Table IV. Stabilization Energy (Relative to CH_3^+) of Polysubstituted Methoxy- and Fluoromethyl Cations

Ion	SE ± 3 kcal/mole
$CH_3OCH_2^+$	66
$(CH_3O)_2C^+H$	85
$(CH_3O)_3C^+$	90
FCH_2^+	27
F_2CH^+	26
F_3C^+	14

Table V. Stabilization Energy of Monosubstituted Methyl Radical and Cation

R	SE ($RCH_2\cdot$), kcal/mole	SE (RCH_2^+), kcal/mole
CN	+11 ± 3	−10 ± 3
H	(0)	(0)
CH_3	9 ± 3	37 ± 3
F	13 ± 3	27 ± 3
Cl	14 ± 4	30 ± 4
Br	19 ± 5	37 ± 5
OCH_3	20 ± 3	66 ± 3

In Table V are given the stabilization energies of some monosubstituted methyl radicals and ions. The radical stabilization by substituents with an unshared pair are one-fourth to one-half as large as the stabilization energies for the corresponding cation. This ratio is generally somewhat less (as seems reasonable[43]) than that of 1:2 which is anticipated by the relative delocalization energy from HMO calculations for $3(\ddot{X}CH_2\cdot)$ and $2(\ddot{X}CH_2)$ π-electron systems. If the mean observed ratio of roughly 1:3 applies to the as yet uninvestigated $\cdot CH_2N(CH_3)_2$ radical, the previously obtained SE for the ion[2] anticipates the very low dissociation energy $D[(CH_3)_2NCH_2\text{–}H] = 70$ kcal/mole.

The cyano substituent stabilizes the radical,[44] but, as indicated in Table V, this substituent has a destabilizing effect on the ion. The repulsion associated with the valence-bond structure, $^+CH_2\text{–}C^+{=}N{:}^-$, evidently exceeds any resonance stabilization derived from the structures: $^+CH_2C{\equiv}\ddot{N}{:} \leftrightarrow CH_2{=}C{=}N{:}^+$.

Acknowledgment. This work was supported in part by Grants No. 1221-C and 833-A1 of the Petroleum Research Fund. We also wish to thank the National Science Foundation for providing funds to assist in the purchase of the mass spectrometer.

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Ion–Molecule Reactions in Liquid Hydrocarbons *via* Photoionization with Vacuum Ultraviolet Radiation. The Polymerization of Isobutene

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Abstract: The uncertainty of the effects of the catalyst fragments and solvent molecules in a conventional cationic polymerization system leads to many approximations in the kinetic description of the reaction. A system was developed which completely eliminates these variables and which leads to the simplification of the kinetic expressions. This system is comprised of an ultraviolet source capable of producing photons of sufficient energy to ionize a monomer molecule and a reaction cell in which the ionized fragments are separated by an electric field. The monomer molecules are ionized in the vapor phase and the positive ion fragments caused to drift into the liquid monomer. These positively charged fragments initiate the bulk polymerization of the monomer in the absence of counterions and solvent molecules. An extensive investigation of the isobutene system led to the postulation of molecular weight limitation by solubility of the polymer *via* a unimolecular transfer mechanism. This unimolecular transfer mechanism also explains some of the seemingly anamolous results reported in the literature for the conventional cationic polymerization of isobutene. A complete description of the apparatus is given.

Ionic polymerizations involve the attack of an ion or an ion pair on a neutral molecule. The nature of the formation of the ion pair as well as the nature of the attack on the ion are very little understood processes. Almost all investigations have been limited to a study of chemical initiation with the production of an ion pair in a liquid medium.[1–10] This does not allow one to study primary reactions very easily, since reaction times are extremely short. Furthermore, the system is usually complicated by the presence of solvents and the unknown effect of the counterion in solution, making

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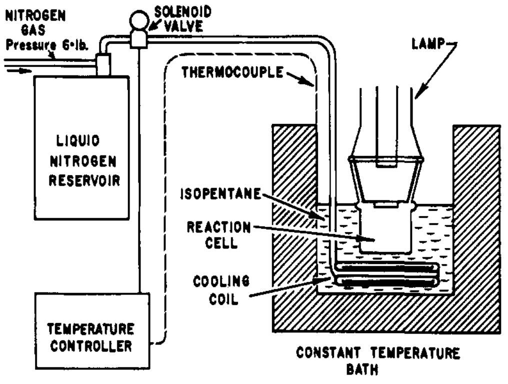

Figure 1. Cooling system.

