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Penultimate-Unit Effects in Free-Radical Copolymerization

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ABSTRACT: Recent important experimental and theoretical results on free-radical copolymerization are reviewed for better understanding of the nature of propagation and chain-transfer reactions. Experiments have yielded much evidence of the existence of the penultimate-unit effect (PUE), of which there are two types. In one, the implicit PUE (IPUE), the effect appears only in the absolute values of the rate constants of propagation, k_p, and chain-transfer, λ, and not explicitly in the monomer reactivity ratios, r_1 and r_2, or in the chain-transfer constant, C $(=\lambda/k_p)$. In the other type, the explicit PUE (EPUE), the effect appears in r_1 and r_2 or in C (or in all three) as well as in k_p and λ. The IPUE may originate in the stabilization of the radical by the penultimate group. The phenomenological model based on this idea was consistent with the experimental results of the IPUE type. In particular, the model and the results consistently suggest that the product r_1r_2, a measure of the alternating tendency, may originate in the IPUE and that the IPUE may be a general rule as that $r_1r_2 < 1$ is a rule. The EPUE is a less general phenomenon, which may originate from a specific interaction, electronic or steric, *between the penultimate unit and the monomer* in the transistion state. Presumably, the EPUE could be adequately modeled by the antepenultimate or a higher order model, at least phenomenologically.

Introduction

We have studied the copolymerization of styrene (ST) and methyl methacrylate (MMA) in the absence[1] and presence[2] of a solvent and reached three conclusions. First, the ST/MMA system conforms to the terminal model with respect to composition but fails to conform to it in terms of the absolute values of the propagation rate constant. Second, the penultimate-unit effect (PUE) is responsible for the failure of the terminal model. Third, the termination step of the system can be represented by a diffusion-controlled termination model. There are reasons to believe that the failure of the terminal model as observed in the ST/MMA system is a rule, not an exception.[3-5] Here, we review these and other studies for a better understanding of the nature and origins of the PUE, in hopes of establishing a unified view of this important phenomenon. To this end, the phenomenological model based on the penultimate-unit stabilization hypothesis, which was proposed for propagation reactions,[4] will be extended to chain-transfer reactions. We suggest that the "implicit" PUE, which can be interpreted by the stabilization energy hypothesis, is a general phenomenon that governs not only the absolute rates of propagation and chain-transfer reactions in an explicit form but also the reactivity ratios and hence the copolymer composition in an implicit form.

Ito[6] and Bamford[7] have criticized our interpretation of recent experimental work. In this paper we address their criticisms.

Survey of Experimental Results

Propagation Rate Constants and Rate Constant Ratios. The penultimate model is characterized by eight rate constant k_{ijm}'s, with i, j, and m denoting the penultimate, the terminal, and the monomer unit, respectively (i, j, and m = 1 or 2). Two of them, k_{111} and k_{222}, refer to homopolymerizations, and the remaining six are properly given in the form of ratios r_{11}, r_{22}, r_{21}, r_{12}, s_1, and s_2:

$$r_{ii} = k_{iii}/k_{iij} \quad (i \neq j) \tag{1}$$

$$r_{ji} = k_{jii}/k_{jij} \quad (i \neq j) \tag{2}$$

$$s_i = k_{jii}/k_{iii} \quad (i \neq j) \tag{3}$$

(In many papers, including ours,[1-5,8,9] the penultimate-model reactivity ratios have been denoted as r_i and r_i' for r_{ii} and r_{ji}, respectively. This notation is confusing with the terminal-model reactivity ratio r_i's, so we have adopted the present notation.) The composition of the copolymer depends on r_{ii} and r_{ji} only, whereas the propagation rate constant k_p is a function of all r_{ii}, r_{ji}, s_i, and k_{iii}.[1]

Fukuda et al.[1] studied the bulk copolymerization of ST (1) and MMA (2) by the rotating-sector (RS) method and obtained the following results:

$$r_{11} = r_{21} = 0.523 \tag{4}$$

$$r_{22} = r_{12} = 0.460 \tag{5}$$

$$s_1 = 0.30 \text{ and } s_2 = 0.53 \tag{6}$$

That is, this system shows a strong PUE in k_p but no detectable effect in composition.

