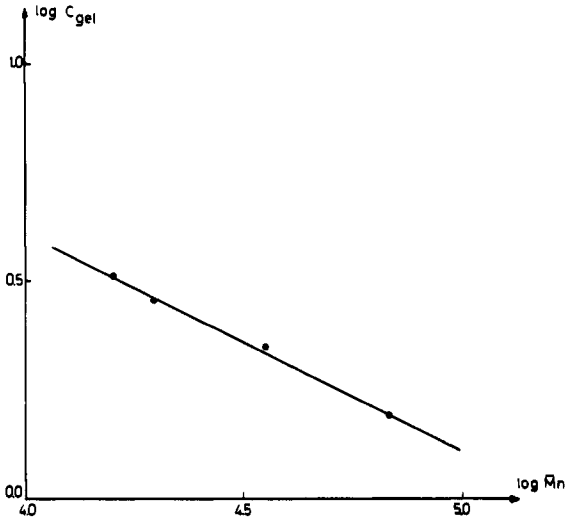

Figure 2. Gel concentration (g·dL^{-1}) vs. PIP length ($\bar{M}_n$) (log–log plot) for magnesium α,ω-dicarboxylato-PIP in toluene at 25 °C.

fluid solutions, which suddenly gel upon increasing the concentration. Figure 1 clearly shows this behavior at 25 °C for a high molecular weight PIP-Mg ($\bar{M}_n$ of carboxy-telechelic-PIP = 7×10^4). At lower concentrations (<1%), the relative viscosity varies regularly as observed also for the nonneutralized PIP. At a given concentration, the influence of the ionic interactions takes over and promotes a sharp asymptotic increase of η_{rel}. The shape of this log η_{rel}–concentration plot (Figure 1) is characteristic of any HTP and expresses the occurrence of a cooperative gelation process. The vertical asymptote of this curve defines the critical gelation concentration (C_{gel}), i.e., the concentration necessary to aggregate the ionic groups and cross-link the difunctional PIP chains dissolved in toluene. The very low values of this C_{gel} (1–1.5 g·dL^{-1}; see also Figure 2) are to be noted.

The relative viscosities were measured by a Desreux-Bisschoff capillary viscosimeter;[20] the shearing conditions were accordingly the same for each experimental determination. At constant PIP length ($\bar{M}_n = 7 \times 10^4$) and solvent (toluene), C_{gel} depends on the temperature in a perfectly reversible manner (1.54 g·dL^{-1} at 25 °C and 1.69 g·dL^{-1} at 50 °C). As reported elsewhere,[16] the greater the size of the divalent cation and the dielectric constant of the solvent, the higher the observed C_{gel}. All these experimental results agree with the dependence of C_{gel} on the electrostatic interactions between the nondissociated ionic groups in nonpolar solvents. It should be accordingly expected that C_{gel} decreases as the carboxylate content of PIP increases, in agreement with Joanny's prediction for ionomers.[15] To check the validity of this statement, C_{gel} has been experimentally related to the length of PIP, all other parameters being kept constant (Figure 2). The behavior of PIP-Mg in toluene at 25 °C is expressed by

$$C_{gel} = 407 \times M^{-0.5} \quad (1)$$

where M is the molecular weight of the carboxy-telechelic-PIP. That means that C_{gel} varies inversely with PIP length or proportionally with the metal carboxylate content of PIP-Mg. It must also be noted that over the whole range of concentration (in toluene at 25 °C) no demixing of the PIP-Mg studied here (see Figure 2) was observed. There is, of course, disagreement between the experimental behavior of halato-telechelic polymers and Joanny's theory developed for ionomers.[15] Therefore, the aggregation process could be fundamentally different for these two types of ion-containing polymers, stressing the deep influence of the distribution of ionic groups along or within the polymeric backbone.

In conclusion, the aggregation of electric dipoles of HTP in nonpolar solvents is closely controlled by the molecular characteristics of the polymeric carrier, besides the well-known parameters of temperature, dielectric constant of the medium, and nature of the ionic group itself.

The validity of eq 1 is now being tested for polybutadiene and polyvinyl aromatic-based HTP, and a theoretical treatment is under study to explain satisfactorily the behavior observed. Information about the regularly organized morphology[21] and the particular rheology[22] of HTP will be reported soon.

