zation tube, a mixture of 1.0 g (6.17 mmol) of 5, 0.605 g (6.05 mmol) of methyl methacrylate, and 1.0 mol % of azobis(isobutyronitrile) (AIBN) was heated at 50 °C for 45 h. After the tube was opened, the mixture was dissolved in $CHCl_3$. After this solution was added to hexane to precipitate the copolymer, the collected solid was dried in vacuo at 70 °C overnight to give 0.74 g (46%) of a white solid copolymer: IR (KBr) 3020, 2980, 2940, 1735 (shoulder), 1720 (s), 1140, 745 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 0.60–1.40 (broad, $CH_2C(CH_3)$), 1.40–2.20 (broad, $CH_2C(CH_3)$), 2.20–2.90 (broad, CH_2CO_2 and $C_6H_4CH_2$), 3.70 (CO_2CH_3), 5.05 (CO_2CH_2), 7.20 (aromatic H's); ^{13}C NMR (25.2 MHz, $CDCl_3$)[12] δ 16.56, 18.80, 21.49 (CH_3), 26.86 (CH_2CO_2), 34.79, 40.42 ($C_6H_4CH_2$), 44.52 (CCO_2CH_3), 51.69 (CO_2CH_3), 54.33 ($CH_2C(CH_3)$), 63.85 (CO_2CH_2), 126.22, 128.63, 129.30, 129.67, 132.94, 140.24 (aromatic C's), 169.81 (CH_2CO_2), 177.55 (CO_2CH_3). Anal. Calcd for $(C_{10}H_{10}O_2)_{0.132}$-$(C_5H_8O_2)_{0.868}$: C, 62.76; H, 7.69. Found: C, 62.77; H, 7.63.

Similar procedures were applied to the syntheses of other copolymers and the identification of their structures.

References and Notes

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(2) A visiting research associate from the Chemistry Institute Academy of Sciences of the People's Republic of China.

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Absolute Rate Constants for the Free Radical Polymerization of Ethylene in the Supercritical Phase

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ABSTRACT: The absolute rate constants for propagation, k_p, and for termination, k_t, were determined for the free radical polymerization of ethylene in supercritical solutions at 130 °C and about 1800 kg/cm^2 using the rotating sector method. Under these conditions, k_t was found to equal 2.0×10^8 L (mol s)$^{-1}$ and k_p to equal 5.4×10^3 L (mol s)$^{-1}$. The magnitude of $k_p k_t^{-1/2}$ calculated from these values is in reasonable agreement with literature values based on isothermal polymerization rates. The value of k_t found in this study, 2×10^8 L (mol s)$^{-1}$, is well within an order of magnitude of values reported for the polymerization of ethylene as saturated liquid and in benzene solution at low pressure. This result cannot be readily accounted for if the termination rate is controlled by segmental diffusion of the polymer chain at a rate controlled by the solvent viscosity.

I. Introduction

Recent compilations[1] of the individual rate constants for propagation, k_p, and for termination, k_t, in vinyl polymerizations contain entries for some monomers other than those listed in earlier summaries.[2] The only published results pertaining to these constants for ethylene appear to be in the publications by Rabel and Ueberreiter,[3] who studied the polymerization of saturated liquid ethylene at about −20 °C, and by Laita and Machacek,[4] who studied the polymerization of ethylene in benzene at 83 °C as a two-phase gas–liquid mixture at pressures well below those required to form a homogeneous solution of the reactants. It seemed desirable to study the polymerization of ethylene in the homogeneous supercritical phase, i.e., at a temperature above about 115 °C and at pressures above about 1500–1900 kg/cm^2, to ensure the miscibility of monomer and polymer at all conversions[5] and so to avoid kinetic complications associated with heterogeneous polymerization. Choice of these conditions also made it possible to perform our experiments within, or very close to, the operating range of most high-pressure reactors producing low-density polyethylene.

At the temperature chosen for these experiments, 130 °C, the rate of polymerization of ethylene initiated thermally is negligible[6] and initiation by oxygen can be avoided if the oxygen content of the ethylene can be kept below several ppm.[5] In principle, therefore, the rotating sector method of intermittent illumination[7] with a photoinitiator should be applicable.