For a ST/MMA/toluene system, Fukuda et al.[2] obtained essentially the same results as those for the bulk system. Results of this solution experiment are evidence for the PUE being responsible for the failure of the terminal model.[2] Here, we start from this point, and therefore, the appropriateness of the penultimate model itself is not discussed in this paper.

Ma et al. observed a PUE in both k_p[8] and composition[9] for the bulk copolymerization of p-chlorostyrene (pCS) and methyl acrylate (MA). They recently found a PUE in k_p (but not in composition) for the ST/ethyl acrylate (EA) system[10a,b] and also for the MMA/vinyl acetate (VA) system.[10a,c] Ito and O'Driscoll,[11] who examined the bulk copolymerization of MMA with butyl methacrylate (BMA) by the spacially intermittent polymerization (SIP) method, observed no PUE in that system.

Davis et al.[12] studied the ST/MMA system by a novel method, the pulsed laser polymerization (PLP) technique[13] and confirmed the results of Fukuda et al. with what seems

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to be higher precision. For the same system, basically the same results were reported by Olaj et al.,[14a] who used another method akin to PLP. Many PLP data are being published by O'Driscoll et al., showing the presence of PUE in k_p (but not in composition) in many other systems.[15]

Chain-Transfer Constants and the Like. In the penultimate-model terminology, the chain-transfer constant, C, is given by[16]

$$C_{ijS} = \lambda_{ijS}/k_{ijj} \tag{7}$$

Here, λ_{ijS} is the rate constant of chain-transfer with i, j, and S denoting the penultimate unit, terminal unit, and transfer agent, respectively. Some years ago, Bamford and Basahel[16] studied the chain-transfer reactions in ST (1)/MMA (2) and ST (1)/MA (3) bulk copolymerizations. With 1-butanethiol (T) as the transfer agent, they found

$$C_{11T} = 22 \tag{8}$$

$$C_{21T} = 22 \tag{9}$$

$$C_{31T} = 20 \tag{10}$$

That is, the three transfer constants are about the same. With carbon tetrabromide (B) as the transfer agent, they found

$$C_{11B} = 337 \tag{11}$$

$$C_{21B} = 60 \tag{12}$$

$$C_{31B} = 302 \tag{13}$$

With this transfer agent, the transfer constant of the styryl radical with MMA as the penultimate unit is about $^1/_5$ that of the styryl radical with either ST or MA as the penultimate unit. This is a result that proves the participation of the penultimate unit in the chain-transfer reaction.

Ito[6] studied the copolymerization of MMA and acrylonitrile (AN) in the presence of ferric chloride (F) as retarder. In this system, the polymer radicals are deactivated mainly by the reaction with the retarder, and the radical-carrying fragment of the retarder does not reinitiate polymerization. Thus, the ratio $C'_{ijF} = \lambda'_{ijF}/k_{ijj}$, where λ'_{ijF} is the rate constant for the reaction with the retarder F, governs the overall copolymerization rate R_p. The experimental R_p data showed

$$C'_{11F} = C'_{21F} \tag{14}$$

$$C'_{22F} = C'_{12F} \tag{15}$$

That is, C' is independent of the penultimate unit in this system.

Termination Rate Constants. There has been controversy regarding the termination step of free-radical copolymerization.[1] Historically, this problem is not independent of the propagation step, so we briefly survey it. In the past, experimental data on the copolymerization velocity, R_p, were usually analyzed on the basis of the terminal-propagation model, and the results were often presented in terms of the cross-termination factor, ϕ, associated with the notion of chemically controlled termination[17]

$$\phi = k_{t12}/(k_{t1}k_{t2})^{1/2} \tag{16}$$

where k_{t12} is the termination rate constant between unlike terminal radicals, and the k_{ti}'s refer to the homopolymerizations. The factor ϕ should be close to unity unless cross-termination is chemically favored over homoterminations. The experimental values of ϕ calculated in this way were often composition-dependent and, in a great majority of systems, much larger than unity:[3,5] for example, the optimum values of ϕ to fit the R_p data were 13 for ST/MMA, 147 for pCS/MA, 1.1 for MMA/BMA, 35 for ST/EA, about 10 for MMA/VA, and 14 for MMA/AN.[5]

Recently, these systems, except for MMA/AN, were examined with the absolute values of k_t by the RS or the SIP method: ST/MMA,[1,2] pCS/MA,[8] MMA/BMA,[11] ST/EA,[10a,b] and MMA/VA.[10a,c] In all of these systems,[14b] the values of copolymerization k_t were always between k_{t1} and k_{t2}, showing no particular preference for cross-termination, which is evidence supporting the notion of diffusion-controlled termination.[11,18] Values of k_t for MMA/AN are still unknown, which will be discussed later.

