

# Radiation-Induced Polymerization by Free Ions

## Part 3.—Rate Constants for Cationic Polymerization \*

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The general kinetics of radiation-induced ionic polymerization are discussed and the effects resulting from impurity termination are analyzed quantitatively. A method is described for the calculation of the propagation rate constants  $k_p$  by combining measurements of polymerization rates with conductivity determinations of the ionic lifetime in the stationary state. The rate constant for cationic propagation by free ions is *ca.*  $4 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$  for both styrene and  $\alpha$ -methylstyrene in the bulk monomer. This large value suggests that the lower results obtained previously for styrene by the use of chemical cationic catalysts refer mainly to ion pairs of varying reactivity.

In cationic polymerizations induced by catalysts, the rate of polymerization is often influenced by the nature of the catalyst and the dielectric constant of the solvent. Thus, in contrast to free radical polymerization, no unique value for the propagation constant  $k_p$  can be specified from existing data on the cationic polymerization of styrene by various catalysts in dichloroethane, the  $k_p$  values ranging from  $3.7 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}$  for iodine<sup>1</sup> at 30° to  $7.7 \text{ M}^{-1} \text{ sec}^{-1}$  for sulphuric acid<sup>2</sup> at 25°. Also,  $k_p$  for the iodine-catalyzed polymerization of isobutyl vinyl ether<sup>3</sup> decreases from  $6.5 \text{ M}^{-1} \text{ sec}^{-1}$  to  $4.5 \times 10^{-2} \text{ M}^{-1} \text{ sec}^{-1}$  when dichloroethane is replaced by n-hexane, a solvent of lower dielectric constant. On the assumption that  $k_p$  values for ionic polymerization are sensitive to the presence and nature of counter ions, such variations in reactivity are attributable to changes in the intimate arrangement of the ion pairs as the structure of the catalyst is altered, and to solvent shifts in the various thermodynamic equilibria which characterize the different states of ion pairs and free ions in each catalyst system. Accordingly, the measured rate constants are composite values representing the weighted contribution from each type of propagating species in the medium.

To interpret the kinetics of ionic polymerization quantitatively, it is desirable to determine the propagation rate constant for free ions since it might depend mainly on the intrinsic reactivity of the monomer with the derived ion. Studies of anionic polymerization by the "living polymer" technique<sup>4,5</sup> have been successful in measuring the relative participation of free ions and ion pairs in the overall polymerization. The  $k_p$  for the free anionic polymerization of styrene in tetrahydrofuran at 25° is close to  $10^5 \text{ M}^{-1} \text{ sec}^{-1}$ , and exceeds by a 1000-fold the corresponding values for propagating ion pairs with alkali metal cations. Other information about the

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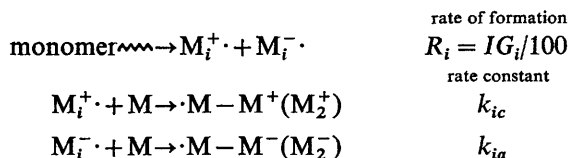
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reactivity of free ions comes from studies of radiation-induced polymerization. Previous estimates of  $k_p$  for free cations in bulk cyclopentadiene <sup>6</sup> ( $6 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$ ) at  $-78^\circ$  and  $\alpha$ -methylstyrene <sup>7</sup> ( $3 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$ ) at  $30^\circ$  have been derived by competitive kinetic methods based on the retarding effect of ammonia and amines on the radiation-induced ionic polymerization. These estimates are several orders of magnitude higher than the typical values obtained in catalytic studies where the conditions favour the existence of ion pairs.<sup>1-3</sup> In this paper, an independent determination of  $k_p$  in radiation-induced cationic polymerization is described from kinetic and conductivity measurements in the stationary state set up on continuous irradiation.

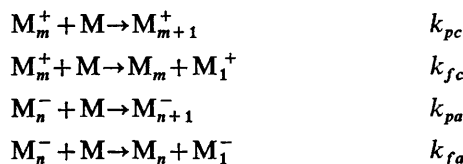
## KINETICS

Because the ions generated by irradiation have only a transient existence, the kinetic treatment of radiation-induced ionic polymerization leads to expressions which are analogous to those derived for homogeneous free radical polymerization.<sup>8</sup> We consider first the case where all the ions in the system are derived from monomer  $M$  according to the following scheme, where  $I$  represents the dose rate in  $\text{eV cm}^{-3} \text{ sec}^{-1}$  and  $G_i$  is the 100 eV yield of free (separated) ions capable of homogeneous initiation.

initiation

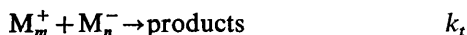


propagation and transfer  
( $m$  or  $n = 1, 2, \dots$ )



termination

( $m$  or  $n = i, 1, 2, \dots$ )



