Determination of absolute rate constants for radical polymerization of diisopropyl fumarate based on a quantitative scavenge of propagating radical

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During polymerization of diisopropyl fumarate (DiPF), the propagating poly(DiPF) radical was scavenged quantitatively by a stable free radical, because of its long-lived nature and high steady-state concentration. By addition of a known amount of 1,3,5-triphenylverdazyl to the polymerization mixture, the concentration of poly(DiPF) radical was determined to be 10^{-5}–10^{-4} mol dm^{-3}, which allowed the evaluation of the propagation rate constant (k_p) from the overall rate of polymerization: $k_p = 0.31 \pm 0.07$ dm^3 mol^{-1} s^{-1} at 30°C. The lifetime of the polymer radical was too long for a rotating sector experiment. The rate constant for bimolecular termination of the radical (k_t) was calculated from the decay of poly(DiPF) radical followed by the scavenger method: $k_t = 0.84$ dm^3 mol^{-1} s^{-1}. These rate constants, which are exceptionally small, are accounted for by the steric factor of the ester alkyl group accumulated along the polymer chain and extremely slow diffusion of the polymer radical. Because the termination rate determined is too slow to interpret the molecular weight of the polymer formed, primary radical termination is to be considered as an additional termination process in the actual polymerization.

(Keywords: diisopropyl fumarate; radical scavenger; radical polymerization; propagation rate constant; termination rate constant)

INTRODUCTION

Recently dialkyl fumarates (DRF) have been found to homopolymerize to high-molecular-weight polymer with the polymethylene structure[1–4]. The bulky ester alkyl group tends to increase the polymerization rate and the molecular weight of the resulting polymer, indicating that the steric factor of the substituent should play an important role in the elementary reactions[4–6].

In a previous paper[7], we have reported the determination of the absolute rate constants for propagation and termination (k_p and k_t, respectively) in the polymerization of diethyl fumarate (DEF) by means of a rotating sector method: $k_p = 0.015$ and $k_t = 164$ dm^3 mol^{-1} s^{-1} at 30°C. Furthermore, the steady-state concentration of the propagating DEF radical was estimated to be of the order of 10^{-5} mol dm^{-3}; as a result, the radical was readily detectable by electron spin resonance (e.s.r.) spectroscopy. However, the rates of propagation and termination allow polymer formation.

The peculiarities in DRF polymerization seem to relate closely to steric effects of the substituents and the main chain, as deduced from the e.s.r. spectra of the polymer radicals[8] and the composition of the spin adduct with 2,4,6-tri-t-butylnitrosobenzene (BNB)[9]. We expected that a radical existing in such an extremely high concentration may permit a direct scavenge with a stable free radical. Although DRF[6,8,10] and some monomers bearing bulky substituents[11–14] have been found to yield e.s.r.-detectable polymer radicals, the radical concentration in the polymerization of common vinyl monomers is too low to be observed by conventional e.s.r. spectroscopy. Direct scavenge of these polymer radicals, including the e.s.r.-detectable ones, has not been attempted.

In the present paper, we chose diisopropyl fumarate (DiPF), which polymerizes faster than DEF, as the monomer, and the absolute values of k_p and k_t were evaluated on the basis of measurement of radical concentration by a direct scavenge with a stable free radical. Determination of the rate constants by the rotating sector method was also attempted. Moreover, decay of the radical, which exists in a very high concentration, was followed by e.s.r. spectroscopy.

EXPERIMENTAL

Materials

DiPF was commercially available and was distilled under reduced pressure. 1,3,5-Triphenylverdazyl was synthesized and purified as described in the literature[15]: $\lambda_{max} = 719$ nm and $\varepsilon_{max} = 4300$ (lit.[15]: $\lambda_{max} = 720$ nm and $\varepsilon_{max} = 4330$). Commercial 1,1′-azocyclohexane-1-carbonitrile (ACN) was recrystallized from methanol. t-Butyl peroxide (TBP) was distilled under reduced pressure.