Discussion

The experimental relations 8 and 9 for the ST (1)/MMA (2) system obtained by Bamford and Basahel[16] indicate the equality $C_{11T} = C_{21T}$ or, equivalently, $k_{211}/k_{111} = \lambda_{21T}/\lambda_{11T}$. Similarly, Ito's results for the MMA/AN system indicate the equality $k_{jii}/k_{iii} = \lambda'_{jiF}/\lambda'_{iiF}$ (eqs 14 and 15).[6] These results have been interpreted as evidence for zero penultimate-unit effect in those systems.[6,7,16] Below we will, as an alternative explanation, reinterpret these transfer results inclusively with other results in the light of penultimate-unit effects and discuss the possible origins of the effects.

Response to Bamford.[7] Equations 4, 6, 8, and 9 can be rearranged to[7]

$$s_1 = k_{211}/k_{111} = k_{212}/k_{112} = \lambda_{21T}/\lambda_{11T} = 0.30 \quad \text{(ST/MMA)} \tag{17}$$

Equation 17 indicates that the rate constants for the two addition reactions and one abstraction reaction of the polystyryl radical decrease by the same factor when the penultimate ST unit is replaced by an MMA unit. Equations 5, 6, 8, 9, 11, and 13 give more such relations:

$$s_2 = k_{122}/k_{222} = k_{121}/k_{221} = 0.53 \quad \text{(ST/MMA)} \tag{18}$$

$$s_1 = k_{311}/k_{111} = \lambda_{31T}/\lambda_{11T} = \lambda_{31B}/\lambda_{11B} \quad \text{(ST/MA)} \tag{19}$$

C_{21B} (eq 12) will be discussed later. A 10% allowance was made for the equalities in eq 19. The value of the s_1 for the (1)/(3) system (eq 19) is unknown. It is probably smaller than unity, as for the similar systems ST/MMA,[1] pCS/MA,[8] and ST/EA.[10a,b]

Bamford[7] has expressed doubt about the reality of eq 17 and similar relations, "based on the characters of the transition states in addition and abstraction reactions, which impose different electronic and steric demands on the reactants".[7] He suggests that if the penultimate unit has significant influence on the radical reactivity (viz., if $s_i \neq 1$), the proportionalities set out in the above equations are unlikely to hold. He concludes that the penultimate unit has negligible influence on radical reactivity, viz., $s_i = 1$.

We do not accept this conclusion because the proportionalities in question are based on experimental results that seem to be correct in essence. For the ST/MMA system, Davis et al.[12] have obtained $s_1 = 0.466$ and $s_2 = 0.175$ at 25 °C by the PLP method and Olaj et al.[14a] have obtained $s_1 = 0.30$ and $s_2 = 0.80$ at 25 °C and $s_1 = 0.37$ and $s_2 = 0.65$ at 40 °C by the modified PLP method. These values and our values (40 °C) given in eqs 17 and 18 may appear very different, raising doubt about the reliability of the measurements. However, the k_p vs composition curves obtained by the three independent groups by different methods are similar, with deviations of similar magnitude from the terminal-model curve (compare Figure 12 in ref 1, Figure 2 in ref 12, and Figure 1 in ref 14). At current levels of experimental accuracy, it seems difficult to establish both s_1 and s_2 with accuracy, even though the PLP method may be more promising than the classical methods. A small difference in k_p produces a large difference in s_1 and s_2 estimated by least-squares curve fitting.[5] We often encounter this difficulty when we try to evaluate two independent parameters on the basis of a single experimental curve of limited accuracy. To avoid the confusion that arises in this way, we have proposed analyzing experimental data by the assumption that $s_1 = s_2 \equiv s$ and have shown that most data can be described by the single parameter, s, as well as by the two parameters.[5] This parameter s may be understood as a certain mean of s_1 and s_2 and can be used as a measure for the PUE. $s = 1$ indicates no PUE, and $s \neq 1$ indicates nonzero PUE in all cases. The k_p data from the three groups mentioned above, when analyzed by this single-parameter treatment, give nearly the same answer in all cases: $s = 0.35 \pm 0.05$. Thus, the existence of a significant PUE in the ST/MMA system is supported by experimental evidence.

