Notes

Reevaluation of the Propagation Rate Constant in the Radiation-Induced Cationic Polymerization of Isobutylene in Solution

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Despite considerable work extending over the past 60 years using a variety of approaches,[1] there is still no general agreement as to the absolute magnitude of bimolecular propagation rate constants (k_p) in carbocationic polymerization. This unsatisfactory situation has prompted several recent reviews[2−7] and is well illustrated by the range of values previously reported for k_p in the polymerization of isobutylene (Table 1).[8−14] For this monomer, a particular concern is the large gap that exists between the set of values[8−11] above 1.0×10^8 M^{-1} s^{-1} and the remainder clustered around 1.0×10^4 M^{-1} s^{-1}.[12−14] The situation is further clouded by the fact that results at both extremes have been reported by the use of the same high-energy radiation method based on the generation of free ions. Thus, while Taylor and Williams[8] obtained 1.5×10^8 M^{-1} s^{-1} for the bulk polymerization of isobutylene, more recently Plesch[14,15] has calculated a value of 9.1×10^3 M^{-1} s^{-1} for the solution polymerization in methylene chloride based on the results of Hayashi, Okamura, and their co-workers.[16]

Plesch[14] has attributed this discrepancy in the derived k_p values to a fundamental difference in propagation mechanisms, arguing that there are both unimolecular and bimolecular modes of propagation. He asserts that the former predominates at high monomer concentrations,[15] as exemplified by the bulk system with a unimolecular rate constant $k_p^1 = k_p[\mathrm{M}]_{\mathrm{bulk}}$, whereas the bimolecular mode is said to apply mainly for dilute solutions. Even so, it is not inherently obvious why there should be such a pronounced falloff in the *apparent (overall)* second-order rate constant $k_p^{\mathrm{app}} = R_p/\{[\mathrm{M}]\sum_i[\mathrm{M}^+]\}$ and that of the related turnover frequency ($k_p^{\mathrm{app}}[\mathrm{M}] = R_p/\sum_i[\mathrm{M}^+]$) upon monomer dilution away from the bulk system. Moreover, this hypothesis of dieidic propagation[14] with such very different time scales for single monomer addition implies that the experimental rate of polymerization should fall precipitously (by as much as a factor of 10^4!) with decreasing monomer concentration [M] in the region defined by the limits $[\mathrm{M}]_{\mathrm{bulk}} > [\mathrm{M}] > \sim 1$ M. Such a huge deceleration in rate does not appear to have been observed in practice, however, casting doubt on this general interpretation in terms of dieidic propagation. The purpose of the present note is to reexamine the basis for the allegedly low value of the bimolecular rate constant k_p derived from an analysis of the radiation-induced polymerization of isobutylene in methylene chloride solution.[14,16] In the interest of conciseness and clarity, the symbols and notation used in the original paper[14] will be retained as far as possible.

The essential step in Plesch's derivation[14] of the rate constant k_p^+ from the results of the Kyoto group[16] is to combine a knowledge of the rate R as a function of monomer concentration m (eq 1) with the slope S (eq 2) of the Mayo plot for 1/DP vs $1/m$. By assuming $c_+ = c_- = c$ and eliminating c, the total free ion concentration of either sign, from eqs 1 and 2, a simple expression is obtained (eq 3) for k_p^+ in terms of an assumed value for k_t and the experimental results R/m and S.[14] At first sight, this is an attractive formulation since it appears to side step the problem of obtaining c and the rate of initiation, R_i. However, it is shown below that exactly the same numerical result for k_p^+ can be obtained through the explicit consideration of c and R_i.