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Molecular Mechanism for $\alpha \rightarrow \delta$ Transformation in Electrically Poled Poly(vinylidene fluoride)

Formation of a polar analogue of the α phase of poly(vinylidene fluoride) (PVF_2) has recently been achieved by Davis et al.,[1] Naegele, Yoon, and Broadhurst,[2] and Davies and Singh.[3] This polar phase (denoted variously as δ, IV, α_p, or II_p) is obtained by conventional or corona poling of thin films of PVF_2 in high electric fields.[1-3] Its

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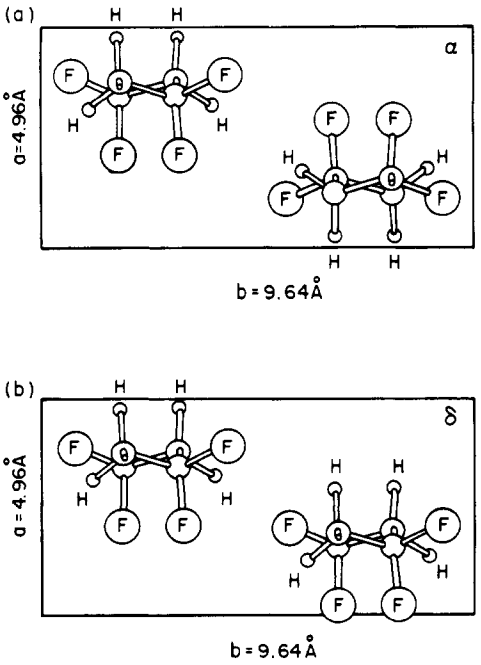

Figure 1. Projections along c of the unit cells of (a) the α phase and (b) the δ phase of PVF_2.

X-ray reflections were observed to be at the same spacings as those of the α form but to have somewhat different intensities;[1-3] at the same time, no significant changes were noted in the locations of infrared absorption bands before and after poling.[1,2] These data imply that the original conformation of α chains (a distorted TGTḠ)[4] and the unit-cell dimensions are preserved after poling; the difference in intensities of X-ray reflections is ascribed to the fact that every second chain has been reoriented by the field so that its dipole component normal to c is now pointing 180° away from its original direction (see Figure 1). In this manner, the initially antipolar arrangement of molecular chains is reversed, and the unit cell acquires a net dipole moment. These conclusions of Davis and co-workers[1] and Naegele et al.[2] have been fully confirmed by a detailed crystal-structure analysis of the δ phase.[5]

The reorientation of dipole vectors during poling has been explicitly assumed to occur by actual physical rotation of alternate crystalline stems about their molecular axes through 180°.[1-3] Intermolecular potential energy calculations[6] have shown that such a 180° rotation is energetically possible in a cooperative manner involving all chains on every second 020 plane. A variation of this process, resulting in rotation of an α chain not all at once, but rather through propagation of a 180° twist along the crystalline stem, has also been investigated.[7] However, these are not the only possible mechanisms that could lead to a reversal of alternate dipole directions; a much simpler model is presented below.

The proposed alternative mechanism would (in its simplest manifestation) involve 90° rotations about every gauche and gauche minus bond of alternate chains in the manner indicated in Figure 2; all rotations would be in the direction of the applied field. This scheme would effectively change the original conformation from TGTḠ to TḠTG. Rotation by 90° corresponds to twice the angle between T and G (or T and Ḡ) positions in these α chains and reflects the distortion in the TGTḠ conformation (G = −Ḡ = 135°) reported by Hasegawa et al.[4] and confirmed recently by Bachmann and Lando.[8] As seen in Figure 2, this model requires alternate molecular chains to pass through an exact cis–trans conformation (equivalent to a 2/1 helix) at the midpoint of the transformational path. For the overall chain direction to be preserved throughout this intramolecular rotational process, the inclination of all main-chain bonds with respect to the c axis must also change continuously, as depicted in Figure 3. At the midpoint of the transformation (2/1 helix), all C–C bonds