Scavenging experiment

The propagating radical was scavenged in an H-shaped sealed tube equipped with a stopcock with Teflon plug as illustrated in *Figure 1*. The polymerization mixture was irradiated by a 100 W high-pressure mercury lamp for a certain period, and immediately after that or after

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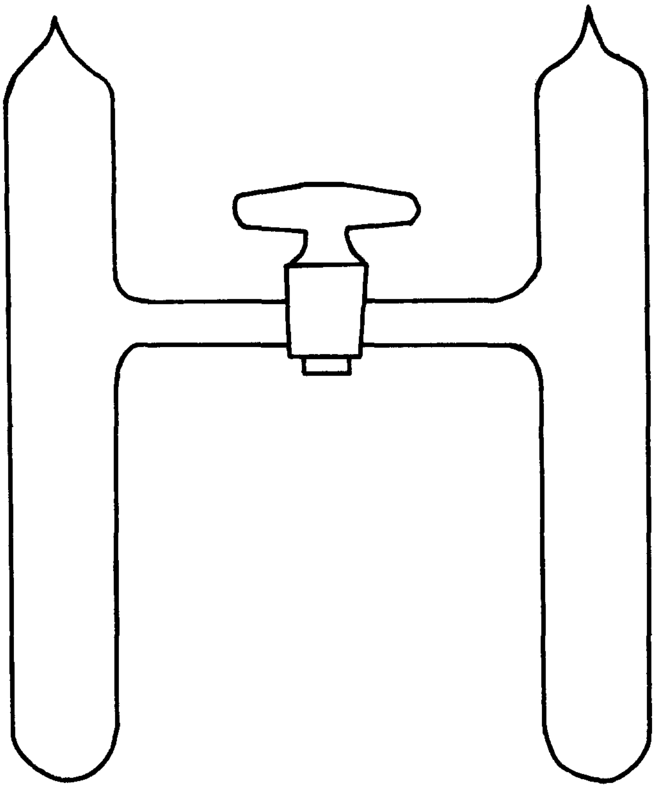

Figure 1 Sealed ampoule used for scavenging poly(DiPF) radical with the verdazyl

a prescribed interval a benzene solution of the verdazyl in the other arm was added to the polymerization mixture through the stopcock for determination of k_p and k_t, respectively. The concentration of unchanged verdazyl was calculated from the absorbance at 720 nm; the visible spectra were recorded on a Shimadzu UV-240 spectrophotometer.

Rotating sector experiment

Determination of the average lifetime of propagating radical (τ) was attempted by the rotating sector method at 40°C; a disc with two 45° cut-outs in symmetrical positions and a 400 W high-pressure mercury lamp were employed. The polymerization in benzene ([DiPF] = 3.29 mol dm^{-3}) was run in a dilatometer of ~10 ml with capillary tubing of ~1 mm inside diameter.

E.s.r. spectroscopy

All the e.s.r. spectra were taken by a JEOL EF2XG spectrometer operating at X band. A sample tube of 3 or 5 mm outer diameter containing DiPF, benzene and TBP sealed under vacuum was irradiated by a 1 kW xenon lamp in the cavity.

RESULTS AND DISCUSSION

Propagation rate constant

Evaluation of the rate constants for the elementary reactions was first attempted by the rotating sector method. The polymerization in benzene sensitized with ACN was initiated by u.v. irradiation: [DiPF] = 3.29 mol dm^{-3} and [ACN] = 0.11 mol dm^{-3}. Based on a plot of the ratio of intermittent (R_{sp}) and continuous rates (R_{cp}) against the flash time, τ was determined graphically as the difference between the theoretical curve for τ of 1 s and one fitting the experimental points by a horizontal shift. The sector used had two 45° cut-outs in symmetrical positions. The value of R_{sp} would decrease from $R_{cp}/2$ to $R_{cp}/4$ with extension of flash time if R_{cp} was proportional to the square root of the initiation rate.

However, change of flash time from 1 s to 3 h brought about only a slight decrease in R_{sp} as shown in *Figure 2*, and τ was approximated as 2 h. Under similar conditions, τ for DEF has been estimated as 166 s, and the long-lived nature of poly(DiPF) radical is noted.