Origins of Penultimate-Unit Effects. Another point we raise here concerns the origin of the PUE. If the effect has its origin in electronic or steric interactions *between the penultimate unit and the monomer or the transfer agent* in the transition state, the effect would be different for different monomers and different transfer agents. Accordingly, the equalities among the rate constant ratios (eqs 17–19) would be unlikely to hold, as Bamford points out. Nevertheless, the experiments indicate the equalities. Perhaps the origin is different. In what follows, we suggest a possible origin.

We have postulated[4] that radical stabilization energies differ not only for different terminal units but also for different penultimate units for some reason or another (electronic or entropic) and have considered the reaction of the type

$$\sim\!\sim\mathrm{M}_i\mathrm{M}_j^{\bullet} + \mathrm{M}_m \xrightarrow{k_{ijm}} \sim\!\sim\mathrm{M}_j\mathrm{M}_m^{\bullet} \qquad (20)$$

The energy change, $\Delta H_{\mathrm{p},ijm}$, associated with this reaction may be given by

$$-\Delta H_{\mathrm{p},ijm} = -(\Delta H_\mathrm{p})_0 + U_{jm} - (U_{ij} + U_m) \qquad (21)$$

where $(\Delta H_\mathrm{p})_0$ is the energy change that would be observed in the absence of all substituent effects, and U_{ij} and U_m are the stabilization energies for radical ij and monomer m, respectively (i, j, and m = 1 or 2). A positive U corresponds to stabilization. A stabilized radical would be slow to react, and a reaction leading to stabilization would be fast. That is, a correlation between s_i's and r_i's is suggested. If we specifically adopt the Evans–Polanyi rule,[19] which states linearity between the activation energy, E_p, and the evolved heat, $-\Delta H_\mathrm{p}$, i.e.

$$E_\mathrm{p} = (E_\mathrm{p})_0 - \alpha(-\Delta H_\mathrm{p}) \qquad (22)$$

where $(E_\mathrm{p})_0$ and α are constants, and if we assume zero PUE for the frequency factors (see below), then we obtain[4]

$$r_{ii} = r_{ji}\ (=r_i) \qquad (i \neq j) \qquad (23)$$

$$r_1 r_2 = s_1 s_2 \qquad (24)$$

and

$$s_i = \exp[-(U_{ji} - U_{ii})(\alpha/RT)] \qquad (i \neq j) \qquad (25)$$

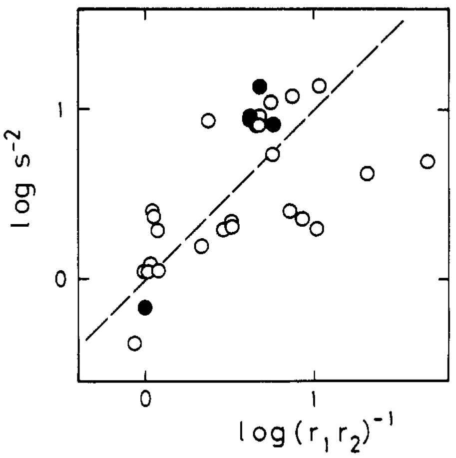

Figure 1. Plot of s^{-2} vs $(r_1r_2)^{-1}$ for various copolymerization systems.[5] Open circles were obtained from the R_p data with the assumption of $\phi = 1$. Closed circles were obtained from the k_p data. The broken line represents eq 24. In this analysis, it is assumed that $s_1 = s_2$ (=s). See the text and ref 5 for details.