$$R = k_p^{\,+} m c_+ \tag{1}$$

$$S = k_t c_- / k_p^{\,+} \tag{2}$$

$$k_p^{\,+} = \{(R/m)(k_t/S)\}^{1/2} \tag{3}$$

Since the validity of eq 3 depends on the assumption that the free ion concentration c is the same in eqs 1 and 2, it is important to stress that this condition $c_+ = c_- = c$ applies only when the termination of the reaction chains occurs solely by the homogeneous second-order recombination of propagating cations and negative ions with the rate constant k_t. It follows that by equalizing the rates of initiation R_i and termination R_t, we have $R_i = R_t = k_t c^2$. Hence $c = (R_i/k_t)^{1/2}$, and according to eqs 1 and 2, R and S are then given by eqs 4 and 5. Also, with this definition of c, R_i can be related to R/m and S (eq 6) by eliminating k_p^+ from eqs 1 and 2. Because of this connecting relation, the same value of k_p^+ will necessarily be obtained from the R/m, S, and k_t parameters using either eq 4 or eq 5.

$$R = k_p^{\,+} m (R_i/k_t)^{1/2} \tag{4}$$

$$S = (R_i k_t)^{1/2} / k_p^{\,+} \tag{5}$$

$$R/m = k_p^{\,+} c = k_t c^2/S = R_i/S \tag{6}$$

It will now be shown that the k_p^+ value obtained from eq 3 is the same as that derived from the so-called Hayashi−Williams equation[4,17,18] (eq 4) which predicts that in the limit of no impurity termination the rate will assume a maximum value and depend on the square root of the rate of initiation R_i and therefore also of the

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Table 1. Reported Propagation Rate Constants in the Carbocationic Polymerization of Isobutylene

catalyst/carbocation source	solvent	T/K	k_p/ M^{-1} s^{-1}	reference
γ radiation	bulk monomer	195−273	1.5×10^8	8
$TiCl_4$	n-hexane	195	$(6 \pm 2) \times 10^8$	9
$AlCl_3$	CH_2Cl_2	195		
$TiCl_4$	hexanes/CH_3Cl (60/40)	193	$(6.5 \pm 3.5) \times 10^8$	10
$TiCl_4$, Me_2AlCl, BCl_3	hexanes/CH_3Cl (60/40)	193−223	$(4.6 \pm 1.1) \times 10^8$	11
$AlCl_3/TiCl_4$	n-heptane	259	0.6×10^4	12
Et_2AlCl/Cl_2	CH_3Cl	225	1.2×10^4	13
γ radiation	CH_2Cl_2	195	0.91×10^4	14, 16
γ radiation	CH_2Cl_2	195	1.8×10^8	this work, 16

radiation dose rate.[18,19] The experimental parameters of $R/m = 7.5 \times 10^{-7}$ s^{-1} and $S = 1.82 \times 10^{-3}$ M yield a value for R_i through eq 6 of 1.37×10^{-9} M s^{-1}, and substitution in either eq 4 or eq 5 along with the previously assumed value of $k_t = 2 \times 10^{11}$ M^{-1} s^{-1} leads to $k_p^+ = 0.91 \times 10^4$ M^{-1} s^{-1}, which is identical with the k_p^+ value reported by Plesch.[14] Accordingly, it is clear that this value for k_p^+ is in fact predicated on a single termination step that occurs only as a result of ion recombination with a mean lifetime, τ_i, for the propagating ion given by $\tau_i = c/k_tc^2 = 1/k_tc = 1/(R_ik_t)^{1/2}$.

We now turn to consider the all-too-common alternative case in radiation-induced ionic polymerization where there is predominant termination of the propagating cations by nucleophilic impurities, as modeled by studies with added water,[20] ammonia, and amines.[21] This leads to the corresponding eqs 7 and 8 for R and S, where [X] is the concentration of the impurity and k_{tx} is the rate constant for the termination reaction of the propagating ion with this impurity.[18,19,22] It is not possible in this case to obtain k_p^+ directly from R and S as in eq 3 or through eqs 4−6, however, and a knowledge of k_{tx}[X] is needed to use eqs 7 and 8; this issue is addressed below.

