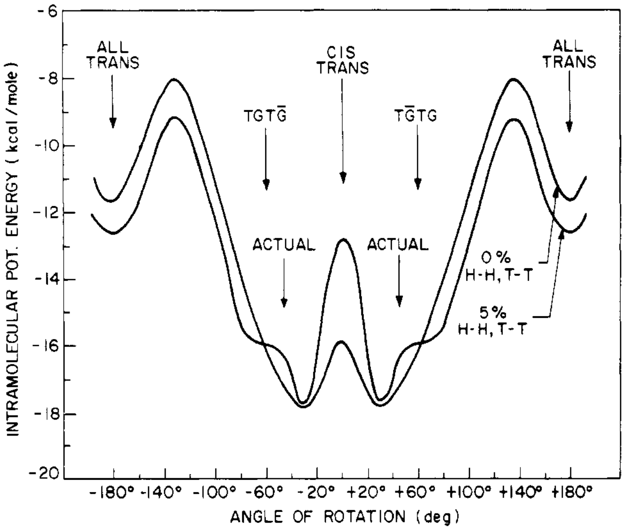

Figure 4. Variation of the intramolecular potential energy with angle θ in a $\mathrm{T}\theta\mathrm{T}\bar{\theta}$ conformation for 0% and 5% head-to-head, tail-to-tail defects (adapted from ref 11).

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 $\mathrm{T}\theta\mathrm{T}\bar{\theta}$ 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(app) is related to $k_{t,ij}$ by

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

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

$$\begin{vmatrix} \mathbf{p}_0(t+1) \\ \mathbf{p}_1(t+1) \\ \mathbf{p}_2(t+1) \\ \mathbf{p}_3(t+1) \\ \vdots \end{vmatrix} = \begin{vmatrix} p_{00} & p_{0\mathrm{tr}} & p_{0\mathrm{tr}} & \cdots \\ p_{10} & p_{1\mathrm{tr}} & p_{1\mathrm{tr}} & \cdots \\ 0 & 1-p_2 & 0 & \cdots \\ 0 & 0 & 1-p_3 & 0 \cdots \\ \vdots & \vdots & & \end{vmatrix} \begin{vmatrix} \mathbf{p}_0(t) \\ \mathbf{p}_1(t) \\ \mathbf{p}_2(t) \\ \mathbf{p}_3(t) \\ \vdots \end{vmatrix} + \begin{vmatrix} R_i(t) \\ 0 \\ 0 \\ 0 \\ \vdots \end{vmatrix} \tag{3}$$

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

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

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

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

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

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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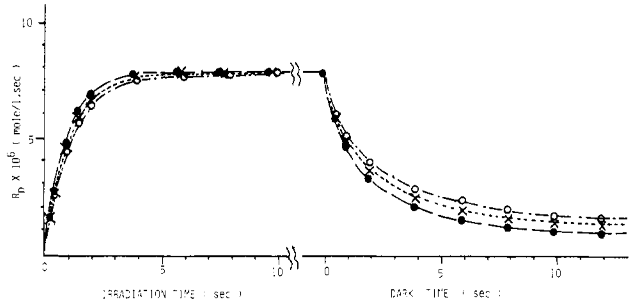

Figure 1. Effect of α on the polymerization rate $R_p(t)$ in the initial and aftereffect stages in photoinduced radical polymerization of styrene at 30 °C: (●) $\alpha = 0.0$; (×) $\alpha = 0.1$; (○) $\alpha = 0.2$.

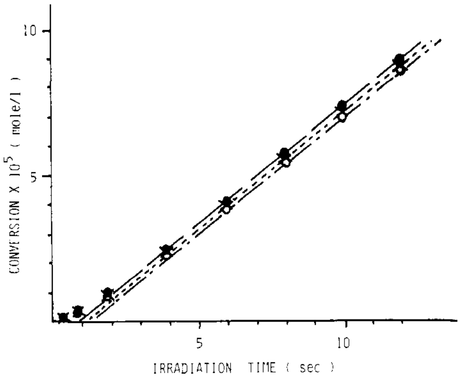

Figure 2. Conversion curves for various model systems: (●) $\alpha = 0.0$; (×) $\alpha = 0.1$; (○) $\alpha = 0.2$.

and second, which are acceptable values for polymerization of styrene at 30 °C under ordinary conditions. The contributions of thermal initiation and minor side reactions were neglected. Respective values of k_{t0} for various α were normalized,[4] so that k_t(app) at steady state coincides with the given value 2.5×10^7 in any model system.