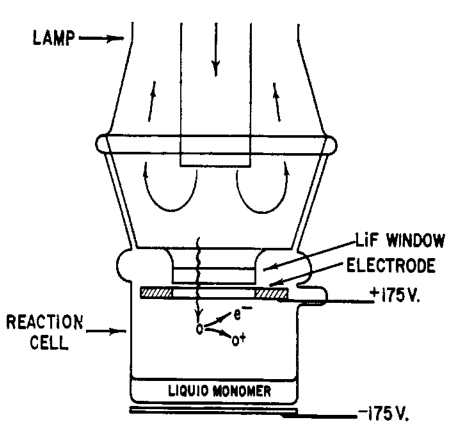

Figure 2. Reaction cell.

isolated studies of the various ion–molecule reactions involved in the polymerization impossible. However, Szwarc, *et al.*,[11,12] have determined the k_p for free ions and ion pairs in the anionic case, and Williams, *et al.*,[13] have determined the k_p for the polymerization of cyclopentadiene by free ions. Evans and his co-workers[14–19] have successfully investigated the effect of solvents and catalysts on the ion-pair equilibrium by absorption studies in the near-ultraviolet, but the question of the necessity of the counterion for polymerization cannot be settled in a chemical system. Alternatively, the study of ion–molecule reactions at very low pressures in the mass spectrometer[20] is limited to very short reaction times and does not allow one to follow through to the final product.

Studies in the high-energy region, using γ and electron radiation, have produced polyisobutene in the molecular weight range of 300,000–500,000.[21–24] Isobutene is a particularly good example since the allylic hydrogens allow one to neglect any free radical contribution in the low-temperature region,[25,26] but high-energy radiation produces, for the most part, free radicals with only a minor component of ions.[27]

It would appear, therefore, that a method of producing free cations in large enough concentrations to initiate a polymerization would be invaluable in the elucidation of the mechanism of cationic polymerization. This would afford a polymerization system free from all the complexities involved in catalyst–cocatalyst reactions and solvent interactions, and also permit the determination of the necessity of an ion pair for polymerization. The objectives of this work were (1) to produce a high enough concentration of free cations to initiate the polymerization,[28] and (2) to study the kinetics of the polymerization without the complications of counterions, solvents, etc.

Experimental Section

Apparatus and Equipment. Monomers. The isobutene used in these experiments was Phillips Petroleum research grade (99.00+ mole % pure).

Light Source. The ultraviolet source used in these experiments was developed in this laboratory and is described in detail elsewhere.[29] However, this source was capable of maintaining a constant output for extended periods of time (120 hr of operation) with a maximum output of 2×10^{17} quanta/sec.

Temperature Control. A low-temperature thermostating bath was designed and constructed for the purpose of maintaining the reaction cell at constant temperature. A diagram of the cooling system is shown in Figure 1. A Brown electronic circular chart temperature controller (Model No. 152R13P-141-13), which operates from a copper–constantan thermocouple immersed in the bath, actuates a solenoid valve which permits the flow of liquid nitrogen from the pressurized storage vessel through a copper line to the bath. Temperatures as low as -186 to $\pm 0.5°$ are easily obtained and can be maintained for prolonged periods of time.