$$R = R_ik_p^+m/\{k_{tx}[X]\} \qquad (7)$$

$$S = k_{tx}[X]/k_p^+ \qquad (8)$$

Comparison of eqs 4 and 7 reveals that the power dependence of R upon R_i or dose rate changes from 0.5 to 1.0 depending on the main termination step.[19] Actually, eqs 4 and 7 are the limiting forms of the more general equation (eq 9) for R that takes into account both termination steps.[18,19] Similarly, the general expression for S from the Mayo equation[23] takes the form of eq 10.

$$R = R_ik_p^+m/\{k_{tx}[X] + (R_ik_t)^{1/2}\} \qquad (9)$$

$$S = \{k_{tx}[X] + (R_ik_t)^{1/2}\}/k_p^+ \qquad (10)$$

By eliminating either k_{tx}[X] from eqs 7 and 8 or of the combined term $\{k_{tx}[X] + (R_ik_t)^{1/2}\}$ from eqs 9 and 10, we regenerate $R/m = R_i/S$ (eq 5), so that this relation is quite independent of the termination step(s). Interestingly, the R_i value of 1.4×10^{-9} M s^{-1} obtained in this way from the experimental results compares very closely with the value of 1.0×10^{-9} M s^{-1} calculated directly from the quoted dose rate of 2.7×10^4 rad/h (4.68×10^{14} eV g^{-1} s^{-1}) using an estimated G_i value for free ion initiation of 0.2 ions/100 eV.[18,19] This agreement with respect to the expected order of magnitude for R_i certainly lends confidence to the experimental values of R/m and S. The crucial question now remains, however, as to which termination step will dominate in the polymerization.

A quick guide to recognizing which of the limiting forms (either eqs 4 and 5 or eqs 7 and 8) will apply is to compare the value of $(R_ik_t)^{1/2}$ with estimates of k_{tx}[X] since both terms are present in the denominator of eq 9 and the numerator of eq 10. Using the previous values of 1.4×10^{-9} M s^{-1} and 2.0×10^{11} M^{-1} s^{-1} for R_i and k_t, respectively, we obtain $(R_ik_t)^{1/2} = \tau_i^{-1} = 1.7 \times 10^1$ s^{-1}. Taking k_{tx} as having a diffusion-controlled value on the order of 10^{10} M^{-1} s^{-1}, it follows that termination by a highly reactive impurity in a concentration as low as 10^{-8} M will already compete very favorably with that from ion recombination ($k_{tx}[X] > (R_ik_t)^{1/2}$) at the dose rate of interest. It is not surprising, therefore, that radiation-induced ionic polymerization is extremely sensitive to minute concentrations of water[20] and other nucleophiles.[21] As a corollary, it is understandable that the highest attainable rates of ionic polymerization with close to the predicted half-power dependence on dose rate (eq 4) have only been achieved through exhaustive drying procedures.[8,18a,22]

We are now in a position to review the experimental work[16] in more detail, and there are two considerations that clearly demonstrate that eqs 7 and 8 rather than eqs 1−5 apply to the R/m and S parameters used by Plesch.[14] First, R is shown in Figure 3 of the Kyoto study[16] to be directly proportional to the first power rather than the half power of dose rate. As has been demonstrated repeatedly, a first-power dependence connotes predominant termination by impurities according to eq 7,[18,19,22] with rates that are considerably lower than those obtained with monomer of higher purity and dryness. Conversely, the observation of a nearly square-root dependence of R on the radiation intensity with the accompanying high "ceiling" rates is the sine qua non for the use of eqs 1−5 and provides the best experimental criterion for the absolute purity of a monomer solution in radiation-induced ionic polymerization.[8,17−19,22] Second, the calculations presented below reveal that the value of R obtained for the associated bulk polymerization of isobutylene in the cited study[16] is at least a factor of 10^4 lower than would be expected if termination were to occur by ionic recombination rather than by impurities. We first proceed by means of eqs 4 and 9 to derive eq 11 which relates the ratio of polymerization rates in the absence (R_0) and presence (R_x) of impurities to the $\{k_{tx}[X]/(R_ik_t)^{1/2}\}$ quotient.