Figure 1 illustrates the time variation of R_p ($\equiv k_p[M]\cdot\sum P_i(t)$) in the first light–dark cycle with a long light period t_l. It is natural that plateau values of R_p are identical for all systems since k_{t0} are normalized. The rate to attain the plateau value, however, is not equal and it decreases with α. Figure 2 shows conversion curves in the initial stages calculated by $\int R_p(t)\,dt$.

Burrel et al.[5] estimated the average lifetime of polymer radicals at steady state, τ_s, from the intersection of time axis t_0 by a tangent to the conversion curve at a steady state: i.e., τ_s is related to t_0 as

$$t_0 = \tau_s \ln 2 \tag{4}$$

This relation does not hold exactly for the $\alpha \neq 0.0$ systems: τ_s calculated from respective conversion curves by this method are 1.4, 1.55, and 1.7 s for α = 0.0, 0.1, and 0.2, whereas respective k_{t0} are normalized to give the same τ_s value of 1.4 s for all systems. Thus, Burrel's method overestimates τ_s by factors of ca. 1.1 and 1.2 for α = 0.1 and 0.2, respectively.

The intermittent method is employed more widely to determine τ_s. In order to calculate the average polymerization rate in sectored UV irradiation $\bar{R}_p(t_l)$, the time variation of $\mathbf{P}(t)$ was followed for several light–dark cycles until the variation attained a dynamic stationary state. Figure 3 shows plots of $\bar{R}_p(t_l)/R_p(s)$ against t_l/τ_s, where $\bar{R}_p(t_l)/R_p(s)$ is calculated by averaging $R_p(t)$ over the light period t_l and the dark period $3t_l$ in dynamic stationary state and $R_p(s)$ denotes R_p at steady state, together with the conventional curve given by Matheson et al.[6] The curves for the $\alpha \neq 0.0$ systems are transformed considerably.[7] Thus, if one tries to determine τ_s by fitting an experimental plot of the $\alpha \neq 0.0$ system to the conventional curve, one fails to get a perfect fit and tends to overestimate τ_s by an indefinite factor, e.g., a factor ranging from 1.1 to 1.7 for α = 0.1.

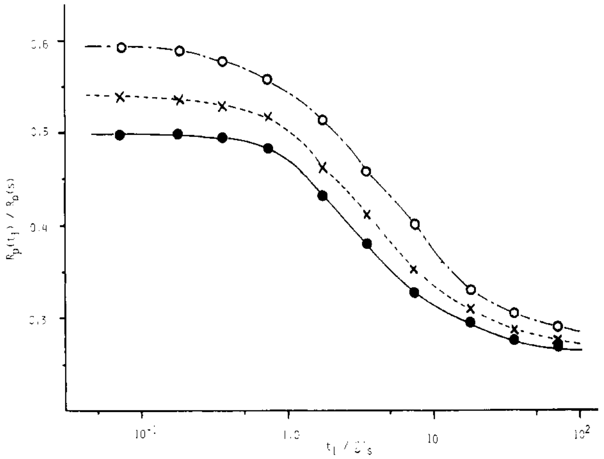

Figure 3. Averaged polymerization rates in intermittent light for different light periods (ratio of light period to dark period is $^1/_3$): (●) $\alpha = 0.0$; (×) $\alpha = 0.1$; (○) $\alpha = 0.2$; (—) conventional curve.

The overestimation of τ_s by a factor of $1 + a$ causes the overestimation of k_p/k_t by the same degree since k_p/k_t is usually calculated from τ_s by employing the relation

$$\tau_s = k_p[M]/2k_tR_p \tag{5}$$

Individual values of k_p and k_t are calculated by combining k_p/k_t and $k_p{}^2/k_t$, which is obtained from other experiments on steady-state polymerization. These procedures finally result in underestimations for the $\alpha \neq 0.0$ systems: they give $k_p/(1 + a)$ and $k_t/(1 + a)^2$, respectively.

Hence, we conclude that the wide dispersion in reported values of k_p and k_t originates partly from the neglect of chain-length dependence of termination rate constant which causes much difficulty in assigning a definitive value to τ_s.

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