Reaction Cell. The reaction cell (Figure 2) consists of a Pyrex body with a nickel electrode sealed into the upper portion of the cell. A standard taper $^{45}/_{50}$ joint affords a means of attaching the cell to the light source. A side arm which is attached to a vacuum system is used to evacuate the reaction cell and to introduce monomer. Ions formed by absorption of the radiation in the vapor phase are separated from their electrons by means of an electric field applied across the cell. This field results in a steady-state concentration of cations in the liquid monomer. The recent work of Vermeil, *et al.*,[30–32] is similar in that the ion pairs are produced by the same type of ionizing radiation, but their work involves the direct irradiation of the liquid monomer. In this case, both electrodes are immersed in the liquid, thereby confining the initiation step to the liquid phase. For kinetic studies, it is simpler to use a system where the initiation takes place in the vapor phase, and the propagation and termination take place in the liquid phase. Our attempt to photopolymerize isobutene by direct irradiation of the monomer did not result in any polymer; however, our conditions of temperature and concentration were considerably different from those of Vermeil.

Typical Reaction. The reaction cell was sealed to the light source with Apiezon W wax, and the cell was evacuated to a pressure of less than 1×10^{-6} torr (usually overnight). Monomer

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was transferred from the monomer cylinder to a trap immersed in liquid nitrogen. The reaction cell was precooled to the desired temperature and the isobutene distilled into the cell. The monomer was stirred by means of a Teflon (Du Pont registered trademark for fluorocarbon film) covered magnet which was coupled with the magnet in the constant-temperature bath, both of which were controlled by a strong magnet mounted on a stirring motor beneath the bath. A potential difference of 350 v dc was applied across the cell, the upper electrode (sealed into the cell) being positive with respect to the lower electrode (positioned outside the reaction cell). Reaction temperatures ranged from -125 to $-140°$. Upon completion of the irradiation, the unreacted monomer was pumped from the reaction cell. The reaction cell was then brought to atmospheric pressure and the polymer transferred to a weighing bottle.

In the experiments using solvents, the solvent was first distilled into the reaction chamber which was precooled to a temperature slightly above the freezing point of the solvent. The monomer was introduced as previously described, and the solution was brought to the desired temperature. Upon completion of the reaction, both the unused monomer and solvent were distilled from the reaction cell.

Mechanism of Reaction. Several experiments were performed in which the polarity of the electrodes was reversed in order to determine whether the reaction was truly one of a cationic mechanism. If the polymer was of free radical origin, reversal of the polarity of the electrodes should not affect the reaction; however, if the polymer was formed cationically, then no product should be formed since the higher concentration of electrons in the monomer would afford a means of rapid termination.

Initiation of Reaction. A right angle cell (Figure 3) was constructed to determine whether the reaction could be initiated in the vapor phase. The lamp was mounted so that the radiation would pass horizontally through the vapor, well above the surface of the liquid monomer. The electrodes were both positioned on the exterior of the reaction cell, and a nitric oxide photometer was positioned at the opposite end of the cell from the lamp to measure any radiation not absorbed by the monomer vapor. The geometry of the cell was such that if no energy was transmitted to the photometer, no stray radiation would reach the liquid monomer even by the shortest reflection path.

Results

In all experiments, except those of reversed polarity, polyisobutene was obtained. A study was made of the variation of molecular weight and yield as a function of monomer temperature and lamp intensity (Table I). The time of irradiation was 90 min with 350 v applied across the cell.

Table I

Temp, °C	Lamp intensity, I_0, $\times 10^{-16}$, quanta/sec	Yield, g	Mol wt $\times 10^{-6}$
-125	1.44	0.0037	2.7
-130	1.44	0.0265	2.2
-135	1.44	0.0737	3.0
-140	1.44	0.0934	3.2
-135	0.65	0.0023	...
-135	1.05	0.0513	3.5
-135	1.44	0.0737	3.0
-135	1.85	0.0839	3.4
-135	3.00	0.1603	3.0

In the experiments in which the polarity of the electrodes was reversed, no polymer was formed. To ensure that the lack of formation of polymer was not due to some impurity in the reaction cell, fresh monomer (from the same monomer source) was distilled into the reaction cell and the polymerization rerun with the polarity of the electrodes in the normal direction. Upon completion of the irradiation, a good yield of polymer was obtained.