Alternatively, the propagating radical was quantitatively scavenged with an appropriate amount of the verdazyl. DiPF monomer was consumed solely by propagation involving addition of poly(DiPF) radical to the monomer, and hence at low conversion (< 10%) the absolute value of k_p can be calculated from the polymerization rate (R_p):

$$R_p = k_p[\text{DiPF}\cdot][\text{DiPF}]$$

where [DiPF·] denotes the concentration of poly(DiPF) radical. After polymerization for a certain period, the verdazyl solution was admitted to the polymerization mixture under vacuum. The absorbance due to the verdazyl was diminished by rapid reaction with the polymer radical, as confirmed by instantaneous consumption of the verdazyl. Fast reactions of poly(DRF) radical with BNB[8], styrene (St)[10] and methyl methacrylate (MMA)[10] may support the quantitative scavenge with the verdazyl. The concentration of the poly(DiPF) radical was calculated from the decrease in the absorbance after normalization for an increase in volume.

Table 1 summarizes the experimental conditions and the radical concentrations determined. Poly(DiPF) radical existed at a concentration as high as 10^{-5}–10^{-4} mol dm^{-3}, in analogy with poly(DEF) radical[7]. The value of R_p was obtained as the slope of the conversion *versus* time plot in *Figure 3*; the linear relations indicate that a steady state was set up throughout the polymerizations. The absolute value of k_p was calculated from R_p:

$$k_p = 0.31 \pm 0.07 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad \text{at } 30°\text{C}$$

Such a small k_p value has never before been evaluated in a homogeneous solution, except for DEF, for which $k_p = 0.015$ dm^3 mol^{-1} s^{-1} at 30°C [7]. Recently k_p values for

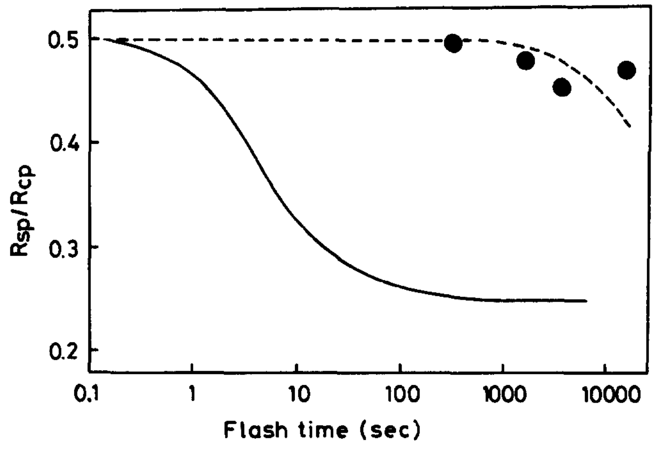

Figure 2 Polymerization of DiPF under intermittent irradiation of u.v. light sensitized with ACN at 40°C: [ACN] = 0.11 mol dm^{-3} and [DiPF] = 3.29 mol dm^{-3}; (——) theoretical curve for τ = 1 s

Table 1 Results of direct determination of the propagating radical concentration in benzene at 30°C

[DiPF] (mol dm^{-3})	[ACN] $\times 10^2$ (mol dm^{-3})	Time (min)	R_p[a] $\times 10^5$ (mol dm^{-3} s^{-1})	[Verdazyl][b] $\times 10^4$ (mol dm^{-3})	[DiPF·] $\times 10^4$ (mol dm^{-3})	k_p (dm^3 mol^{-1} s^{-1})
2.00	10	15	4.9	5.30	1.04	0.24
2.32	5.0	60	5.4	3.04	0.98	0.24
4.94	1.0	5	10.0	5.30	0.54	0.37
4.94	5.0	10	18.6	5.30	1.01	0.37
4.94	5.0	20	18.6	5.30	1.41	0.27
4.94	10	5	25.9	5.30	1.98	0.27
4.94	10	30	25.9	5.30	1.27	0.41
					Average	0.31 ± 0.07