It will be recalled[2,7] that the rotating sector method involves the independent determination of radical lifetimes, τ, polymerization rates under steady illumination, $(R_p)_s$, and initiation rates, R_i. Measurement of the first of these parameters, τ, posed the main difficulty, inasmuch as the reactor chosen was a constant-volume reaction cell in which the reaction rate was monitored by the rate of pressure drop, $\Delta p/\Delta t$. This required use of a leak-free reaction cell and the minimization, or correction, of factors causing pressure changes other than that brought about by the isothermal polymerization induced by the photodecomposition of the initiator. Beyond the correction for deviations from isothermal conditions, this implied use of

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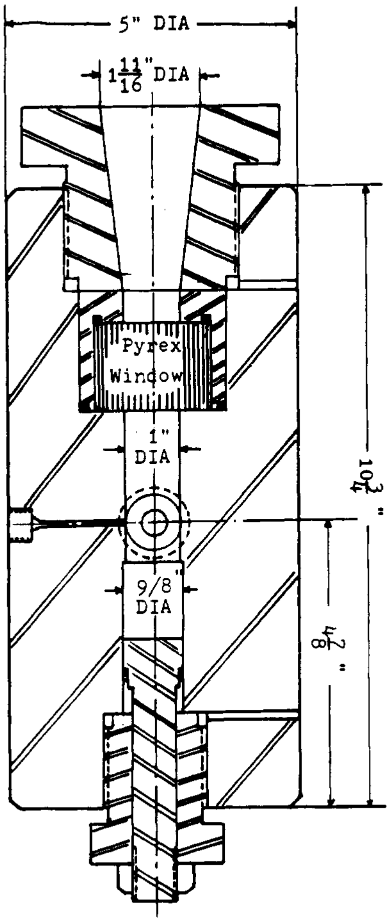

Figure 1. Reaction cell.

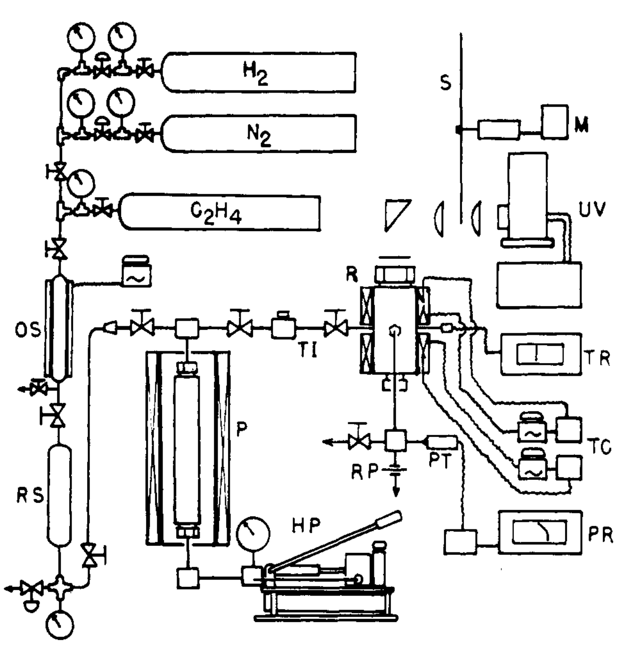

Figure 2. Experimental arrangement.

a photoinitiator which had a negligible dark rate at 130 °C and a reaction cell which could be essentially fully illuminated. This, in turn, required a window with a considerably larger unsupported area than is common in optical pressure vessels. These experimental problems will be discussed in somewhat greater detail in the Experimental Section.

The effect of conversion and solvent viscosity on the individual rate constants k_p and, particularly, k_t has been the subject of much discussion.[8,9] Although the kinetics of vinyl polymerization at moderate to high conversion is a topic of much current interest,[10] the present apparatus allows kinetic measurements to low or moderate conversions (less than about 10%) only, because higher conversions would demand excessive initial pressures or final pressures too low to maintain single-phase supercritical conditions. All experiments to be reported, therefore, were limited to conversions of about 8% or less. As will be seen, the assumption that the rate constants are conversion independent appears to be justified by the results of this study.