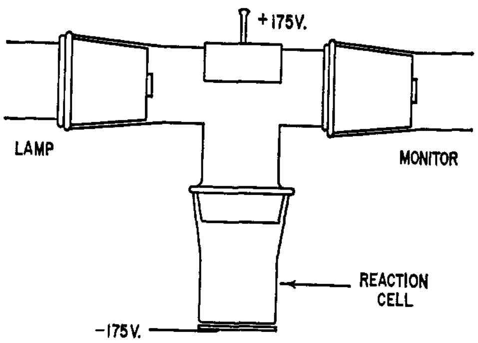


Figure 3. Right angle cell.

The right angle cell experiments showed that the initiation could take place in the vapor phase. Only small yields of polyisobutene were obtained in these experiments, but small yields are to be expected because of the geometry of the cell (*i.e.*, the increased path length the ion must travel to reach the liquid monomer).

A final series of experiments was run to determine what solvent effects would manifest themselves under these reaction conditions. The solvents used, ethyl chloride, isopentane, and toluene, represent a wide spread in dielectric constant. The data from these experiments showed a molecular weight dependency on the solvent.

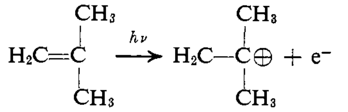
Discussion

It was shown conclusively that the cationic polymerization of isobutene could be initiated by photon impact, and that free cations could be produced in high enough concentrations to give macroscopic yields of polymer. It was also shown that neither solvent nor counterion are necessary for the production of high molecular weight polyisobutene.

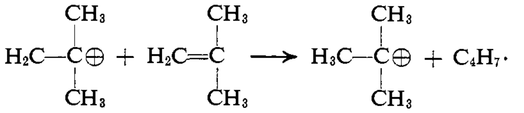
If this polymerization proceeded by a free-radical mechanism, then the reversal of the applied field should have no effect on the formation of the polymer, and, since no polymer was obtained under these conditions, the reaction must be cationic in nature. This is in agreement with the radiation experiments of Collinson, Dainton, and Gillis,[25] and Hoffman,[26] in which they found no free-radical polymerization occurring at $-78°$.

The right angle cell experiments demonstrated that the initiation could take place in the vapor phase, thereby divorcing the initiation step from the propagation and termination steps. In all subsequent experiments the reaction cell was long enough to ensure complete absorption of the radiation by the isobutene vapor in order to minimize the concentration of electrons at the surface of the liquid (*i.e.*, direct irradiation of the liquid at these low field strengths could result in a negative surface charge which in turn would act as an efficient chain terminator).

We can now discuss the kinetics of this system and write the reactions involved in the polymerization. The first step in the reaction is the absorption of a photon by a monomer molecule which produces an ion radical and a free electron (reaction 1). This ion radical then reacts with a second monomer molecule to yield a *t*-butyl carbonium ion and a free radical (reaction 2).



$$\mathrm{H_2C{=}C(CH_3)_2} \xrightarrow{h\nu} \mathrm{H_2C{-}C^{\oplus}(CH_3)_2} + e^- \qquad (1)$$



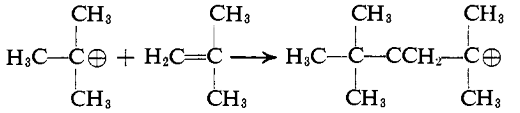
$$\mathrm{H_2C{-}C^{\oplus}(CH_3)_2} + \mathrm{H_2C{=}C(CH_3)_2} \longrightarrow \mathrm{H_3C{-}C^{\oplus}(CH_3)_2} + \mathrm{C_4H_7\cdot} \qquad (2)$$

Reaction 2 has been observed in the mass spectrograph[20] under conditions very similar to those in the reaction cell (*i.e.*, vapor phase, reduced pressure, applied electric field, etc.). Early experiments showed no difference in molecular weight of product obtained with and without the addition of DPPH (1,1-diphenyl-2-picrylhydrazyl) to the reaction, showing there is no significant contribution of free radical coupling reactions to the over-all mechanism. In addition, the reversed field experiments show that the free radical formed in reaction 2 is of no consequence in the ensuing series of reactions.