A considerable simplification is possible if a single rate constant  $k_t$  can be used to describe the termination process by charge neutralization. Then, employing the notation adopted in part 2, we have the relations,

$$R_i = k_t \sum_m \sum_n [M_m^+][M_n^-],$$

and

$$C_{\pm} = \sum_m [M_m^+] = \sum_n [M_n^-] = (R_i/k_t)^{\frac{1}{2}}. \quad (1)$$

From the definition of  $\tau$  as the mean lifetime in the stationary state, then

$$\tau = C_{\pm}/R_i = (1/R_i k_t)^{\frac{1}{2}}. \quad (2)$$

The  $\tau$  values derived from the conductivity data of part 2 determines the lifetime of a propagating ion (including its participation in transfer steps) provided that for the particular species,

$$\tau \gg 1/k_i[M]. \quad (4)$$

If this condition does not apply, then the initiation step through the reaction of the appropriate radical-ion is sufficiently slow to reduce the propagating lifetime to a value,  $\tau - (k_i[M])^{-1}$ , significantly lower than  $\tau$ . On the other hand, assuming that (4) holds, the total concentration of ions (of either sign) is made up almost entirely of propagating species, and it follows that for long kinetic chains, the rate of polymerization  $R_p$  is given by

$$R_p = (k_{pc} + k_{pa})[M]C_{\pm},$$

which can also be expressed as

$$R_p = (k_{pc} + k_{pa})[M]\tau R_i. \quad (5)$$

By the same assumption (4), the kinetic chain length  $\nu$  and the 100 eV yield of monomer disappearance  $G(-m)$  are given by

$$\nu = (k_{pc} + k_{pa})[M]\tau \quad (6)$$

and,

$$G(-m) = (k_{pc} + k_{pa})[M]\tau G_i. \quad (7)$$

The relative contributions of positive and negative ions to the total  $R_p$  cannot be resolved from a kinetic analysis of the overall homopolymerization, and recourse must be made to other evidence. We have chosen to represent  $k_i$  and  $R_p$  in terms of  $\tau$  because  $\tau$  is obtained directly from the conductivity data. This feature is unique to the present case, for by contrast in free radical polymerization, the determination of  $\tau$  is generally realized by non-stationary state methods such as the rotating sector technique.<sup>8</sup> This latter method is also applicable to the study of radiation-induced free ion polymerization but in such a case (as in free radical polymerization),  $\tau$  is deduced solely from measurements of polymerization rate as a function of sector speed and the method is indirect.<sup>8</sup>

A test of the validity of this general scheme is provided by the dependence of  $R_p$  on  $I$ . Combining (2) and (5), we obtain the analogue of the expression in free radical polymerization,

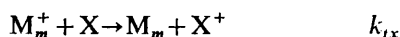
$$R_p = (k_{pc} + k_{pa})[M](R_i/k_i)^{\frac{1}{2}}, \quad (8)$$

which predicts a square-root dependence on dose rate. This relationship is independent of whether only one or both types of charged species are propagating freely in the monomer, provided that (4) holds for both, or for the species (cation or anion) which makes the predominant contribution to  $R_p$ . A combination of a high  $k_p$  and a low  $k_i$  for species belonging to the same charge type might result in a significant departure from a square-root dependence if this charge type were responsible for the bulk of the polymerization rate. Under these circumstances,

$$\nu = k_p[M]\tau - k_p/k_i, \quad (9)$$

and the magnitude of the second term governs the deviation from the square-root behaviour. For long kinetic chains ( $\nu > 10^4$ ) this deviation is small unless  $k_p/k_i$  exceeds  $10^2$ . Corresponding situations in free radical polymerizations ( $k_p \gg k_t$ ) have been analyzed and predicted<sup>9</sup> to give similar deviations from simple relations such as (8). However, in the present case, any observed deviation from (8) is more readily explicable in terms of competing termination processes.

Hitherto we have treated the simple case where the lifetime  $\tau$  of an ion with respect to neutralization is also a strict measure of its propagation lifetime, subject to condition (4). Now we consider the situation where the propagating ion may undergo competitive termination by reaction with an impurity X,



in addition to the charge neutralization process. This reaction does not imply termination by charge transfer; rather, termination is more likely to occur in cationic processes by proton transfer or by addition of the ion to a base. In the ensuing kinetics,  $X^+$  refers to all such impurity ions generated by reactions of the propagating ion. The kinetics can be presented more compactly for one major propagating species, and we arbitrarily take this to be the cation, but the expressions may be easily extended to two propagating species.