$$R_0/R_x = \{k_{tx}[X] + (R_ik_t)^{1/2}\}/(R_ik_t)^{1/2} = 1 + \{k_{tx}[X]/(R_ik_t)^{1/2}\} \qquad (11)$$

From wide experience in the practice of radiation-induced ionic polymerization, it is reasonable to assume that the level of impurity contamination in the assembled apparatus used for sample preparation will remain similar throughout a given set of experiments. Accordingly, since $(R_ik_t)^{1/2}$ is already known (1.7×10^1 s^{-1}), we can use eq 11 to estimate k_{tx}[X] in these experiments by the Kyoto group[16] through a comparison of their reference value for R_x in the bulk monomer with the benchmark or ceiling value for R_0 obtained at the same dose rate under the most stringent conditions of drying where the rate approaches the limiting value[8] according to eq 4. Significantly, it is found that R_x from Figure 4 of ref 16 is only 1.67×10^{-6} M s^{-1} at a dose rate of 2.7×10^4 rad/h (4.68×10^{14} eV g^{-1} s^{-1}), whereas the corresponding R_0 interpolated from the data of ref 8 has the much higher value of 3.25×10^{-2} M s^{-1}. Thus, $R_0/R_x \approx 2 \times 10^4$, and hence from eq 11, $k_{tx}[X] \approx 3.4 \times 10^5$ s^{-1}. Evidently, a severe inequality $k_{tx}[X] \gg (R_ik_t)^{1/2}$ applies to the results of these experiments,[16] and the recalculation of k_p^+ by eq 9 with this k_{tx}[X] value of 3.4×10^5 s^{-1} leads to a revised figure of 1.8×10^8 M^{-1} s^{-1}. The order of magnitude of k_p^+ obtained in this way is not very sensitive to the scatter in the experimental rate data,[8,16] and in particular, there is little likelihood that the k_p^+ value has been seriously overestimated by this procedure.

In summary, it is shown that the low value of the rate constant $k_p^+ = 0.9 \times 10^4$ M^{-1} s^{-1} reported by Plesch[14] rests on the assumption[26] that the lifetime of the propagating ion is governed by the rate of ionic recombination with the value $\tau_i = (R_ik_t)^{-1/2} = 5.9 \times 10^{-2}$ s, whereas under the conditions that prevailed in the Kyoto experiments,[16] the true *propagating* lifetime is determined by reaction with impurities and is given by $\tau_x = \{k_{tx}[X]\}^{-1} = 2.9 \times 10^{-6}$ s. Consequently, the calculation of the rate constant from the observed rate data is seriously underestimated by the ratio of τ_i to τ_x,[25] which is on the order of 10^4. The analysis given in the present paper leads to a much higher revised value of 1.8×10^8 M^{-1} s^{-1} for k_p^+ in the solution polymerization of isobutylene. This result is in essential agreement with the previous determination of 1.5×10^8 M^{-1} s^{-1} obtained under the most stringent anhydrous conditions in the bulk system[26] with high rates that conformed closely to the Hayashi–Williams relation. The level of consistency between the two results[27] is remarkable considering that the very different limiting forms of eq 9 have been used in these situations. Therefore, this additional test case provides further support for the kinetic model[18,19] that has been widely employed with considerable success in analyzing the results of radiation-induced ionic polymerization.[8,18,19 22]

