melting point depression, ΔT_m, at constant PVF_2 content is insensitive to the ratio of two methacrylate polymers because the binary in-