[a] Calculated from conversion–time plot
[b] Concentration of the verdazyl solution added to the polymerization mixture

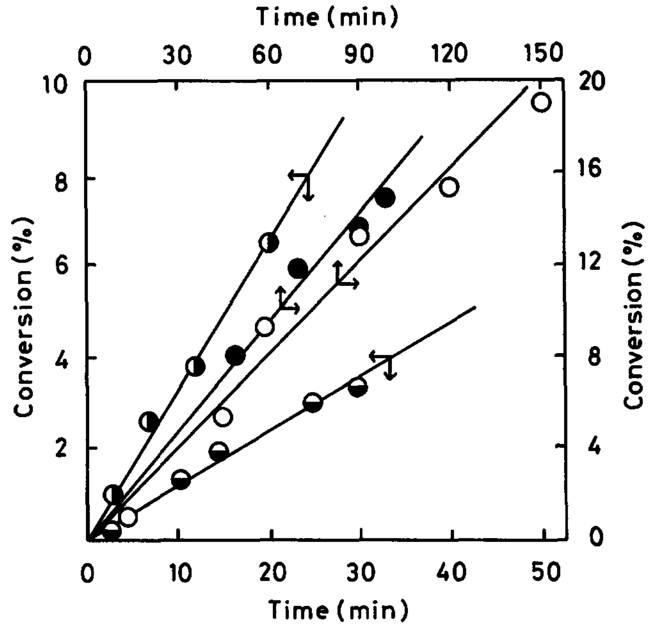

Figure 3 Plot of DiPF conversion *versus* time for polymerization with u.v. irradiation at 30°C: ◑, [DiPF] = 4.94 mol dm^{-3} and [ACN] = 0.10 mol dm^{-3}; ●, [DiPF] = 2.00 mol dm^{-3} and [ACN] = 0.10 mol dm^{-3}; ○, [DiPF] = 2.32 mol dm^{-3} and [ACN] = 0.05 mol dm^{-3}; ◒, [DiPF] = 4.94 mol dm^{-3} and [ACN] = 0.01 mol dm^{-3}

itaconic esters and *N*-cyclohexylmaleimide have been estimated[12–14] to be 1–10 dm^3 mol^{-1} s^{-1}, but the k_p values for DEF and DiPF are even smaller than these. The existence of the radical in such an exceptionally high concentration seems to prove the extremely low reactivities in termination and other reactions by which the radical may lose its activity. 1-Cyano-1-cyclohexyl radical from the sensitizer should disappear before mixing with the verdazyl solution, because of a much shorter lifetime and a much lower steady-state concentration.

The small k_p value for DiPF can be qualitatively interpreted in terms of steric interaction between the bulky substituents of the monomer and the polymer radical during propagation, in agreement with the considerable steric hindrance in the addition of a bulky radical to DEF[16]. As expected from the fast reactions with the verdazyl and other compounds[8,10], the low reactivity of poly(DiPF) radical during polymerization is not due to chemical inertness. Relief of internal strain in the monomer by conversion of the carbon–carbon double bond to a single bond during polymerization could facilitate propagation. Probably a balance between steric hindrance and the relief of internal strain allows propagation of DRF, though the reactants could approach each other to promote bond formation with a limited probability. The larger k_p value for DiPF than for DEF[7] is considered to arise from greater internal strain.

Rate constant for cross-propagation

The reactivities of DiPF and poly(DiPF) radical towards the reference polymer radical and monomer, respectively, were estimated as rate constants for cross-propagation in copolymerization. Monomer reactivity ratios, r_1 and r_2, for copolymerizations of DiPF (M_1) with styrene (St) and methyl acrylate (MA) (M_2) have been reported:

$$r_1 = 0.06 \text{ and } r_2 = 0.40 \qquad \text{for } M_2 = \text{St}^{17}$$

$$r_1 = 0.09 \text{ and } r_2 = 1.88 \qquad \text{for } M_2 = \text{MA}^{18}$$

The absolute values of k_p ($= k_{22}$) for St and MA have been determined as 55 and 720 dm^3 mol^{-1} s^{-1} at 30°C[19], respectively, and hence the rate constants for cross-propagation k_{12} ($= k_{11}/r_1$) and k_{21} ($= k_{22}/r_2$) were obtained as summarized in *Table 2* together with the data for DEF and poly(DEF) radical.