Now we extend this model to the transfer reaction of the type

$$\sim\!\sim\mathrm{M}_i\mathrm{M}_j^{\bullet} + \mathrm{S} \xrightarrow{\lambda_{ijS}} \sim\!\sim\mathrm{M}_j\mathrm{X} + \mathrm{A}^{\bullet} \qquad (26)$$

where S (=AX) denotes the transfer agent. Within the framework of this model, one would expect that the ratio t_i

$$t_i = \lambda_{jiS}/\lambda_{iiS} \qquad (i \neq j) \qquad (27)$$

is a function only of U_{ji} and U_{ii}, as s_i is. In fact, similar assumptions to those for the propagation reaction lead to

$$t_i = \exp[-(U_{ji} - U_{ii})(\beta/RT)] \qquad (i \neq j) \qquad (28)$$

where β is the Evans–Polanyi coefficient analogous to the α in eq 22.

The Evans–Polanyi rule requires similarity of potential energy curves of closely similar reactions.[19] This requirement seems to be nearly ideally met in our penultimate-unit stabilization arguments, because we are questioning only those relative changes caused by replacement of the penultimate monomer with the other kind of monomer. The associated change in the shape of the potential energy curve should be minor, for we have ruled out possible interactions between the penultimate unit and the monomer (see above). In a sense, ruling out such interactions may be equivalent to assuming similarity of the potential energy curves. Moreover, the change in stabilization energy itself appears to be generally small. As will be described later, the value of s is estimated to range from 1 down to about 0.3 in most systems (cf. Figure 1). For example, the ST/MMA system has an s value of about 0.35 (see above), the associated activation energy being only about 0.6 kcal/mol. Thus, the Evans–Polanyi rule should be a particularly good approximation in our problem, for reactions of the same type.

We now discuss the propriety of this "stabilization energy model" (the SE model) in light of experimental results and consider some possible origins of PUE.

(i) According to the penultimate model, static or structural properties of copolymers such as composition and sequence distribution depend only on r_{ij}'s.[1,4,9,20] Equation 23 indicates that the PUE of the stabilization energetic origin, if any is present, does *not explicitly* appear in composition. This is consistent with composition curves of most systems being described well by the terminal model.

(ii) $r_1r_2 < 1$ in most systems.[21] With this applied to eq 24, we have an indication that the PUE (of the assumed origin) is a general rule rather than an exception; that is, $s_1s_2 < 1$ in most systems. Viewed differently, eq 24 indicates that the products r_1r_2 and s_1s_2 are governed by the same effect. It follows that the composition is under an *implicit* influence of the PUE. The available k_p data,[1,2,8,10-12,14a] though still few, all suggest the reality of eq 24. For example, the ST/MMA system ($r_1r_2 = 0.24$) has a significant PUE ($s_1s_2 = 0.16$),[1] whereas the MMA/BMA system ($r_1r_2 = 1.00$) does not.[11] It is strongly requested that more experiments be done to provide accurate k_p data to test the present ideas more extensively. (Notably, many PLP data are being provided by the Canadian group,[15] which are apparently in support of eq 24.)

The reality of eq 24 is also suggested by the raw data of polymerization rate R_p amply available in the literature. As already noted, the available k_t data indicate that the termination step is diffusion-controlled. The chemical model with $\phi = 1$ is numerically close to the diffusion model, so it is reasonable to adopt the $\phi = 1$ model, for simplicity, in the analysis of the R_p vs composition curves for approximate information on the propagation step. The results of such an analysis[5] are given in Figure 1, which shows positive correlation between r_1r_2 and s^2. (This analysis assumes that $s_1 = s_2 = s$ for the reason mentioned before. See ref 5 for more details.)