From the work of Lampe and Field,[20] it is possible to calculate the maximum residence time of the ion radical in the vapor phase by use of the equation

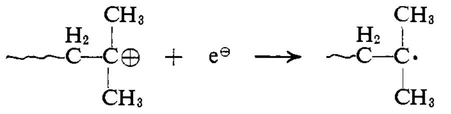
$$\tau_p = (2m_i d)^{1/2}/eE$$

where m_i is the mass of the ion, d is the distance the ion must travel to reach the liquid phase, e is the electronic charge, and E is the strength of the applied field. Using a value of 6 cm for d and assuming no collisions of the ion in the vapor phase, the maximum residence time is calculated to be approximately 4×10^{-6} sec. If reaction 2 occurs through collision in the vapor phase, the residence time of the ion radical will be less than 4×10^{-6} sec. The initiating species can be considered as the *t*-butyl carbonium ion. This ion can react in two ways: it can absorb an electron and form a free radical in which case it will remain dormant, or it can attack another monomer molecule and propagate (reaction 3).



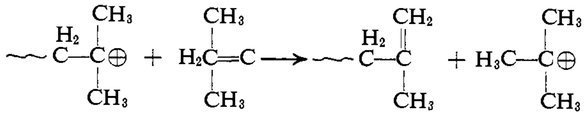
$$\mathrm{H_3C{-}C^{\oplus}(CH_3)_2} + \mathrm{H_2C{=}C(CH_3)_2} \longrightarrow \mathrm{H_3C{-}C(CH_3)_2{-}CCH_2{-}C^{\oplus}(CH_3)_2} \qquad (3)$$

The only true termination reaction in which the positive specie is lost is the electron-capture process in reaction 4. Some of the electrons liberated in the ionization process will migrate to the liquid monomer and afford a means of chain termination. This may happen to a large extent, since the current flow through the circuit is less than 10^{-12} amp. Therefore, if the electrodes become saturated, the formation of any additional ion pairs would only flood the reaction cell with free electrons which can either recombine with the cations in the vapor phase or the active centers in the liquid phase. However, one need only consider that the reaction soon reaches a steady state and that the number of active centers present at steady-state conditions is governed by the potential applied across the cell and the intensity of the source.



$$\sim\!\sim\mathrm{CH_2{-}C^{\oplus}(CH_3)_2} + e^{\ominus} \longrightarrow \sim\!\sim\mathrm{CH_2{-}C\cdot(CH_3)_2} \qquad (4)$$

Chain transfer, on the other hand, can only take place with another monomer molecule by a proton shift from the active end of the polymeric chain to a monomer molecule[33-36] (reaction 5).



$$\sim\!\sim\mathrm{CH_2{-}C^{\oplus}(CH_3)_2} + \mathrm{H_2C{=}C(CH_3)_2} \longrightarrow \sim\!\sim\mathrm{CH_2{-}C({=}CH_2)(CH_3)} + \mathrm{H_3C{-}C^{\oplus}(CH_3)_2} \qquad (5)$$

The over-all reaction may then be summarized as

Initiation

$$\mathrm{M} \xrightarrow{h\nu} \mathrm{M}\cdot^{+} + e^{\ominus} \qquad (6)$$

$$\mathrm{M}\cdot^{+} + \mathrm{M} \longrightarrow \mathrm{M}^{+} + \mathrm{M}\cdot \qquad (7)$$

Propagation

$$\mathrm{M}_{n-1}{}^{+} + \mathrm{M} \xrightarrow{k_p} \mathrm{M}_n{}^{+} \qquad (8)$$