II. Experimental Section

1. **Reaction Cell.** The method of determining rates from the pressure drop in an isothermal reactor required that the reaction cell be leak-free. This was ensured through use of a Bridgman seal at the bottom of the reactor (Figure 1), whereas the type of window seal between two sets of elastomeric O-rings found successful in an earlier design[11] was again found to be suitable. The large unsupported area of the window, 1 in. in diameter and unavailable in standard high-pressure optical bombs, did not result in failure of the window, provided the clearances between the window and its metal keeper were properly designed and machined. The lower end of the reactor was enlarged to a diameter slightly greater than 1 in. to allow insertion of a motor to agitate the reaction mixture. This motor, intended for use with reaction mixtures containing premixed polymer, was not inserted in the experiments to be described. The reaction vessel was designed and built by McCartney Manufacturing Co., with modifications introduced in our machine shop. Successful experiments were carried out with both quartz and Pyrex windows. Most experiments reported here were carried out with windows made from annealed polished plate 7740 Pyrex, obtained from Swift Glass Co. Viton A O-rings (Durometer hardness 75) were used in most experiments. The reaction temperature was sensed by a thermocouple inserted into one of the ports at the reactor's center.

2. **Experimental Arrangement.** Major components of the experimental arrangement are shown in Figure 2. The reactor R was heated by cast-in-aluminum heaters and its temperature was controlled by temperature controllers TC which received signals from thermocouples located in the walls of the heaters. The pressure was measured by pressure transducer PT (STD Cell, BLH Electronics) and recorded on an Esterline Angus Recorder, Model L-1101S. The ethylene was purified in deoxygenator OS (CuO BASF catalyst R3-11) and liquefied prior to pumping in the chilled cylinder P, which contained a floating piston (Autoclave Engineers) operated by hand pump HP. The light source UV was a high-intensity mercury–xenon arc lamp (Schoeffel Instruments, Model L-165), operated by Schoeffel power supply LPS 255 HR. The source had an emission band centered at 365 nm, which matched an absorption band of the photoinitiator (see below). Motor M drove the sectored disk S. Quartz lenses and mirrors were used in the conventional manner to focus the light beam in the plane of the rotating disk and to obtain a collimated beam which filled the reaction cell. The spectra of photoinitiator, inhibitors, and the light source were measured by means of a grating monochromator (Schoeffel Instruments, Model GM 100) in conjunction with a photometer (Schoeffel Instruments, Model M 460). The effect of the relative source intensity on the decomposition rate of the initiator was determined by a measurement of the photometer current.

3. **Addition of Reactants.** Most of the deoxygenated ethylene was introduced into the reactor at room temperature by means of the hand pump actuated floating piston, followed by the desired amounts of initiator and inhibitor, where required, in about 1 cm^3 of heptane or benzene. The latter were injected from a syringe through a side port in a valve separating piston and reactor. The solvents caused a small amount of chain transfer, which had no effect on k_p and k_t. The required amount of the remaining ethylene was then added. (The ethylene was added in two stages to allow mixing of initiator and inhibitor at low pressure.) The room-temperature pressure required to generate the desired reaction pressure at the reaction temperature was determined from the P–V–T properties of ethylene.[12] The reactor was then heated,

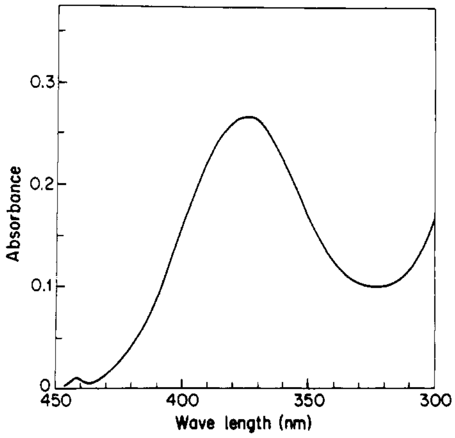

Figure 3. Absorption spectrum of 1-(*tert*-butylazo)-1-phenoxycyclohexane in benzene solution.

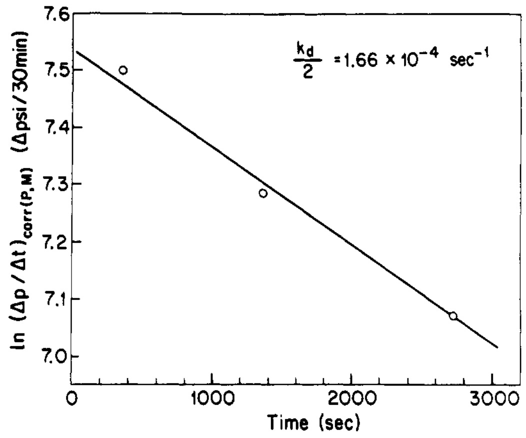

Figure 4. Polymerization rates (arbitrary units) during periods of steady illumination after correction for monomer depletion and the kinetic effect of pressure for run A-08 vs. time.

and reaction rates could be determined after the temperature, pressure, and light intensity had stabilized. Details of the equipment and procedures are discussed in ref 13.