The stationary state equations for chain termination and charge neutralization in the presence of an impurity  $X$  are

$$R_i = k_t \sum_m [M_m^+][Y^-] + k_{tx} \sum_m [M_m^+][X], \quad (10)$$

$$R_i = k_t \sum_m [M_m^+][Y^-] + k_i [X^+][Y^-], \quad (11)$$

where  $[Y^-]$  represents the *total* negative ion concentration. The identity,

$$k_{tx} \sum_m [M_m^+][X] = k_i [X^+][Y^-] \quad (12)$$

is implied by these equations and conforms to a stationary state assumption for  $[X^+]$ . Proceeding as before with the assumption of a single rate constant  $k_t$  in eqn. (12) for bimolecular reactions between charged species, and from the equation of charge conservation,

$$\sum_m [M_m^+] + [X^+] = [Y^-],$$

then

$$[Y^-] = (R_i/k_t)^{\frac{1}{2}}, \quad (13)$$

whence

$$\sum_m [M_m^+] = R_i / ((R_i/k_t)^{\frac{1}{2}} + k_{tx}[X]), \quad (14)$$

and

$$R_p = R_i k_p [M] / ((R_i/k_t)^{\frac{1}{2}} + k_{tx}[X]). \quad (15)$$

The last equation may be rewritten in the form

$$R_p = R_i \tau' k_p [M] \quad (16)$$

where  $\tau'$  is defined by the relation,

$$1/\tau' = 1/\tau + 1/\tau_s \quad (17)$$

and  $\tau_s = 1/k_{tx}[X]$ . Thus  $\tau'$  is the mean lifetime of the propagating ion subject to two competitive (parallel) termination reactions with independent characteristic lifetimes  $\tau$  and  $\tau_s$ .

#### STYRENE

The above determination of  $k_p$  rests upon a knowledge of  $R_p$ ,  $\tau$ ,  $[M]$ , and  $R_i$  at any particular dose rate. In the calculations of table 1,  $R_p$  values are taken from part 1,  $\tau$  determinations from part 2, and  $R_i$  values are based upon a  $G_i$  value of 0.1. The direct experimental determination of  $G_i$  by the conductivity method in monomeric systems is difficult (see part 2). Also, because of the prevalence of chain transfer in styrene polymerization (part 1),  $G_i$  cannot be determined from a combination of rate and molecular weight data. The justification for using  $G_i = 0.1$  is that this is the most reliable value available for hydrocarbons at or near room temperature (see part 2). Our approach implies that all ions which achieve separation are capable of initiating polymerization.

The two dose rates in table 1 were chosen so as to span the available conductivity and polymerization data. An apparent increase in  $k_p$  with dose rate is attributable to the dependence of  $\sigma$  and  $R_p$  on  $I^n$  where the exponent  $n$  is greater than the theoretical value of 0.50 in each case. In this regard, the most severe limitation is imposed by the dependence of  $R_p$  on  $I^{0.62}$  since this implies the coexistence of a small amount of impurity termination together with the charge neutralization process. From eqn. (15) the relative importance of impurity termination diminishes as the dose rate increases. Therefore the value of  $k_p$  as determined at the highest available dose rate represents the closest approximation to the true value, but because the effect of impurity termination cannot be neglected, this value still represents a lower limit because we have used

TABLE 1.—RADIATION-INDUCED POLYMERIZATION OF STYRENE <sup>a</sup>

$I$	eV cm <sup>-3</sup> sec <sup>-1</sup>	$1.00 \times 10^{14}$	$1.00 \times 10^{15}$
$I'$	eV g <sup>-1</sup> sec <sup>-1</sup>	$1.10 \times 10^{14}$	$1.10 \times 10^{15}$
$R_i = 1.66 \times 10^{-24} I$	M sec <sup>-1</sup>	$1.66 \times 10^{-10}$	$1.66 \times 10^{-9}$
$\sigma^b$	ohm <sup>-1</sup> cm <sup>-1</sup>	$1.22 \times 10^{-12}$	$4.15 \times 10^{-12}$
$\tau = \epsilon/3.6 \times 10^{12} \pi \sigma$	sec	0.175	0.0514
$R_p^c$	M sec <sup>-1</sup>	$6.4 \times 10^{-4}$	$2.6 \times 10^{-3}$
$k_p = R_p/[M]\tau R_i$	M <sup>-1</sup> sec <sup>-1</sup>	$2.5 \times 10^6$	$3.5 \times 10^6$
$k_t = \tau^{-2} R_i^{-1}$	M <sup>-1</sup> sec <sup>-1</sup>	$2.0 \times 10^{11}$	$2.3 \times 10^{11}$

<sup>a</sup> temperature 15°C, [M] = 8.75 M, dielectric constant  $\epsilon = 2.41$ ; <sup>b</sup> from part 2; <sup>c</sup> from part 1.