Monomeric DiPF and DEF are rather more reactive towards poly(St) radical than St and MA. However, poly(DRF) radicals were found to be much less reactive

Table 2 Rate constants for propagation and cross-propagation at 30°C

Polymer radical	Monomer	Rate constant (dm^3 mol^{-1} s^{-1})
DiPF	St	5.17[a]
DiPF	MA	3.44[a]
DEF	St	0.75[a]
MA	DiPF	383[b]
MA	St	4000[b,c]
MA	MA	720
St	DiPF	138[b]
St	DEF	190[b]
St	MA	73[b,c]

[a] Evaluated as k_{12} from r_1 and k_{11}
[b] Evaluated as k_{21} from r_2 and k_{22}
[c] For copolymerization of MA(M_1)-St(M_2), $r_1 = 0.18$ and $r_2 = 0.75$[17]

towards St and MA monomer than the polymer radicals from the vinyl monomers by factors of 10^3–10^4. The observed tendencies imply that the small k_p values for DiPF and DEF can be ascribed to the inherently less reactive nature of their polymer radicals, especially towards a sterically hindered monomer, probably due to steric hindrance around the radical centre[9] and rigid main chain as expected from the molecular model[5].

Termination rate constant

After interruption of u.v. irradiation of the polymerization mixture, among the elementary reactions, propagation and mutual reaction of poly(DiPF) radical proceeded in the dark. As already mentioned, the termination rate of DiPF seemed to be too slow for the rotating sector experiment. Owing to the long-lived nature, we evaluated k_t by means of the scavenger method or e.s.r. spectroscopy in the dark. If poly(DiPF) radical was consumed exclusively by bimolecular termination under these conditions, the second-order rate equation for termination would be:

$$[\mathrm{DiPF}\cdot]_0/[\mathrm{DiPF}\cdot]_t = 1 + k_t[\mathrm{DiPF}\cdot]_0 t$$

where $[\mathrm{DiPF}\cdot]_0$ and $[\mathrm{DiPF}\cdot]_t$ denote the radical concentrations at reaction times 0 and t, respectively. Close adherence to second-order kinetics with respect to the radical concentration is confirmed by the linear relationship illustrated in *Figure 4*. Apparently, poly(DiPF) radical lost its activity by mutual reaction, which was so slow that about 25% of the radicals still remained after being left in the dark for 7 h.

The absolute value of k_t was calculated from the slope of the straight line with unit intercept on the ordinate using the initial concentration of the radical:

$$k_t = 0.84\ \mathrm{dm^3\,mol^{-1}\,s^{-1}} \quad \text{at } 30°\mathrm{C}$$

This is much smaller than values for vinyl monomers by at least a factor of 10^7, and even smaller than those for the itaconates and maleimide, for which k_t values of the order of 10^4–$10^5\ \mathrm{dm^3\,mol^{-1}\,s^{-1}}$ have been reported[12–14]. The k_t value for DiPF seems to be the smallest of those for radically polymerizable monomers in homogeneous solution.