Termination

$$\mathrm{M}_n{}^{+} + e^- \xrightarrow{k_t} \mathrm{M}_n\cdot \qquad (9)$$

Transfer

$$\mathrm{M}_n{}^{+} + \mathrm{M} \xrightarrow{k_{tr}} M_n + \mathrm{M}^{+} \qquad (10)$$

If all of the photons are absorbed in the vapor phase and a certain fraction, α, form cations which survive long enough to initiate polymerization, then the rate of initiation may be written

$$R_i = \alpha I_0 \qquad (11)$$

where I_0 is the intensity of the lamp, and α is a function only of the applied voltage. From reactions 8, 9, and 10, the rates of propagation, termination, and transfer may be written

$$R_p = k_p[\mathrm{M}^+][\mathrm{M}] \qquad (12)$$

$$R_t = k_t[\mathrm{M}^+][e^-] \qquad (13)$$

$$R_{tr} = k_{tr}[\mathrm{M}^+][\mathrm{M}] \qquad (14)$$

Under steady-state conditions, the rate of initiation must be equal to the rate of termination, and therefore

$$\alpha I_0 = k_t[\mathrm{M}^+][e^-] \qquad (15)$$

Equation 15 states that the product of the concenration of electrons, $[e^-]$, and the concentration of cations, $[\mathrm{M}^+]$, is dependent on the lamp intensity. However, the concentration of electrons in the liquid phase will be dependent on the strength of the applied field, and hence

$$[e^-] = \beta V_{app}{}^{-1} \qquad (16)$$

where β is a proportionality constant and V_{app} is the applied voltage. Substitution of this relationship into eq 15 then yields

$$[\mathrm{M}^+] = \frac{\alpha I_0 V_{app}}{\beta k_t} \qquad (17)$$

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(33) P. H. Plesch, *J. Chem. Soc.*, 543 (1950).

(34 M. St. C. Flett and P. H. Plesch, *ibid.*, 3355 (1952).

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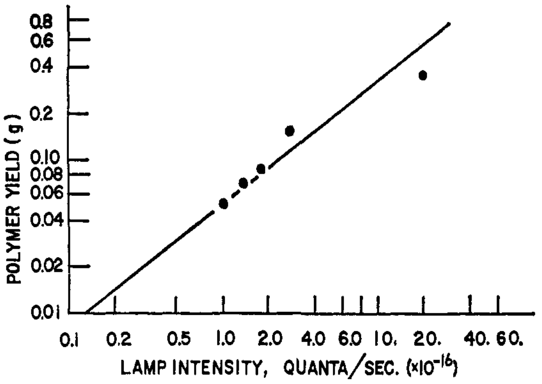

Figure 4.

This equation points out that the concentration of active centers in the liquid phase should be a linear function of the lamp intensity at constant applied voltage. Since $[M^+]$ determines the yield, a plot of yield *vs.* lamp intensity should be linear (Figure 4).

The number-average degree of polymerization may be expressed as

$$\overline{DP}_n = \frac{\text{rate of propagation}}{\text{rate of termination + rate of transfer}} \tag{18}$$

Substitution of eq 12, 14, and 15 into eq 18 yields

$$\overline{DP}_n = \frac{k_p[M^+][M]}{\alpha I_0 + k_{tr}[M^+][M]} \tag{19}$$

If we now substitute eq 17 into eq 19 and rearrange, we obtain

$$\overline{DP}_n = \frac{k_p[M]}{\beta k_t V_{app}^{-1} + k_{tr}[M]} \tag{20}$$

If termination predominates (*i.e.*, $\beta k_t V_{app}^{-1} \gg k_{tr}[M]$), then $\overline{DP}_n$ should be a function of V_{app}. Table II shows this not to be the case; hence, one is led to conclude that $k_{tr}[M] \gg \beta k_t V_{app}^{-1}$, and the voltage term can be neglected. Therefore, eq 20 reduces to

Table II[a]