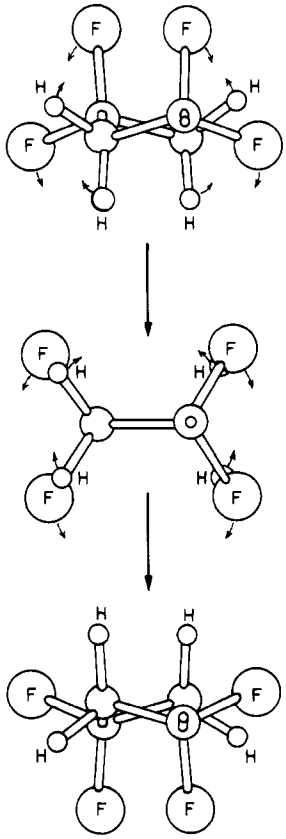

Figure 2. Pattern of intramolecular rotations in the distorted TGTḠ conformation leading to reversal of its dipole component normal to the chain; view is along the c axis of the unit cell.

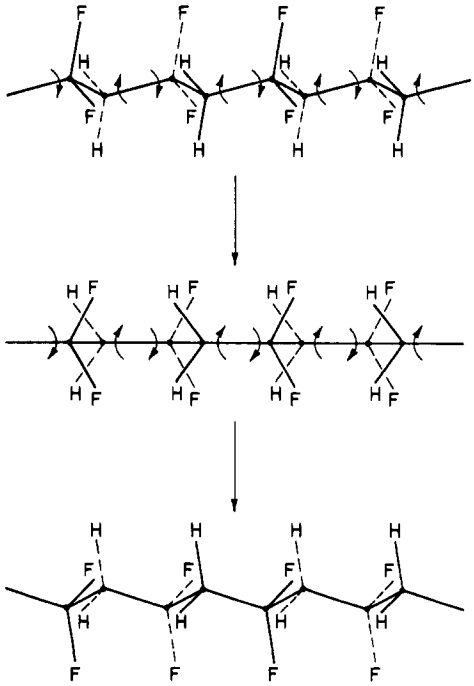

Figure 3. Pattern of intramolecular rotations in the distorted TGTḠ conformation leading to reversal of its dipole component normal to the chain; view is along the b axis of the unit cell.

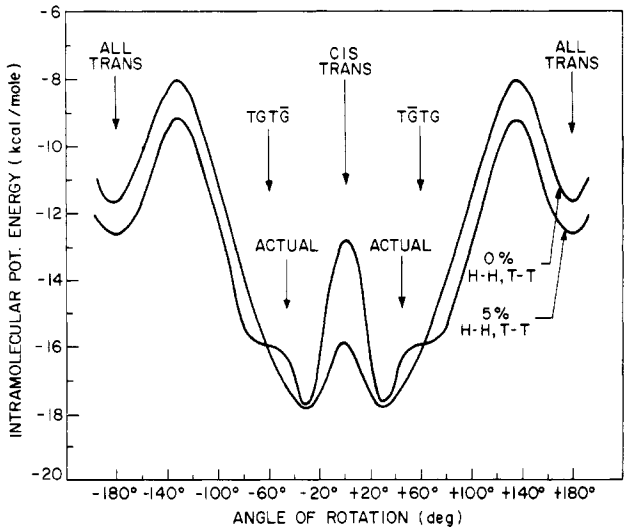

Figure 4. Variation of the intramolecular potential energy with angle θ in a $T\theta T\bar{\theta}$ conformation for 0% and 5% head-to-head, tail-to-tail defects (adapted from ref 11).

define a plane parallel to the original c direction; ultimately, their inclination to this c axis will be the reverse of the original.

Clearly, this transitory cis–trans conformation represents a localized peak in intramolecular potential energy of the crystalline stems; nevertheless, it is by no means an unrealistic temporary conformation, since 2/1 helices had for years been considered probable conformations for the stable α phase.[9,10] An estimate of the strain involved during passage through the cis–trans conformation may be made by using the detailed energetic calculations of Farmer, Hopfinger, and Lando.[11] Figure 4 is adapted from their Figure 1 and shows the variation of intramolecular potential energy (employing both steric and electrostatic terms) for a $T\theta T\bar{\theta}$ conformation with both the value of the angle of rotation (θ) and the content of inverted monomeric units ("head-to-head", "tail-to-tail" or H–H, T–T). It is seen that the potential energy maximum for the 2/1 helix is relatively low even for 5% defects (the Kureha polymer used by most investigators[1,3] in the field-induced $\alpha \rightarrow \delta$ transformation has a H–H, T–T content of 3.8%).[12] In fact, the potential energy of the 2/1 helix is seen in Figure 4 to be lower than that of the stable all-trans conformation of the β phase.