4. Reactants. Ethylene gas was obtained from Phillips Petroleum Co. and deoxygenated by passage through the deoxygenator.

The photoinitiator was 1-(*tert*-butylazo)-1-phenoxycyclohexane (TBPC) obtained through the courtesy of Dr. C. J. Dyball, Lucidol Division of the Pennwalt Corp. TBPC was stated to be 95% pure and was used without further purification. The absorption spectrum of TBPC in benzene is shown in Figure 3. The major absorption band, centered at 375 nm, matches well one of the emission bands of the light source. The rates of polymerization caused by the thermal decomposition of TBPC at a temperature as high as 145 °C were negligible.

Diphenylpicrylhydrazyl (DPPH) was one of the inhibitors used in this study. Examination of its ESR spectrum indicated that it was thermally stable at 130 °C but unstable when illuminated by unfiltered light from our source. In the presence of a 365-nm isolation filter, which inactivated the absorption centered at 508 nm yet permitted a sufficient rate of initiator decomposition, the photodecomposition or DPPH was sufficiently slow to allow its use as inhibitor.

The other inhibitor used was hydroquinone (HQ). Its absorbance above 330 nm was small, and it was thermally and photochemically stable under the experimental conditions when a 360-nm cutoff filter or a 365-nm isolation filter was used.

5. Polymer Properties. Infrared spectra, intrinsic viscosities, and gel permeation chromatograms of polymer recovered in these experiments were obtained (courtesy of Sumitomo Chemical). The properties were those expected of low-density polyethylene made at the temperature and pressure of these experiments,[5] except for the somewhat low molecular weights ($\bar{M}_n$ = 58000–170000). These indicated that, in addition to the anticipated small chain transfer activity expected from heptane or benzene, some leakage of oil across the floating piston caused an additional small reduction in molecular weight. In the absence of these impurities, a molecular weight of about 200000 would have been expected, since β scission of polymer radicals controls the molecular chain length.[5]

6. Calculations. As already mentioned, determination of the rate constants k_p and k_t from the radical lifetimes, τ, requires an independent determination of the rate of polymerization under steady illumination, $(R_p)_s$, and of the rate of initiation, R_i. The latter is a function of the initiation efficiency, ϵ. If k_t is defined according to a frequently followed convention,[18] the relation between $(R_p)_s$ and R_i is given by $(R_p)_s = k_p[M](R_i/2k_t)^{1/2}$, and k_p and k_t can be calculated by means of the following equations:

$$\epsilon = \frac{f}{2}\,\frac{\text{amt of inhibitor present}}{\text{amt of initiator consumed}} \qquad (1)$$

where f is the number of chains intercepted by a single inhibitor molecule, and

$$R_i = 2\epsilon k_d[\text{In}] \qquad (2)$$

where k_d is the rate constant for initiator decomposition and [In] is the initiator concentration. It also follows[2] that

$$k_t = 1/(2R_i\tau^2) \qquad (3)$$

and

$$k_p = (R_p)_s/([M]R_i\tau_s) \qquad (4)$$

The calculation of τ from a comparison of polymerization rates under steady illumination and at various sector speeds is well-known,[2,7] but some special problems arise in the present context. First, small temperature fluctuations, which caused significant changes in the reaction pressure, were found to be unavoidable because of the bulkiness of the reaction cell. These changes were followed by recording the temperature at the reaction site. The beginning and the end of the time interval, Δt, was then chosen so that it coincided with points at which the reaction temperature was at a predetermined value near 130 °C. The Δp, from which the reaction rate was calculated then corresponded to two points along an isothermal reaction coordinate.

Second, the quantity $\Delta p/\Delta t$ from which R_p and $(R_p)_s$ are to be calculated must be corrected for initiator and monomer depletion during any one run and for the effect of pressure on the rate of polymerization. The drop in reaction rate due to initiator depletion in successive periods of steady illumination provides the means of calculating the rate constant for the photodecomposition of initiator, k_d. We then have for a given run carried out at a given initial initiator concentration, $[\text{In}]_0$, and at constant light intensity

$$(\Delta p/\Delta t)_{\text{corr}(P,M)} = (\text{const}) \exp(-k_d t/2) \qquad (5)$$

where the symbol on the left-hand side represents the rate of pressure drop corrected for monomer depletion and the kinetic effect of pressure. The former correction is obtained from the P-V-T properties of ethylene[11] and the latter from the activation volume for polymerization, ΔV, assumed here to equal −23 cm^3/mol.[5,14] The initiator concentration at any time is then calculated from

$$[\text{In}] = [\text{In}]_0 \exp(-k_d t) \qquad (6)$$

where $[\text{In}]_0$ represents the initiator concentration at time zero. Further details of the calculations are discussed in section III and in ref 13.