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References and Notes

(1) (a) Evans, A. G.; Polanyi, M. *Nature (London)* **1943**, *152*, 738; *J. Chem. Soc.* **1947**, 252. (b) Evans, A. G.; Holden, D.; Plesch, P. H.; Polanyi, M.; Skinner, H. A.; Weinberger, M. A. *Nature (London)* **1946**, *157*, 102. (c) Evans, A. G.; Meadows, G. W. *Trans. Faraday Soc.* **1950**, *46*, 327. (d) Pepper, D. C. *Sci. Proc. R. Dublin Soc.* **1951**, *25*, 131–163. (e) *Cationic Polymerisation and Related Complexes*; Plesch, P. H., Ed.; Heffer: Cambridge, England, 1953. (f) Plesch, P. H. In *The Chemistry of Cationic Polymerization*; Plesch, P. H., Ed.; Pergamon Press Ltd.: Oxford, England, 1963; pp 141–208. (g) Pepper, D. C. *Makromol. Chem* **1974**, *175*, 1077; *J. Polym. Sci. Symp.* **1975**, *50*, 51. (h) Kennedy, J. P. *Cationic Polymerization of Olefins: A Critical Inventory*; Wiley-Interscience: New York, 1975; pp 86–136. (i) Ledwith, A.; Sherrington, D. C. In *Comprehensive Chemical Kinetics*; Bamford, C. H., Tipper, C. F. H., Eds.; Elsevier: Amsterdam, 1975; Vol. 15, Chapter 2, pp 67–131. (j) Kennedy, J. P.; Marechal, E. *Carbocationic Polymerization*; Wiley-Interscience: New York, 1982. (k) *Cationic Polymerization and Related Processes*; Goethals, E. J., Ed.; Academic Press: London, 1984. (l) Plesch, P. H. *Prog. React. Kinet.* **1993**, *18*, 1–62. (m) Matyjaszewski, K.; Pugh, C. In *Cationic Polymerization: Mechanisms, Synthesis, and Applications*; Matyjaszewski, K., Ed.: Decker: New York, 1996; p 204. (n) *Cationic Polymerization*; ACS Symposium Series No. 665; Faust, R., Shaffer, T. D., Eds.; American Chemical Society: Washington, DC, 1997. (o) Plesch, P. H. *Developments in the Theory of Cationoid Polymerisations (1946–2001)*; Rapra Technology Ltd.: Shawbury, Shrewsbury, England, 2002. (p) Odian, G. *Principles of Polymerization*, 4th ed.; Wiley-Interscience: New York, 2004; pp 392–397.

(2) (a) Mayr, H.; Patz, M. *Macromol. Symp.* **1996**, *107*, 99–110 *(IUPAC International Symposium on Ionic Polymerisation, 1995).* (b) Mayr, H.; Schimmel, H.; Kobayashi, S.; Kotani, M.; Prabakaran, T. R. *Macromolecules* **2002**, *35*, 4611–4615.

(3) Mayr, H.; Roth, M.; Lang, G. In *Cationic Polymerization*; ACS Symposium Series No. 665; Faust, R., Shaffer, T. D., Eds.; American Chemical Society: Washington, DC, 1997; Chapter 3, pp 25–40.

(4) Bywater, S. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 4467–4477.

(5) Plesch, P. H. *Macromolecules* **2001**, *34*, 1143–1147.

(6) Sigwalt, P.; Moreau, M.; Polton, A. *Macromol. Symp.* **2002**, *183*, 35–42 *(IUPAC International Symposium on Ionic Polymerisation, 2001).*

(7) Plesch, P. H. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 2537–2544.

(8) Taylor, R. B.; Williams, F. *J. Am. Chem. Soc.* **1969**, *91*, 3728; **1967**, *89*, 6539.

(9) Roth, M.; Mayr, H. *Macromolecules* **1996**, *29*, 6104.

(10) Schlaad, H.; Kwon, Y.; Sipos, L.; Faust, R.; Charleux, B. *Macromolecules* **2000**, *33*, 8225.

(11) Sipos, L.; De, P.; Faust, R. *Macromolecules* **2003**, *36*, 8282.