Neither the proposed new model nor the one invoking physical rotation of molecular stems by 180° is backed by experimental data. However, reorientation of dipoles by the mechanism suggested in this paper involves only minor and energetically reasonable internal rotations, as well as few, if any, steric intermolecular interactions. In general, the chain-rotation mechanism is expected to require a higher total input of energy, although a firm conclusion must await a detailed energetic comparison of the two models.

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Reexamination of the Method for Determining Radical Polymerization Rate Constants

In the kinetic studies of radical polymerization, reaction rates have usually been assumed to be independent of chain length. Several workers,[1-3] however, observed that the termination rate constant decreases appreciably with chain length and some effects on polymerization kinetics have been discussed.[4]

Here we discuss how much error would be caused by the neglect of the chain-length dependence of termination rate constant in determining k_p and k_t in radical polymerization of styrene.

The rate constant for termination between radicals of DP (degree of polymerization) i and j is assumed to be expressed as

$$k_{t,ij} = k_{t0} i^{-\alpha} j^{-\alpha} \tag{1}$$

Thus, the apparent termination rate constant $k_t(\text{app})$ is related to $k_{t,ij}$ by

$$k_t(\text{app}) = \sum\sum k_{t,ij} P_i P_j / (\sum P_i)^2 \tag{2}$$

where P_i denotes the concentration of radical of DP i.

The chain-length distribution of radicals at time t can be represented by a vector $\mathbf{P}(t)$ of which the element $P_i(t)$ denotes the concentration of radical of DP i and the time evolution of vector $\mathbf{P}(t)$ is given by

$$\begin{vmatrix} P_0(t+1) \\ P_1(t+1) \\ P_2(t+1) \\ P_3(t+1) \\ \cdot \\ \cdot \\ \cdot \end{vmatrix} = \begin{vmatrix} p_{00} & p_{0tr} & p_{0tr} & \cdots \\ p_{10} & p_{1tr} & p_{1tr} & \cdots \\ 0 & 1-p_2 & 0 & \cdots \\ 0 & 0 & 1-p_3 & 0 \cdots \\ \cdot & \cdot & & \\ \cdot & \cdot & & \\ \cdot & \cdot & & \end{vmatrix} \cdot \begin{vmatrix} P_0(t) \\ P_1(t) \\ P_2(t) \\ P_3(t) \\ \cdot \\ \cdot \\ \cdot \end{vmatrix} + \begin{vmatrix} R_i(t) \\ 0 \\ 0 \\ 0 \\ \cdot \\ \cdot \\ \cdot \end{vmatrix} \tag{3}$$

$$p_{00} = -(k_i[\mathrm{M}] + k_{prt}\sum \mathbf{P}_j(t))\Delta t$$

$$p_{0tr} = k_{trI}[\mathrm{I}]\Delta t$$

$$p_{10} = k_i[\mathrm{M}]\Delta t$$

$$p_{1tr} = k_{trM}[\mathrm{M}]\Delta t$$

$$p_i = (k_{trI}[\mathrm{I}] + k_{trM}[\mathrm{M}] + k_{prt}\mathbf{P}_0(t) + \sum_j k_{t,ij} P_j(t))\Delta t$$

where the unit of time ($\equiv\Delta t$) is equal to $1/k_p[\mathrm{M}]$ and $P_0(t)$ denotes the concentration of initiator radical of which the supply per unit time in the light period is R_i, with ordinary abbreviations for other rate constants. In actual calculations, the unit time is chosen as 0.01 s, the unit of chain length is accordingly $k_p[\mathrm{M}]/100$, and the contribution of chains longer than 10^5 DP is neglected.

The time variation of $\mathbf{P}(t)$ in the nonstationary polymerization of bulk styrene induced by sectored UV irradiation was calculated for the model systems with $\alpha = 0.0$, 0.1, and 0.2, employing tentative values of $k_p = 55$, $k_t = 2.5 \times 10^7$, $c_M = 2.5 \times 10^{-5}$, and $R_i = 1.0 \times 10^{-8}$ in mole, liter,

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