III. Results

1. Radical Lifetimes. Table I lists the data for a particular run carried out with intermittent illumination. The polymerization rates are proportional to the rate of pressure drop, $\Delta p/\Delta t$, listed in the second column. The rate of initiator decomposition, expressed in terms of the rate constant k_d, is calculated by comparing polymerization rates in the three intervals with steady illumination, making use of eq 5. The results are shown in Figure 4,

Table I
Analysis of Run A-08[a]

duration of light flash, s	rate of pressure drop, psi/30 min	mean pressure, kg/cm²	monomer concn, mol/L	initiator concn × 10^{-5}, mol/L	correction factors: pressure	correction factors: monomer	correction factors: initiator	$R_p/(R_p)_s$
0.900	756	1846	17.39	8.464	1.0	1.0	1.0	0.40
steady	1746	1816	17.11	7.680	1.020	1.016	1.050	
3.625	489	1781	16.78	6.866	1.045	1.036	1.110	0.31
0.250	706	1766	16.64	6.484	1.055	1.045	1.143	0.49
steady	1285	1743	16.42	5.501	1.072	1.059	1.240	
0.688	483	1712	16.13	4.575	1.094	1.078	1.360	0.43
0.0868	512	1697	15.99	4.257	1.105	1.088	1.410	0.48
steady	954	1677	15.80	3.496	1.120	1.100	1.556	

[a] Polymerization temperature, 130 °C; initial pressure, 1862.5 kg/cm²; initial initiator concentration, 8.613 × 10^{-5} mol/L; initial ethylene concentration, 17.54 mol/L; photometer current, 1.8 μA; filter, cutoff (360 nm); sector, r = 3 (ratio of dark to light period).

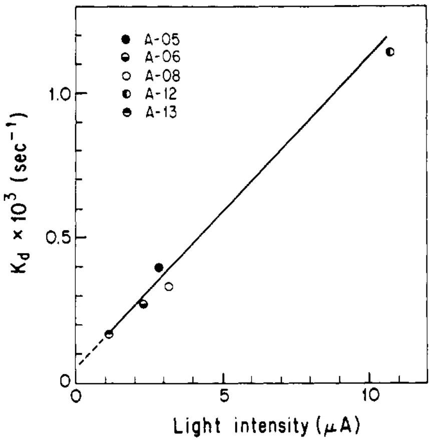

Figure 5. Rate constant for initiator decomposition vs. light intensity (arbitrary units).

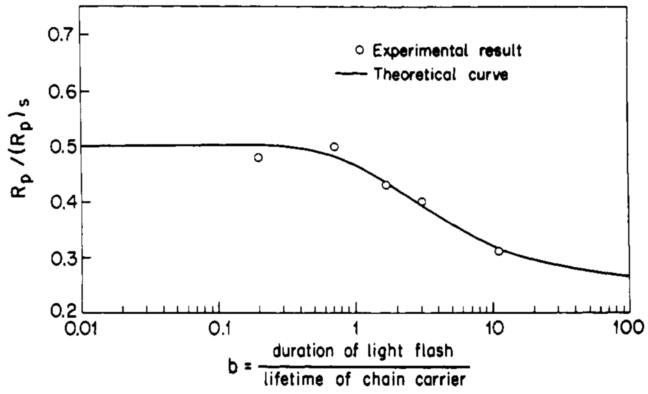

Figure 6. Reduced polymerization rate for intermittent illumination vs. reduced time. Run A-08.