Applied voltage	$I_0 \times 10^{-17}$ quanta/sec	Mol wt $\times 10^{-6}$	Yield, g
90	2.0	3.25	0.3648
370	2.0	3.13	0.3358
900	2.0	3.70	0.3979

[a] Yields were obtained after 90 min of irradiation.

$$\overline{DP}_n = k_p/k_{tr} \tag{21}$$

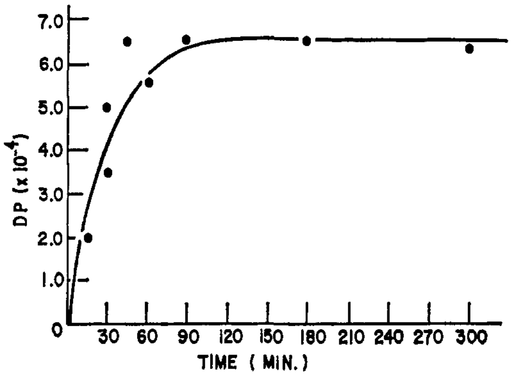

Figure 5.

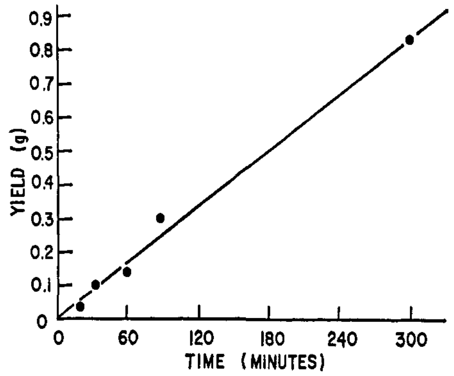

Figure 6.

Since the $\overline{DP}_n$ is equal to the ratio of the two rate constants (k_p/k_{tr}), one would expect the $\overline{DP}_n$ to be independent on time. Figure 5 shows, however, that the $\overline{DP}_n$ is time dependent during the first part of the reaction. The fact that the monomer is consumed at a uniform rate (Figure 6) suggests that the initial dependency of molecular weight on reaction time is due to some impurity acting as a chain-transfer agent. This transfer reaction must involve the consumption of this impurity, X, in a manner similar to that shown in reactions 22 and 23. Upon complete consumption of

$$\sim\!\sim M^+ + X \xrightarrow{k_{tr}'} \sim\!\sim MX + H^+ \tag{22}$$

$$H^+ + M \longrightarrow HM^+ \tag{23}$$

X, the only transfer process which can take place is that which involves active polymer and monomer. If this process is included in the equation for the degree of polymerization, then eq 20 becomes (neglecting the termination process)

$$\overline{DP}_n = \frac{k_p[M]}{k_{tr}[M] + k_{tr}'[X]} \tag{24}$$

which can also be written as

$$\lim_{[X] \to 0} \overline{DP}_n = k_p/k_{tr} \tag{25}$$

This type of scavenging process to remove impurities from the polymerization medium has also been suggested in conventional systems. Plesch, *et al.*,[37] have listed "threshold" concentrations for various Friedel–Crafts catalysts, below which no polymerization of isobutene was observed. Furthermore, they suggest that the S-shaped time–temperature curve may signify the presence of a poison which is present in the preliminary stage of the reaction.

Equation 17 indicates that the concentration of cations, and hence the yield, should be dependent upon the applied field if the electrodes are saturated. The data in Table II show, however, that the yield is not dependent on the applied voltage, and, therefore, the molecular weight is not limited by a flooding of the

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(37) P. H. Plesch, M. Polanyi, and H. A. Skinner, *J. Chem. Soc.*, 257 (1947).

reaction cell with excess electrons. This is further substantiated by the fact that the yield is dependent on lamp intensity (Table I). However, the fact that the yield is a linear function of time (Figure 6) indicates that the system has reached the steady state.