(iii) For the chain-transfer reaction, the combination of eqs 25 and 28 gives

$$k_{jii}/k_{iii} = \gamma(\lambda_{jiS}/\lambda_{iiS}) \qquad (i \neq j) \tag{29}$$

$$\gamma = \exp[(\beta - \alpha)(U_{ji} - U_{ii})/RT] \qquad (i \neq j) \tag{30}$$

Because the coefficients α and β concern different types of reactions, we cannot expect their general equality. From theoretical considerations, Evans et al.[22] suggested a value of about 0.4 for α. Kagiya and Sumida[23] have obtained $\alpha = 0.35$ on the basis of experimental data. Semenov[19c,24] suggested a value of 0.25 for reactions of the type

$$A^\bullet + BX \rightarrow AX + B^\bullet \tag{31}$$

These results suggest that $|\beta - \alpha|$ is small, if not zero, and hence γ may not be very far from unity unless $U_{ji} - U_{ii}$ is large. If we assume that $\alpha = 0.35$ and $\beta = 0.25$ and solve eqs 25 and 30 for γ, we have $\gamma = 0.7$ for the ST/MMA system with $s_1 = 0.30$ (eq 17). This magnitude of γ seems compatible with the experimental results, which are that $\gamma \cong 1$ (eqs 17 and 19).

(iv) The transfer reaction of the radical $\sim$MMA–ST$^\bullet$ to carbon tetrabromide (B) appears different from that above. Equations 11 and 12 are rearranged to give

$$k_{211}/k_{111} = (337/60)(\lambda_{21B}/\lambda_{11B}) \tag{32}$$

That is, γ is as large as 5.6 in this reaction. This magnitude of γ is outside the scope of the SE model and suggests a PUE of different origin. Bamford and Basahel suggested a steric effect caused by close contacts in the transition state between the bulky bromine atom and the α-methyl group of the penultimate MMA unit.[25] This system is the only known example that exhibits an *explicit* PUE in chain transfer and similar reactions, including the retardation reaction to be discussed later. In propagation reactions, several systems have a composition curve that cannot be described by the terminal model. Many authors attribute this phenomenon to a PUE.[9,26,27] If this is correct, we have $r_{ii} \neq r_{ji}$, an explicit PUE. The ST/AN system is one example.[26,27] A dipolar repulsive interaction in the transition state between the cyano groups on the monomer and the penultimate unit was suggested as a possible origin of PUE in this system.[27]

The above suggests that there are two PUEs of different origin. One type is the implicit PUE (IPUE), which manifests itself only in absolute values of the rate constants k_p and λ or, equivalently, s_i and t_i. The IPUE is characterized by the equalities or near equalities of r_{ii} with r_{ji} and s_i with t_i. The other type is the explicit PUE (EPUE), which manifests itself in the inequalities of r_{ii} with r_{ji} or s_i with t_i (or both) and in absolute values of the rate constants.

That our SE model is consistent in every respect with the experimental results of the IPUE type suggests that a possible origin of IPUE is the stabilization (or destabilization) of the radical by the penultimate group. The correlation between r_1r_2 and s_1s_2 suggested by the model and experiments indicates that IPUE is a very general phenomenon. A possible origin of EPUE may be a specific interaction, electronic or steric, between the penultimate group and the monomer or the transfer agent in the transition state. Just as the terminal model, even though formally valid to describe the composition of the IPUE system, fails to describe the absolute rate constants of those systems, the penultimate model, while valid to describe the composition and the transfer constant C of the EPUE systems, would probably fail to describe the absolute rate constants of the same systems. Introduction of the antepenultimate or a higher order model would be necessary for adequate description of EPUE systems. This discussion suggests that EPUE is a higher order effect than IPUE and hence a less general phenomenon. Few systems of the EPUE type are known actually.

Response to Ito.[6] On the basis of the results shown in eqs 14 and 15, Ito concludes that the propagation step of the MMA/AN system has no "abnormality" and that it conforms to the terminal model.[6] Clearly, his experiments showed the equalities

$$s_i = k_{jii}/k_{iii} = \lambda'_{jiF}/\lambda'_{iiF} \qquad (i \neq j) \tag{33}$$

but not the equality of s_i to unity. Such experiments provide no information per se on absolute values of k_p or s_i (see also ref 28). The equalities themselves are not necessarily in conflict with the IPUE hypothesis for this system, as already suggested.