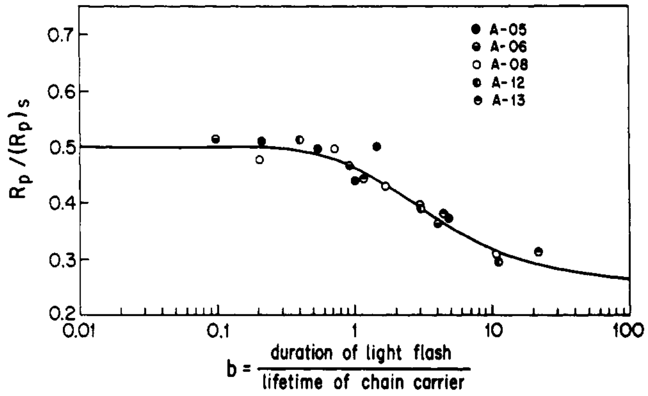

Figure 7. Reduced polymerization rate for intermittent illumination vs. reduced time. All runs.

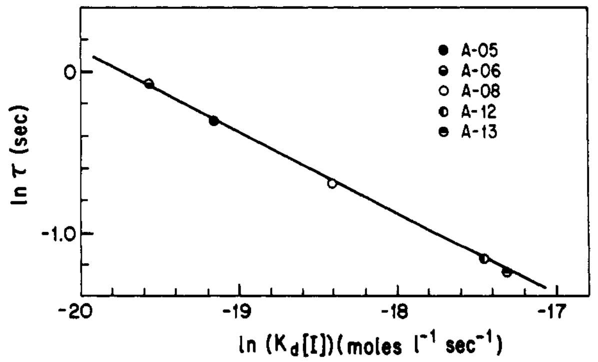

Figure 8. Radical lifetime vs. rate of initiator decomposition.

which yields the value of k_d characteristic for this particular intensity of illumination. A similar analysis of the periods with steady illumination in four other runs yields Figure 5, which establishes the linearity between light intensity and the rate constant k_d.

The initiator concentrations during each interval of intermittent illumination are calculated next from eq 6 (column 5), together with the correction factor for initiator depletion (column 8) by which the observed values of $\Delta p/\Delta t$ must be adjusted. The correction factors for the pressure effects on the polymerization rate (column 6) and on the monomer concentration (column 7) for the periods of intermittent illumination are then calculated, as described in section II.6. Application of these three correction factors to the observed values of $\Delta p/\Delta t$ measured for the periods of intermittent illumination yields the adjusted rates, which should depend only on the dimensionless time, b.[7] Figure 6 shows a plot of the adjusted polymerization rates, expressed as fractions of the rates under steady illumination, $R_p/(R_p)_s$. The figure was constructed in the usual manner by shifting the data along the time axis to obtain the best possible fit along the theoretical curve.[7] The four other runs, carried out under intermittent illumination, were analyzed in a similar manner, each yielding a value of the radical lifetime, τ, at a particular value of the rate of initiation. Data from all runs are plotted jointly in Figure 7.

The absolute value of the rate of initiation is as yet undefined—because the initiator efficiency, ϵ, is as yet unknown—and must be determined from the inhibition period. However, an important test of the adequacy of the analytical treatment can now be made with the help of Figure 8. Bimolecular radical termination requires that Figure 8 have a slope of $-^1/_2$, and the observed slope of −0.52 is in good agreement with that assumption. The satisfactory conformance of Figures 6 and 7 with the theory

Table II
Rates of Polymerization

run no.	pressure, kg/cm^2	monomer concn, mol/L	initiator concn $\times 10^5$, mol/L	$k_d \times 10^4$, s^{-1}	$(R_p)_s \times 10^4$, mol/(L s)
A-05	1887	16.71	1.068	4.403	3.40
A-06	1823	16.79	1.174	2.701	2.24
A-08	1817	17.11	7.680	3.321	6.50
A-12	1923	17.20	0.875	11.42	5.48
A-13	1764	15.85	17.46	1.713	7.59
A-17	1650	15.42	4.673	2.83	2.94
A-18	1716	15.87	12.35	2.83	7.42
A-19	1657	15.05	3.349	2.83	3.97
A-20	1799	16.10	6.261	2.83	6.75
A-21	1854	16.35	5.738	2.83	6.31
A-22	1781	16.09	4.076	2.83	3.42

Table III
Efficiency of Initiation

run no.	inhibitor	induction period, min	initiator consumed during induction period, mol/L $\times 10^5$	inhibitor added, mol/L $\times 10^6$	efficiency	
					$f = 2$	$f = 1$
A-18	DPPH	5.73	1.770	7.72	0.44	0.22
A-19	DPPH	10.5	1.561	7.72	0.50	0.25
A-17	DPPH	16.1	4.567	16.10	0.34	0.17
A-20	HQ	5.31	0.823	7.86		0.48
A-21	HQ	11.4	1.681	15.73		0.47
A-22	HQ	16.2	2.297	23.59		0.51

of the rotating sector, applied to vinyl polymerizations obeying the classical polymerization kinetics with bimolecular termination, appears to provide convincing evidence that correct radical lifetimes, interpretable according to eq 3 and 4, have been measured. These equations show also that the determination of the individual rate constants k_p and k_t requires knowledge of the polymerization rates R_p and initiation rates R_i.