(12) Marek, M.; Chmelir, M. *J. Polym. Sci.* **1968**, *177*, 3225.

(13) Magagnini, P. L.; Cesca, S.; Giusti, P.; Priola, A.; DiMaina, M. *Makromol. Chem.* **1977**, *178*, 2235.

(14) Plesch, P. H. *Philos. Trans. R. Soc.* **1993**, *A342*, 469.

(15) The main argument[14] for the unimolecular rate-determining mode in the radiation-induced cationic polymerization of bulk monomers is that the reaction rate appears to be of zero order with respect to monomer concentration up to fairly high conversions. However, in a recent comprehensive review of propagation rate constants in vinyl polymerization, Bywater[4] has pointed out that Plesch's evidence is not entirely convincing since it is difficult to distinguish between linear and curved plots of conversion against time (or against the equivalent radiation dose at a constant dose rate) up to 20% conversion; moreover, truly reliable data bearing on this question is said to be scanty.[4]

(16) Ueno, K.; Yamaoka, H.; Hayashi, K.; Okamura, S. *Int. J. Appl. Radiat. Isot.* **1966**, *17*, 595.

(17) (a) Szwarc, M.; van Beylen, M. *Ionic Polymerization and Living Polymers*; Chapman and Hall: London, 1993; pp 264–270. (b) Szwarc, M. *Ionic Polymerization Fundamentals*; Hanser: Munich, 1996; pp 76–79. (c) Stannett, V. T.; Silverman, J.; Garnett, J. L. In *Comprehensive Polymer Science*; Allen, G., Ed.; Pergamon: Oxford, 1989; Vol. 4, Chapter 19, pp 323–327.

(18) (a) Williams, F.; Hayashi, Ka; Ueno, K.; Hayashi, K.; Okamura, S. *Trans. Faraday Soc.* **1967**, *63*, 1501. (b) *C&E News* **1966**, *44*, (May 23) pp 48–49. (c) Bonin, M. A.; Busler, W. R.; Williams, F. *J. Am. Chem. Soc.* **1965**, *87*, 199. (d) Williams, F. *Discuss. Faraday Soc.* **1963**, *36*, 254–256.

(19) (a) Williams, F. In *Fundamental Processes in Radiation Chemistry*; Ausloos, P., Ed.; Wiley-Interscience: New York, 1968; Chapter 8, pp 515–598. (b) Williams, F. *J. Macromol. Sci., Chem.* **1972**, *A6*, 919–949.

(20) (a) Bates, T. H.; Best, J. V. F.; Williams, F. *Nature (London)* **1960**, *188*, 469. (b) Bates, T. H.; Williams, F. *Nature (London)* **1960**, *187*, 665. (c) Brownstein, S.; Bywater, S.; Worsfold, D. J. *Makromol. Chem.* **1961**, *48*, 127. (d) Best, J. V. F.; Bates, T. H.; Williams, F. *Trans. Faraday Soc.* **1962**, *58*, 192. (e) Ueno, K.; Hayashi, K.; Okamura, S. *Polymer* **1966**, *7*, 431. (f) Huang, R. Y. M.; Westlake, J. F. *J. Polym. Sci., Part A1* **1970**, *8*, 49. (g) Huang, R. Y. M.; Westlake, J. F. *J. Polym. Sci., Part B* **1969**, *7*, 713.

(21) (a) Bonin, M. A.; Busler, W. R.; Williams, F. *J. Am. Chem. Soc.* **1962**, *84*, 355. (b) Hubmann, E.; Taylor, R. B.; Williams,

F. *Trans. Faraday Soc.* **1966**, *62*, 88. (c) Cordischi, D.; Mele, A.; Rufo, R. *Trans. Faraday Soc.* **1968**, *64*, 2794.