The s_i values of this system are not known yet. We would expect them to be smaller than unity, for two unrelated reasons. First, this system has a value of r_1r_2 much smaller than unity ($r_1r_2 = 0.18$). Equation 24 with this value suggests that there is a significant IPUE. Second, if we simulate the R_p curve of the MMA/AN system *with no retarder*[29] by assuming the $\phi = 1$ model for the termination step (see above), we obtain a value of s ($= s_1 = s_2$) of 0.3 (Figure 2). If instead we simulate the same data by assuming the terminal-propagation model ($s_i = 1$), as was done by Ito,[6] we obtain $\phi = 14$ (Figure 2). Then, once again, we are confronted with the classical paradox as to the origin of large ϕ.[3] Thus, our explanation is consistent not only with the IPUE arguments but also with the current notion of diffusion-controlled termination. Ito's explanation is based on the notion of chemically

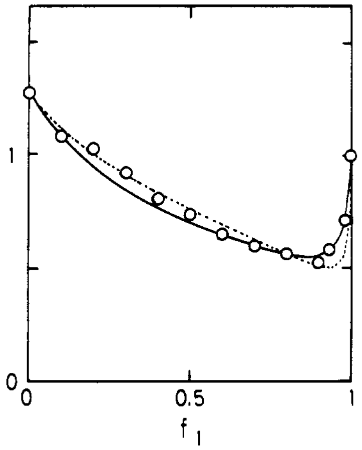

Figure 2. Plot of R_p/R_{p1} vs composition f_1 for AN (1)/MMA (2) copolymerization, with experimental data (circles) cited from ref 29. The solid curve was calculated with the penultimate model with s ($=s_1 = s_2$) = 0.3, and the dotted curve was calculated with the Walling equation[17] with ϕ = 14. The initiation rate was assumed to be constant.

controlled termination, which is probably mistaken in light of the evidence in support of the diffusion idea (see above and also ref 3). A final conclusion should, however, be provided by the absolute measurements of k_p.

Supplementary Comments. We have suggested that radical stabilization by the penultimate unit is a possible origin of IPUE. The recent ESR studies by Sato et al.[30,31] on some model systems seem to support this idea, even though their systems may not be equivalent to the usual copolymerization systems.

The product r_1r_2 is a measure for the 1–2 alternating bonds in the copolymer chain. Here, we suggest that r_1r_2 depends on IPUE (cf. eq 24). This implies a new clue for an understanding of the general alternating tendency ($r_1r_2 < 1$), which is generally believed to be related with the polarities of *the radical and the monomer* but has never been interpreted with theoretical rigor in the framework of the terminal model (see, e.g., the *Q*–*e* scheme[21,32] and the criticisms of it[33]). The polarities of *the terminal and penultimate groups* may have something to do with the radical stabilization.

The mechanism of radical stabilization by the penultimate group is not obvious but might be clarified by advanced quantum chemical studies. Using the method of ab initio unrestricted Hartree–Fock molecular orbital, Imoto et al.[34,35] succeeded in perhaps the first a priori interpretation of the experimentally observed activation energies of common homopropagation reactions. They noted, however, that similar calculations with the same model, which corresponds to the terminal model, failed to explain the cross-propagations, i.e., copolymerizations.[35] Imoto suggests the necessity of incorporation of a penultimate unit into their model.[35]

Finally, we note the important point already raised by Bamford[16] and Imoto[35] that homopolymerizations should not be considered to be irrelevant to PUEs.

Conclusions

The general existence of the PUE in free-radical copolymerization is well evidenced by the recent studies. Two types of PUE exist. One type, the IPUE, is manifested only in absolute values of the rate constants of propagation, k_p, and chain-transfer reaction, λ, and is characterized by the equalities or near equalities of r_{ii} with r_{ji} and of s_i with t_i. The other type, the EPUE, is manifested in the inequalities of r_{ii} with r_{ji} and/or of s_i with t_i as well as in k_p and λ.

A possible origin of IPUE is the stabilization of the radical by the penultimate group. The phenomenological model based on this idea (the SE model) is consistent in every respect with the available experimental data of the IPUE type. In particular, the SE model and experiments suggest a close correlation between r_1r_2 and s_1s_2. This correlation indicates that r_1r_2 may be of the IPUE origin and that the IPUE is no less a general rule than that $r_1r_2 < 1$ is.

The EPUE is a less general phenomenon. The origin of the EPUE may be a specific interaction between *the penultimate unit and the monomer* (or the transfer agent). The EPUE would be adequately described by the antepenultimate or a higher order model.

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