2. Polymerization Rates. Polymerization rates under steady illumination, $(R_p)_s$, were calculated from the polymer yield and $\Delta p/\Delta t$ as described in section II.6 for the five runs carried out under intermittent illumination, as well as for six other runs designed to determine the length of the inhibition period (see below). The results are tabulated in Table II, together with the values of the rate constant for initiator decomposition, k_d, calculated according to eq 5. The magnitudes of $(R_p)_s$, the pressure, and the concentration terms represent average values for the first period of steady illumination in each run.

3. Initiation Rates. Initiation rates were determined by measuring the length of the inhibition periods in the presence of diphenylpicrylhydrazyl (DPPH) or hydroquinone (HQ). DPPH, the preferred inhibitor in vinyl polymerization, exhibited a long period of retardation, as also found by Laita,[4] while HQ was found to inhibit efficiently, exhibiting a sharp onset of polymerization, without initial retardation, at the end of the inhibition period. Nonetheless, inhibition periods could be defined readily with both inhibitors by extrapolation of the data from the period in which polymerization was uninhibited. Because of the sharper inhibition periods, HQ must be considered to be the preferred inhibitor with ethylene. It exhibits the required proportionality between its concentration and the length of the inhibition period (Figure 9).

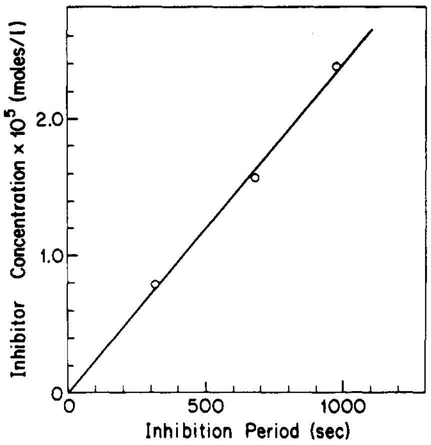

Figure 9. Inhibitor concentration (hydroquinone) vs. length of inhibition period.

Table IV
Absolute Rate Constants[a]

run no.	τ, s	$R_i \times 10^9$, mol/(L s)	$(R_p)_s \times 10^4$, mol/(L s)	$k_t \times 10^{-8}$, L/(mol s)	$k_p \times 10^{-3}$, L/(mol s)
A-05	0.73	4.70	3.40	2.0	5.93
A-06	0.93	3.18	2.24	1.8	4.51
A-08	0.32	25.5	6.50	1.9	4.65
A-12	0.50	10.0	5.48	2.0	6.37
A-13	0.29	29.9	7.59	2.0	5.52

[a] Because of an error in calculation, the values of R_i in a preliminary report of this research were stated to be too small by a factor of 2, and those of k_t too large by the same factor (Takahashi, T.; Ehrlich, P. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1981**, *22*, 203).

The efficiency of initiation, ϵ, can then be obtained from eq 1 after calculation of the amount of initiator consumed during the inhibition period through use of eq 6 with k_d values from Figure 5, provided f, the number of chains intercepted per inhibitor molecule, is known. Literature data suggest that f should be close to 2 for DPPH with ethylene, whereas the efficient inhibition with HQ suggests the choice of $f = 1$ for that inhibitor. Table III shows the results of these calculations. The value $\epsilon = 0.5$ is consistent with the choice of $f = 2$ for DPPH and $f = 1$ for HQ. We choose that value of ϵ for our calculations of k_p and k_t.

4. Absolute Rate Constants. The rate constant for termination, k_t, can now be calculated for each of the five runs carried out with intermittent illumination through use of eq 2 and 3. The results are shown in Table IV.

As already implied by the results of Figure 7, k_t is found to be independent of the initiation rate and equals 2.0 × 10^8 L/(mol s).

The magnitude of k_p can be calculated either from eq 4 or from the values of k_t and of $k_p k_t^{-1/2}$, calculated from R_p according to the equation $R_p = k_p[M](\epsilon k_d/k_t)^{1/2}[In]^{1/2}$. The results are listed in the last column of Table IV.