$\tau$  instead of  $\tau'$  (cf. eqn. (5) and (16)), where  $\tau \gg \tau'$ . Since the determination of  $k_p$  is most sensitive to the absolute value of  $R_p$  at a particular dose rate, we compare the values of  $R_p$  used in table 1 (from part 1) with those obtained by Metz and his co-workers<sup>10</sup> under the most rigorous conditions of dryness. The interpolated  $R_p$  values of these latter workers at a dose rate of  $1.1 \times 10^{14}$  eV g<sup>-1</sup> sec<sup>-1</sup> are  $6.9 \times 10^{-4}$  M sec<sup>-1</sup> and  $6.7 \times 10^{-4}$  M sec<sup>-1</sup> at 0 and 25° respectively which are in excellent agreement with the value of  $6.4 \times 10^{-4}$  M sec<sup>-1</sup> in table 1. At the higher dose rate ( $1.1 \times 10^{15}$  eV g<sup>-1</sup> sec<sup>-1</sup>) the corresponding values of Metz *et al.* are  $3.3 \times 10^{-3}$  M sec<sup>-1</sup> and  $2.2 \times 10^{-3}$  M sec<sup>-1</sup> (by extrapolation) which are again near to the value of table 1 ( $2.6 \times 10^{-3}$  M sec<sup>-1</sup> at 15°). Therefore confidence can be placed in the  $R_p$  values, at least to the extent that they represent the highest values measured under the appropriate conditions, although these values fall short of the ultimate rates which would be attained in the absence of any impurity.

Now the presence of a terminating impurity lowers the absolute value of  $R_p$  ( $I$ ) and raises the value of the exponent  $n$  above 0.5 in the relation,  $R_p \propto I^n$ . A quantitative treatment of this effect can be carried through on the basis of eqn. (15) by using numerical values for the rate constants  $k_p$ ,  $k_t$ , and  $k_{tx}$ , and the results are presented graphically in fig. 1.

The values chosen for  $k_p$  and  $k_t$  are essentially based on those derived in table 1, but we have used  $k_p = 5 \times 10^6$  M<sup>-1</sup> sec<sup>-1</sup> as a reference point for our calculations since the values of  $k_p$  in table 1 are lower limits. Unfortunately, no direct extrapolation method can be used to obtain the true  $k_p$  from the experimental data unless the amount of impurity is estimated and its rate constant  $k_{tx}$  is known precisely. The value of  $k_{tx}$  chosen for the calculations of fig. 1 is the diffusion-controlled value of  $10^{10}$  M<sup>-1</sup> sec<sup>-1</sup>. The value of  $k_t$  given in table 1 and used in fig. 1 ( $2 \times 10^{11}$  M<sup>-1</sup> sec<sup>-1</sup>), is large in comparison with the rate constant for the bimolecular termination reaction between polymeric free radicals which is generally of the order of  $10^7$  M<sup>-1</sup> sec<sup>-1</sup>. This is consistent with the conclusion of part 2 that a mobile ionic species (presumably of low

propagation efficiency) is present in the system and it largely governs the value of  $k_t$ . In turn this justifies the use of one value of  $k_t$  in the kinetic treatment, because differences which arise in the diffusion coefficients for polymeric ions of varying length then have less influence on the rate constants for ionic recombination.

The curves plotted in fig. 1 show that as the amount of impurity increases, the absolute value of  $R_p$  decreases and the exponent  $n$  increases from 0.5 to 1.0. The straight line (curve I) corresponding to the square root dependence is the asymptote to the impurity curves, but at the higher impurity concentrations, the asymptotic value

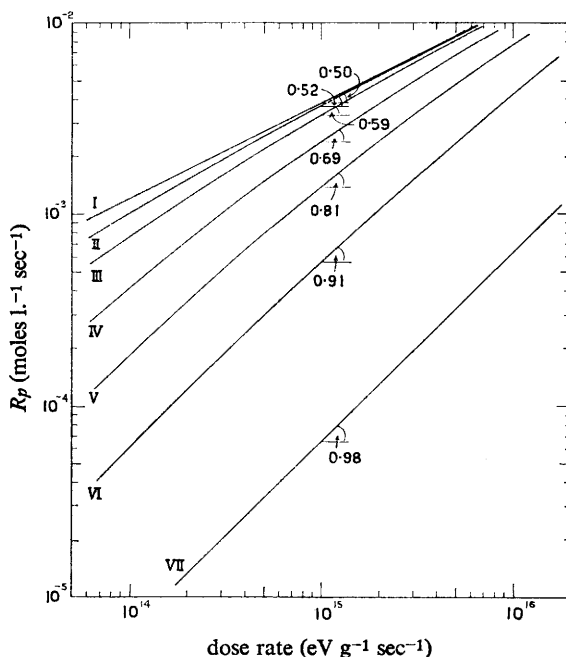


FIG. 1.—Calculated Dose Rate Dependence of  $R_p$  for Styrene as a function of impurity concentration  $[X]$ .