(22) Exponents close to the limiting half-power dependence of R_0 on the dose rate predicted by the Hayashi–Williams equation[17–19] have also been obtained with styrene,[18a] α-methylstyrene,[18a] isobutyl vinyl ether,[18a] and several other monomers. Some leading references are: (a) Naylor, D. M.; Stannett, V. T.; Deffieux, A.; Sigwalt, P. *Polymer* **1990**, *31*, 954. (b) Bonin, M. A.; Calvert, M. L.; Miller, W. L.; Williams, F. *J. Polym. Sci., Part B* **1964**, *2*, 143. (c) Metz, D. J. *Adv. Chem. Ser.* **1966**, *66*, 170. (d) Du Plessis, T. A.; Stannett, V. T.; Goineau, A. M. *J. Polym. Sci., Part A1* **1974**, *12*, 2457. (e) Potter, R. C.; Metz, D. J. *J. Polym. Sci., Part A1* **1971**, *9*, 441. (f) Potter, R. C.; Johnson, C. L.; Metz, D. J.; Bretton, R. H. *J. Polym. Sci., Part A1* **1966**, *4*, 419. (g) Potter, R. C.; Bretton, R. H.; Metz, D. J. *J. Polym. Sci., Part A1* **1966**, *4*, 2295. (h) Chawla, A. S.; Huang, R. Y. M. *J. Polym. Sci., Part A1* **1975**, *13*, 1271.

(23) The Mayo equation derived for free cation polymerization[18,19] in the general case of transfer to monomer and where the termination of the propagating carbocation can proceed by both second-order ion recombination and reaction with impurities is $1/\mathrm{DP} = k_{\mathrm{tr}}/k_{\mathrm{p}}^{+} + \{k_{\mathrm{tx}}[\mathrm{X}] + (R_{\mathrm{i}}k_{\mathrm{t}})^{1/2}\}/k_{\mathrm{p}}^{+}m$. Hence, the slope S of the plot of 1/DP against $1/m$ is given by eq 10 while the limiting forms of S that apply to the inequalities $(R_{\mathrm{i}}k_{\mathrm{t}})^{1/2} \gg k_{\mathrm{tx}}[\mathrm{X}]$ and $k_{\mathrm{tx}}[\mathrm{X}] \gg (R_{\mathrm{i}}k_{\mathrm{t}})^{1/2}$ discussed in this Note are given by eqs 5 and 8, respectively.

(24) Although this assumption is not made explicitly in ref 14 and perhaps is not obvious immediately from eq 3, the equivalence of eq 3 to eqs 4 and 5 establishes the point, as discussed in the text. One might also note that in the expression for k_{p}^{+} in eq 3 the only rate constant that is used is k_{t}, which is that for ionic recombination.

(25) Essentially, this low value of k_{p}^{+} for isobutylene in ref 14 results from prorating the observed rate of polymerization over the *maximum* propagating lifetime τ_i of the carbocation, whereas the higher correct value results from using the much shorter actual lifetime, τ_x.

(26) The value of k_{p}^{+} derived for the bulk system[8] assumes that the monomer concentration in the latter is given by $[\mathrm{M}]_{\mathrm{bulk.}}$ It is noteworthy that the use of $[\mathrm{M}]_{\mathrm{bulk}}$ in the corresponding expression for the rate of free-radical polymerization yields values of the bimolecular rate constant that likewise are very similar to those obtained in solution. See, e.g., Table 1 in: Manders, B. G.; Chambard, G.; Kingma, W. J.; Klumperman, B.; van Herk, A.; German, A. L. *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *34*, 2473–2497.

(27) By Ockham's principle (pluralitas non est ponenda sine necessitate), the reconciliation between the values of k_{p}^{+} calculated for the bulk and solution polymerization indicates that the dieidic propagation hypothesis[14] is unnecessary to explain the results for the radiation-induced polymerization of isobutylene. This conclusion does not, of course, necessarily hold for the radiation-induced cationic polymerization of other monomers.

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