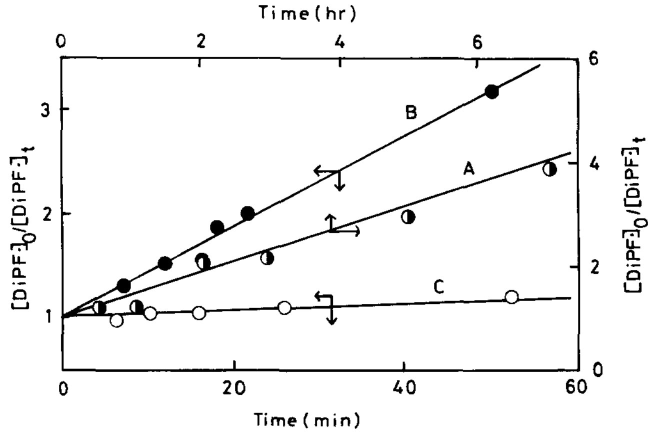

Figure 4 Second-order plot for mutual termination of poly(DiPF) radical based on scavenging with the verdazyl at [DiPF] = 2.30 mol dm^{-3} and [ACN] = 0.10 mol dm^{-3} in benzene (A); amplitude of the e.s.r. spectrum at [DiPF] = 4.94 mol dm^{-3} and [TBP] = 0.10 mol dm^{-3} in bulk (B); and amplitude of the e.s.r. spectrum at [DiPF] = 2.00 mol dm^{-3} and [TBP] = 0.10 mol dm^{-3} in benzene (C)

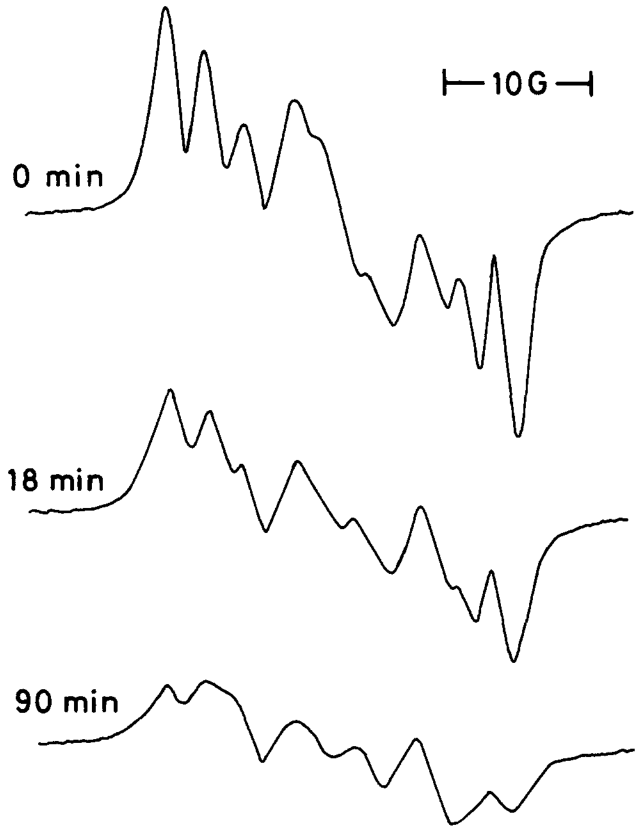

Figure 5 Decrease in intensity of the e.s.r. spectrum due to poly(DiPF) radical after interruption of u.v. irradiation in bulk: [DiPF] = 4.94 mol dm^{-3} and [TBP] = 0.10 mol dm^{-3}

Figure 5 shows the variation in the e.s.r. spectrum of poly(DiPF) radical in the dark. A second-order plot on the basis of the amplitude of the outermost signal is also obtainable as in *Figure 4*, indicating that the slope of the straight line depends on the monomer concentration. Since the slopes corresponding to $k_t[\mathrm{DiPF}\cdot]$ are 7.2×10^{-4} in bulk and $1.9 \times 10^{-4}\ \mathrm{s^{-1}}$ in benzene, the concentrations of poly(DiPF) radical are calculated to be 8.6×10^{-4} and $2.3 \times 10^{-4}\ \mathrm{mol\,dm^{-3}}$, respectively, from the k_t value determined by the scavenger method. Because DiPF monomer is a poor solvent for poly(DiPF), the higher radical concentration estimated in bulk could be ascribed to heterogeneous polymerization. Although the polymerization conditions were not the same in the H-shaped sealed ampoule and the e.s.r. tube, the radical concentrations determined are quite close to those in *Table 1*.