If the Arrhenius plot shown by Kennedy and Thomas[38,39] were linear from -60 to $-135°$, one would predict a molecular weight of 2.1×10^7 for polyisobutene prepared at $-135°$, and an activation energy of approximately -3.7 kcal/mole. However, at temperatures below $-100°$ the molecular weight of the polymer becomes nearly independent of temperature, and one calculates an activation energy of -0.17 kcal/mole. This indicates that at the lower temperatures (below $-100°$) a molecular weight limiting mechanism other than bimolecular chain transfer has become important and is consuming $\sim$3.5 kcal/mole. We have observed that the molecular weights of polymers prepared in solution at these low temperatures do not increase with increasing dielectric constant of the medium, but rather with increasing solubility of the polymer in the solvent (Table III).

Table III

Solvent	Dielectric constant of pure solvent at $-135°$	Mol wt $\times 10^{-6}$
Isobutene	$\sim$2	3.13
Toluene	2.74[a]	2.50
Isopentane	2.04	1.32
Ethyl chloride	21.5[a]	0.06

[a] Extrapolated.

If a propagating molecule attains a molecular weight high enough so it is no longer soluble in the polymerization medium, this molecule will precipitate from the solution, and, in all probability, the active site will be buried within the molecule. The rate at which this precipitated molecule reacts with monomer will depend on the rate of diffusion of the monomer to the active site; however, once the monomer reaches the active site, the probability of addition or transfer is still dependent upon the ratio of the rate constants in eq 21. Therefore, although the over-all rate is diffusion controlled, $\overline{DP}_n$ is not diffusion controlled, and hence the diffusion rate cannot be used to explain the limiting of the molecular weight. On the other hand, if this precipitated cation were stable and would remain as a living cation, then the accumulation of an appreciable amount of this product would result in a partial neutralization of the potential applied across the reaction cell. This in turn would result in fewer active cations in the solution, and the yield of polymer would decrease with time until the electrodes were completely neutralized by the precipitated cations, at which time polymerization would cease. However, Figure 6 shows that the yield is quite linear with time. This precipitated cation can then only alleviate itself of its positive charge in a unimolecular transfer process. This process would certainly account for the change in activation energy required by the Arrhenius plot, and can be written simply as

$$M^+ \xrightarrow{k_{tr}''} M + S^+ \qquad (26)$$

The ejected specie must be able to diffuse through the polymer chain with ease so that it can then attack a monomer molecule to continue the polymerization. If this transfer process is included in the reaction scheme, then a term which will account for the seemingly anomalous behavior of the low-temperature polymerization is introduced into the equation describing $\overline{DP}_n$

$$\overline{DP}_n = \frac{k_p[M][M^+]}{k_{tr}[M][M^+] + k_{tr}''[M^+]} \qquad (27)$$

which can be written

$$\overline{DP}_n = \frac{k_p}{k_{tr} + k_{tr}''/[M]} \qquad (28)$$

When the polymer molecule remains in solution, the bimolecular transfer process predominates ($k_{tr} \gg k_{tr}''/[M]$), and eq 28 becomes simply

$$\overline{DP}_n = k_p/k_{tr}$$

However, if the monomer supply to the active center is depleted, such as in the precipitated molecule, then $k_{tr}''/[M]$ becomes significant, and the complete expression (eq 28) must be used to describe $\overline{DP}_n$, and if $k_{tr}''/[M]$ becomes much greater than k_{tr}, then

$$\overline{DP}_n = \frac{k_p}{k_{tr}}[M] \qquad (29)$$

Equation 29 suggests that precipitation of the polymer molecule is not necessary to observe this dependence of $\overline{DP}_n$ on monomer concentration, but that, even in very dilute solution where the time necessary for collision between the propagating ion and a monomer molecule is extended, this unimolecular transfer process should manifest itself. The results reported by Kennedy and Thomas[40] give excellent support to this transfer mechanism. They observed that the molecular weight of polyisobutene produced from a methyl chloride solution decreased extremely rapidly with decreasing monomer concentration in solutions containing less than 20 vol % monomer.

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