I,  $[X] = 0$ ; II,  $[X] = 10^{-10}$  M; III,  $[X] = 3 \times 10^{-10}$  M; IV,  $[X] = 10^{-9}$  M; V,  $[X] = 3 \times 10^{-9}$  M; VI,  $[X] = 10^{-8}$  M; VII,  $[X] = 10^{-7}$  M.

$$\begin{aligned} G_i &= 0.1, \\ k_t &= 2 \times 10^{11} \text{ M}^{-1} \text{ sec}^{-1}, \\ k_{tx} &= 10^{10} \text{ M}^{-1} \text{ sec}^{-1}, \\ k_p &= 5 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}, \end{aligned}$$

$$\begin{aligned} R_p &\propto I^n, \\ R_i &= G_i I / 100, \\ R_p &= k_p [M] \left\{ \frac{R_i}{k_{tx}[X] + (R_i k_t)^{\frac{1}{2}}} \right\} \end{aligned}$$

is not reached within the practical dose rate range. The experimental curve given in part 1 with  $R_p \propto I^{0.62}$  corresponds to behaviour intermediate between curves III and IV, and therefore implies an impurity concentration between  $3 \times 10^{-10}$  and  $10^{-9}$  M on the basis of these calculations. This treatment based on eqn. (15) assumes that a constant adventitious impurity concentration  $[X]$  is maintained during the course of the irradiation, even at the low levels ( $10^{-10}$  to  $10^{-7}$  M) indicated by the calculations. It follows from (12) that the ratio  $[X^+]/[X]$  cannot exceed  $k_{tx}/k_t$ , no matter how high the dose rate, so that the stationary-state concentration of impurity ions is always small by comparison with the total amount of impurity. A more stringent

restriction on the applicability of this treatment is the tacit assumption that the impurity is not "consumed" as the irradiation proceeds, but that X (or a species of equivalent retarding power) is regenerated in the charge neutralization of  $X^+$ , thereby conserving the concentration of X at a stationary level. Undoubtedly, an effect of this type is operating to some extent, otherwise it would be difficult to explain why minute concentrations of water are so effective in curbing the polymerization rate. Other evidence for this type of behaviour is illustrated by the results obtained with trimethylamine (part 1). The effects of adventitious ion scavengers in radiation-induced polymerization are therefore entirely different in scope from the effects which often arise in free radical polymerization where traces of inhibitors are efficiently removed from the system on the irradiation proceeds.

We attributed (part 1) most of the polymerization of styrene under dry conditions to a cationic process. Therefore the  $k_p$  values in table 1 refer to cationic propagation. It is not known whether the absence of significant anionic polymerization is due to slow initiation and/or propagation in the bulk monomer. If a  $k_{pr}$  value of *ca.*  $10^5 \text{ M}^{-1} \text{ sec}^{-1}$  applied as for the free anionic polymerization of styrene in tetrahydrofuran,<sup>4,5</sup> then even if the initiation step were not limiting, the contribution of anionic propagation would only represent a maximum of about 3 % of the total observed rate of polymerization. It is clearly difficult to exclude such a small contribution on the available evidence.

We now compare the current rates of radiation-induced ionic polymerization for bulk styrene under extremely anhydrous conditions with results collected by Chapiro<sup>9</sup> and which refer solely to the free radical reaction in a "wet" system. By analogies between the kinetic treatments of free ion and free radical polymerization (cf. eqn. (8)), and ignoring the effect of impurity termination in the former case, it follows that

$$\frac{k_p(\text{ionic})}{k_p(\text{radical})} = \frac{R_p(\text{ionic})}{R_p(\text{radical})} \left\{ \frac{k_t(\text{ionic})G_i(\text{radical})}{k_t(\text{radical})G_i(\text{ionic})} \right\}^{\frac{1}{2}} \quad (18)$$

Essentially, the rate of free radical polymerization may be regarded as an internal standard to which the rate of ionic polymerization may be compared so as to give an absolute value of  $k_p$  (ionic) if all the remaining constants are known. We compare the  $R_p$  values in the two cases at a dose rate of 10 rads/sec or  $6.24 \times 10^{14} \text{ eV g}^{-1} \text{ sec}^{-1}$  since this is the highest dose rate for which the relation  $R_p \propto I^{0.5}$  applies in the free radical polymerization.<sup>9</sup> At lower dose rates, the ratio  $R_p$  (ionic)/ $R_p$  (free radical) would be lowered by virtue of the  $R_p \propto I^{0.62}$  relation for the ionic polymerization, and this would increase the importance of impurity termination in this latter case leading to an increasing deviation from the conditions under which eqn. (18) holds rigorously, i.e., no impurity termination. The values which are used in the calculation are:

$I' = 6.24 \times 10^{14} \text{ eV g}^{-1} \text{ sec}^{-1}$ ,	ref.
$R_p$ (ionic) = $1.85 \times 10^{-3} \text{ M sec}^{-1}$ ,	part 1
$R_p$ (radical) = $4.0 \times 10^{-6} \text{ M sec}^{-1}$ at $20^\circ\text{C}$ ,	9
$k_t$ (ionic) = $2.2 \times 10^{11} \text{ M}^{-1} \text{ sec}^{-1}$ ,	this work
$k_t$ (radical) = $4.4 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$ at $20^\circ\text{C}$ ,	11
$G_i$ (ionic) = 0.1 ions/100 eV,	part 2
$G_i$ (radical) = 0.6 radicals/100 eV,	9

and these lead to a ratio

$$k_p(\text{ionic})/k_p(\text{radical}) = 8.0 \times 10^4.$$



The data for the free radical polymerization refer to 20°, at which temperature the interpolated  $k_p$  (radical) is  $35.3 \text{ M}^{-1} \text{ sec}^{-1}$  from the findings of Matheson *et al.*<sup>11</sup> for the bulk polymerization. Therefore this value leads to  $k_p$  (ionic) =  $2.8 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$ , which is consistent with the range of values previously recorded in table 1. However, the two methods of calculation are not strictly independent, for they both rely on the experimental values of  $R_p$  and  $\tau$  (or  $k_t = \tau^{-2} R_i^{-1}$ ) for the free ion polymerization.

These values of  $k_p$  which are based directly or indirectly on the conductivity method are lower limits. On the other hand, the determination by the amine retardation method should set an upper limit to  $k_{pc}$ , and in part 1 this was calculated to be about  $4 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$  but the precision was poor, and the reliability of the value is questionable because of the difficulties associated with the application of this method to styrene (see part 1). Consequently, more confidence is attached to the determination by the conductivity method,  $k_{pc} > 3.5 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$ , and it is unlikely that the limiting value of  $k_{pc}$  exceeds  $10^7 \text{ M}^{-1} \text{ sec}^{-1}$  since the observed dose rate dependence of  $R_p$  is so close to 0.5.

#### $\alpha$ -METHYLSTYRENE

A similar calculation of  $k_p$  for  $\alpha$ -methylstyrene according to eqn. (5) is set out in table 2. The excellent agreement between the  $k_p$  values at the two dose rates is

TABLE 2.—RADIATION-INDUCED POLYMERIZATION OF  $\alpha$ -METHYLSTYRENE <sup>a</sup>

$I$	$\text{eV cm}^{-3} \text{ sec}^{-1}$	$1.00 \times 10^{-14}$	$1.00 \times 10^{15}$
$I'$	$\text{eV g}^{-1} \text{ sec}^{-1}$	$1.10 \times 10^{14}$	$1.10 \times 10^{15}$
$R_i = 1.66 \times 10^{-24} I$	$\text{M sec}^{-1}$	$1.66 \times 10^{-10}$	$1.66 \times 10^{-9}$
$\sigma^b$	$\text{ohm}^{-1} \text{ cm}^{-1}$	$1.16 \times 10^{-12}$	$3.75 \times 10^{-12}$
$\tau = \epsilon/3.6 \times 10^{12} \pi \sigma$	$\text{sec}$	0.201	0.062
$R_p^c$	$\text{M sec}^{-1}$	$1.2 \times 10^{-3}$	$3.5 \times 10^{-3}$
$k_p = R_p/[M]\tau R_i$	$\text{M}^{-1} \text{ sec}^{-1}$	$4.6 \times 10^6$	$4.3 \times 10^6$
$k_t = \tau^{-2} R_i^{-1}$	$\text{M}^{-1} \text{ sec}^{-1}$	$1.5 \times 10^{11}$	$1.6 \times 10^{11}$

<sup>a</sup> at 0°C,  $[M] = 7.84 \text{ M}$ ; dielectric constant  $\epsilon = 2.64$ ; <sup>b</sup> from part 2; <sup>c</sup> ref. (12).