The average value for k_p is found to be 5.4 × 10^3 L/(mol s). With this value, $k_p k_t^{-1/2}$ becomes 0.38 $(L/(mol\ s))^{1/2}$. This value might be compared with 0.48 $(L/(mol\ s))^{1/2}$ obtained for $\epsilon^{1/2} k_p k_t^{-1/2}$ obtained by Symcox and Ehrlich[12] from rate data at 129 °C and 1800 kg/cm^2 for the homogeneous polymerization carried out in the presence of propane, using di-*tert*-butyl peroxide, DTBP, as initiator. The efficiency of DTBP is usually assumed to approach 1, and so the agreement between these studies should be considered to be as good as can be expected. There appears to be agreement as to the validity of the values of $k_p k_t^{-1/2}$ quoted above for the homogeneous polymerization of ethylene and their approximate dependence on temperature and pressure.[5,15] The present study therefore lends further support to these values. We must now attempt to interpret the individual results for k_p and k_t.

IV. Discussion

It is uncertain whether a significant comparison can be made between the individual values of k_p and k_t found in this study and those reported by Rabel and Ueberreiter[3] for ethylene polymerized at its saturation pressure at −20 °C and by Laita and Machacek[4] at 83 °C at relatively low pressure in benzene as a liquid–gas mixture of unknown phase composition where, presumably, most or all of the polymerization occurred in the liquid phase. An additional difficulty in interpreting the latter study arises from the fact that a high incidence of monomolecular termination was concluded to have occurred. Since k_p should be more sensitive to variations in temperature and pressure than k_t, we restrict our comments to a comparison of the values of k_t reported in the three studies. We note that the values of k_t reported by Rabel and Ueberreiter of 4.6 × 10^8 L $(mol\ s)^{-1}$ and of 1.05 × 10^9 L $(mol\ s)^{-1}$ reported by Laita and Machacek are within factors of approximately 2 and 5, respectively, of those reported here.

Our ability to obtain consistent results lends substantial justification to our assumption of a conversion-independent k_t as well as k_p to at least 8% conversion. One may cite in this connection also the apparent absence of a reported Trommsdorff effect in bulk polyethylene reactors operated to conversions higher than 30%.

The two sets of observation, the apparent insensitivity of both rate constants to solvent environment and conversion, suggest perhaps that the rotational dynamics of the isolated polyethylene chain control the kinetics under all conditions cited. This conclusion is consistent with the failure of models which make segmental diffusion of the polymer chain through a viscous solvent medium the controlling mechanism, which determines the magnitude of k_t, such as the recent model of Mahabadi and O'Driscoll.[9] That model predicts a value of k_t at least 2 orders of magnitude greater than that observed at an estimated solvent viscosity of 0.08 cP.[16] We are thus faced with the seeming paradox of what looks like a diffusion-controlled termination step by virtue of its modest rate ($k_t \ll 10^{11}$ L mol^{-1} s^{-1}) coupled with an apparent insensitivity of that rate to solvent viscosity, conversion, and molecular weight, which was much lower in the two other studies. We must note, however, that the low viscosity of the monomer solvent places the system outside of the range of vinyl polymers for which reliable absolute rate data are available and whose kinetics appear to be controlled by segmental diffusion of chain ends through a resisting solvent medium. Conceivably, the "internal viscosity" of the reacting polymer chain controls the rate of chain termination of polyethylene under all conditions referred to.[17] Admittedly, this statement reflects our inability to propose an established and quantitative model which appears capable of accounting for all observations cited.

An attempt might be made to compare k_p and k_t for ethylene with the magnitude of these constants reported for other monomers. A common reference condition is 60 °C and atmospheric pressure. If we assume the activation volume and activation energy for k_t to be negligible, k_t at the reference conditions remains at 2.0 × 10^8 L/(mol s). Assuming the corresponding values for k_p to be −23 cm^3/mol and 6 kcal/mol, respectively,[5] the reference value for k_p at 60 °C and 1 atm becomes 5 × 10^2 L/(mol s), identical with that reported by Laita and Machacek close to this reference condition.[4] This value is only about 3 times that reported for styrene and much smaller than those reported for vinyl acetate, vinyl chloride, and tetrafluoroethylene. A much higher value than 5 × 10^2 for k_p of ethylene would be expected if resonance stabilization were to exert the strongly predominant control on k_p in all these cases.[4]

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