The persistence of poly(DiPF) radical confirmed by the different methods seems to be due mainly to the nature of the polymer chain. The 1,2-dicarbethoxy-1-ethyl radical (succinyl radical), which is structurally akin to the terminal unit of poly(DEF) radical, has been detected at low temperatures as short-lived species[20], and no spectroscopic similarity with poly(DEF) radical was found. Furthermore, the rate constant for the dimerization reaction of triphenylmethyl radical, 374 dm^3 mol^{-1} s^{-1} at 30°C[21], is much greater in magnitude than k_t for DiPF. In this regard, not only the considerable steric hindrance around the radical centre but also the less flexible nature of poly(DiPF) chain[5] leads to extremely slow mutual reaction of the polymer radical.

On the basis of the k_t value determined, the time required to reach the steady state of the poly(DiPF) radical can be estimated using the kinetic equation for ordinary radical polymerization[22]. Such a calculation reveals that the concentration of poly(DiPF) radical increases slowly to attain the steady-state concentration, of the order of 10^{-4} mol dm^{-3}, unlike the following observations in DiPF polymerization. A conversion–time plot for the polymerization gave a straight line through the origin as in *Figure 3*, and the e.s.r. spectrum of poly(DiPF) radical reached a stationary state within a short time after the start. We conclude that the termination rate expected from the k_t value determined by the scavenger method is much slower than the actual rate.

Decomposition of ACN was not induced under the conditions for k_t determination by the scavenger method, but primary radical termination (PRT) may be involved in the rotating sector experiment and in the usual polymerization reaction, in which initiation, propagation and all of the termination processes take place simultaneously as the elementary reaction. When the propagating radical loses its activity solely by the mutual reaction of poly(DiPF) radical, the degree of polymerization ($\bar{P}_n$) of the resulting polymer is expressed by:

$$\bar{P}_n = R_p/R_t = k_p[\text{DiPF}]/(k_t[\text{DiPF}\cdot])$$

R_p may be of the order of 10^{-4} mol dm^{-3} s^{-1} on the basis of the numerical values in *Table 1* and the estimate of $\bar{P}_n$ is of the order of 10^4, which seems to be considerably higher than that of the polymer actually isolated by one or two orders[4]. This discrepancy may arise from the contribution of PRT, and the denominator of the above equation should involve the PRT term:

$$\bar{P}_n = k_p[\text{DiPF}]/(k_t[\text{DiPF}\cdot] + k_{\text{PRT}}[\text{R}\cdot])$$

where $[\text{R}\cdot]$ denotes the concentration of the primary radical. Comparison of $\bar{P}_n$ for the polymer with the estimate shows that the rate of PRT is approximately more than 10 times that of the mutual termination of poly(DiPF) radical.

The type of termination process that could be monitored is dependent on the experimental technique. The propagating radical produced in the initiation lost its activity through the mutual reaction of poly(DiPF) radical and PRT in the rotating sector experiment. However, the termination rate determined by the scavenger method represents merely the rate of the mutual reaction of poly(DiPF) radical. The large difference in the k_t values for DEF[7], 164 dm^3 mol^{-1} s^{-1} at 30°C, and DiPF may be due to the contribution of PRT, because the rate constants for DEF and DiPF were determined by the rotating sector and scavenger methods, respectively.

A study of polymerization involving PRT indicated that the kinetic order with respect to initiator should be smaller than 0.5[23]. Usually PRT consists of the participation of a relatively stable radical in termination. In DRF polymerization, however, the much less reactive poly(DRF) radical reacts with the reactive primary radical. The same kinetic equation predicts that the square-root dependence could be valid for DRF polymerization involving PRT, depending on the magnitudes of the rate constants of the individual elementary reactions and the concentration of the reactants.

CONCLUSIONS

During polymerization of diisopropyl fumarate, the propagating radical was found to be present in a high concentration, of the order of 10^{-4} mol dm^{-3}. The absolute rate constants for propagation and mutual termination of the polymer radical (k_p and k_t, respectively) were determined by a quantitative scavenge with a stable free radical: $k_p = 0.31 \pm 0.07$ and $k_t = 0.84$ dm^3 mol^{-1} s^{-1} at 30°C. These rate constants, which are exceptionally small in magnitude, were accounted for by severe steric hindrance and slow diffusion of the polymer radical.

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