essentially due to the dependence of  $R_p$  on  $I^{0.48}$  as reported by Metz.<sup>12</sup> These data have been used because the  $R_p(I)$  values are the highest yet attained for this monomer, and may even correspond to the absolute limit in view of the square-root dependence on dose rate. The absolute rates for this monomer are extremely sensitive<sup>13</sup> to the experimental techniques which are used in baking out the glass apparatus and in drying the monomer, and the increased refinement of procedure<sup>12</sup> has led to a substantial improvement in the rates. Thus, at 0° and a dose rate of  $4.2 \times 10^{15} \text{ eV g}^{-1} \text{ sec}^{-1}$ , the *highest* value of  $R_p$  from several runs involving different preirradiation procedures is reported<sup>12</sup> to be  $7 \times 10^{-3} \text{ M sec}^{-1}$ , whereas data<sup>13</sup> obtained under less rigorous conditions of sample preparation gave a value of  $R_p = 1.6 \times 10^{-3} \text{ M sec}^{-1}$ . The situation is parallel to that discussed for styrene, and as indicated by the kinetic treatment, the criterion of dose rate dependence provides a reliable guide to the determination of the ultimate limit for the rates of radiation-induced ionic polymerization.

The value of  $k_p$  ( $4 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$ ) deduced in table 2 is in satisfactory agreement with a determination<sup>7</sup> of  $k_{pc}$  ( $3 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$ ) by means of the amine retardation method. This value given by the conductivity method is not a lower limit because in this instance,  $R_p$  is not limited by impurity termination. No evidence has been obtained<sup>7,13</sup> for a substantial anionic contribution to the propagation reaction.



However, there is the possibility that anionic polymerization predominates only under extremely dry conditions (i.e., corresponding to the  $R_p \propto I^{0.5}$  dependence) but this would require that anionic termination (to water) occur more readily than cationic termination at any given level of water concentration, and also that  $k_{pa}$  exceed  $k_{pc}$ . No independent verification exists for the former requirement, and the second proposition is inconsistent <sup>7</sup> with other evidence. In the absence of concrete evidence for anionic propagation, the close agreement between the  $k_{pc}$  value determined from amine retardation <sup>7</sup> and the  $k_p$  (ionic) from this work confirms that the cationic propagation is the most important mode of polymerization in this system.

#### ISOBUTYL VINYL ETHER

In fig. 2, the available data for the polymerization of isobutyl vinyl ether from this (part 2) and previous work <sup>14</sup> show that  $R_p \propto I^{0.63}$ . The conductivity results

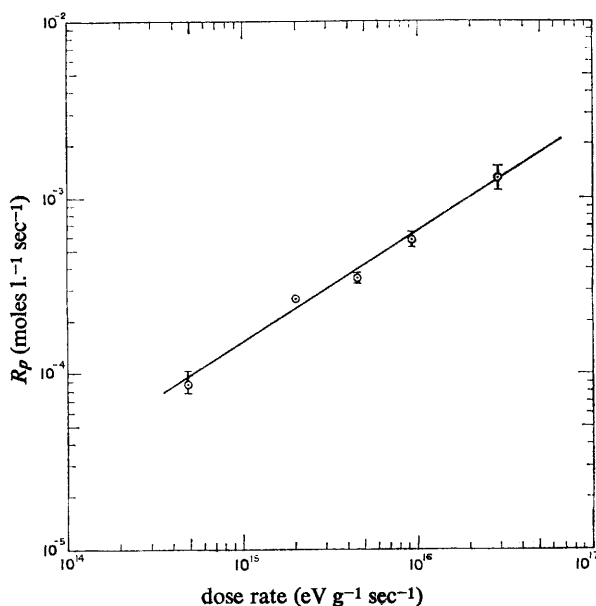


FIG. 2.—Dose rate dependence of isobutyl vinyl ether at 30°.

$$R_p \propto I^{0.63}$$

TABLE 3.—RADIATION-INDUCED POLYMERIZATION OF ISOBUTYL VINYL ETHER <sup>a</sup>

$I$	eV cm <sup>-3</sup> sec <sup>-1</sup>	$1.00 \times 10^{15}$
$I'$	eV g <sup>-1</sup> sec <sup>-1</sup>	$1.32 \times 10^{15}$
$R_i = 1.66 \times 10^{-24} I$	M sec <sup>-1</sup>	$1.66 \times 10^{-9}$
$\sigma^b$	ohm <sup>-1</sup> cm <sup>-1</sup>	$7.1 \times 10^{-12}$
$\tau = \epsilon/3.6 \times 10^{12} \pi \sigma$	sec	0.0423
$R_p^c$	M sec <sup>-1</sup>	$1.8 \times 10^{-4}$
$k_p = R_p/[M]\tau R_i$	M <sup>-1</sup> sec <sup>-1</sup>	$3.4 \times 10^5$
$k_t = \tau^{-2} R_i^{-1}$	M <sup>-1</sup> sec <sup>-1</sup>	$3.4 \times 10^{11}$

<sup>a</sup> [M] = 7.6 M; dielectric constant  $\epsilon = 3.40$ ; <sup>b</sup> from part 2; <sup>c</sup> ref. (14) and fig. 2.

are combined with the value of  $R_p$  at a dose rate of  $1.0 \times 10^{15}$  eV cm<sup>-3</sup> sec<sup>-1</sup> to give a rate constant  $k_{pc}$  of  $3 \times 10^5$  M<sup>-1</sup> sec<sup>-1</sup>, as summarized in table 3. This value is

taken to be the cationic propagation constant on the basis of previous evidence.<sup>14</sup> As for styrene, the dose rate dependence of  $R_p$  suggests that the resulting  $k_{pc}$  is slightly low and additional work<sup>21</sup> on isobutyl vinyl ether indicates a higher value. For the present, the  $k_{pc}$  value in table 3 should be regarded as tentative.

## SUMMARY AND CONCLUSIONS

The propagation rate constants are summarized and compared in table 4 with the values obtained in other work under a variety of conditions and with different catalyst systems. For styrene the rate constants for both free cationic and free anionic propagation are orders of magnitude greater than for either free radical or ion pair propagation. Moreover, the  $k_p$  for the free cation is at least 50 times greater

TABLE 4.—PROPAGATION RATE CONSTANTS IN ADDITION POLYMERIZATION

monomer	catalyst	solvent	temp.	$k_p$ $M^{-1} \text{ sec}^{-1}$	activation energy kcal/mole	ref.
styrene	radiation	bulk	15°	$3.5 \times 10^6$	~0	this paper 15
styrene	free anion	tetrahydrofuran (THF)	25°	$6.5 \times 10^4$ $1.3 \times 10^5$		4 5
styrene	free radical	bulk	20°	35	7.8	11
styrene	anionic ion pair ( $\text{Na}^+$ counter ion)	THF	25°	80		4
styrene	cationic					
	$\text{H}_2\text{SO}_4$	$\text{C}_2\text{H}_4\text{Cl}_2$	25°	7.7		2
	$\text{HClO}_4$	$\text{C}_2\text{H}_4\text{Cl}_2$	25°	17	8.3	16
	$\text{I}_2$	$\text{C}_2\text{H}_4\text{Cl}_2$	30°	$4 \times 10^{-3}$	6.5	1
	$\text{SnCl}_4$	$\text{C}_2\text{H}_4\text{Cl}_2$	30°	0.41		17
$\alpha$ -methylstyrene	radiation	bulk	0°	$4 \times 10^6$		this paper
	free cation	bulk	30°	$3 \times 10^6$	~0	7,13
$\alpha$ -methylstyrene	anionic ion pair ( $\text{Na}^+$ counter ion)	THF	25°	2.5		18
isobutyl vinyl ether	radiation	bulk	ca. 30°	$3 \times 10^5$		this paper
	free cation				6.6	14
isobutyl vinyl ether	cationic	$\text{C}_2\text{H}_4\text{Cl}_2$		6.5		3
	$\text{I}_2$	n-hexane		$4.5 \times 10^{-2}$		3
cyclopentadiene	radiation	bulk	-78°	$6 \times 10^8$	<2	6
	free cation					

than for the free anion. The reactivity of the free cation greatly exceeds that of the cation pairs in conventional catalytic systems, as illustrated by a comparison of the results for both styrene and isobutyl vinyl ether. The temperature dependence of free cationic polymerization is generally small with an overall activation energy not exceeding 2 kcal/mole although isobutyl vinyl ether is an exception. From the magnitude of the rate constants for the free cationic polymerization of styrene,

$\alpha$ -methylstyrene, and cyclopentadiene, the pre-exponential factor  $A_p$  for these monomers must be about  $10^7$  to  $10^9 \text{ M}^{-1} \text{ sec}^{-1}$ . Thus,  $A_p$  for styrene should be about  $10^8 \text{ M}^{-1} \text{ sec}^{-1}$  for free carbonium ion polymerization, a value similar to that attained in free radical propagation<sup>11</sup> ( $A_p = 2.2 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$ ). Hence the much lower rate constant for free radical propagation is due to the high activation energy. For the cation pairs, an appreciable activation energy is involved in some instances,<sup>1,16</sup> and the  $A_p$  values are also decreased from the free ion value, depending upon the extent to which the free rotation of the incoming monomer unit is restricted by the counter ion in the transition state.<sup>1</sup> Finally, original ideas concerning the high reactivity of free cations in polymerization<sup>19,20</sup> are fully borne out by the present results.

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