Polymer Bulletin 26, 543–548 (1991)

Polymer Bulletin

Contribution of primary radical termination to radical polymerization of diethyl fumarate estimated from absolute rate constants

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Summary

Diethyl fumarate was radically polymerized under UV irradiation and concentration of the propagating radical was determined to be of the order of 10^{-5} mol/L by scavenge with a stable free radical. The absolute rate constant for propagation (k_p) was evaluated from the overall rate of polymerization at 30°C: $k_p = (2.9 \pm 0.3) \times 10^{-2}$ L/mol•s. The rate constant for mutual termination of the polymer radical (k_t) was calculated from the decreasing rate of the radical concentration in the dark: $k_t = 8.0$ L/mol•s. The k_t value determined is one twentieth of that evaluated previously by a rotating sector method. This discrepancy is accounted for by contribution of much faster primary radical termination.

Introduction

Radical high polymerization of dialkyl fumarate (DRF) has attracted much attention, because of peculiar features of polymerization to poly(substituted methylene)(1-4). One of the features of DRF polymerization is faster polymerization of DRF with the bulkier ester alkyl group to the higher molecular weight polymer, and importance of the steric effect relating to the size of the alkyl group has been noted.

We have determined the rate constants of propagation (k_p) and termination (k_t) for diethyl fumarate (DEF)(5) and diisopropyl fumarate (DiPF)(6) by a rotating sector method and a quantitative scavenge of the propagating radical of which life-time was too long to be evaluated by the rotating sector method, respectively. The ESR signals due to the polymer radicals presenting in extraordinarily high concentrations were readily detected, and bimolecular termination of the radical from the fumarate was followed by ESR spectroscopy. According to these experiments, $k_p = 0.015$ and $k_t = 164$ L/mol•s for DEF(5), and $k_p = 0.31$ and $k_t = 0.84$ L/mol•s for DiPF(6) have been evaluated at 30°C.

These rate constants are much smaller than those of most of conventional monomers of which k_p and k_t are of the orders of 10^2 and 10^7 L/mol•s, respectively. Polymerizations of dialkyl itaconates(7,8) and N-cyclohexylmaleimide(9) have also been featured by the presence of the polymer radical in high concentrations and the small rate

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*To whom offprint requests should be sent constants for propagation and termination. Although the substituents of DRF and poly(DRF) radical as well as those of the itaconates and maleimide monomers and their polymer radicals hinder considerably the elementary reactions, a balance of the propagation and termination rates allows polymerization irrespective of the magnitudes of the respective rate constants. Therefore these polymerizations have exemplified a new possibility in polymerization of monomers bearing large substituents.

In the course of our studies on DRF polymerization, we have suspected a considerable participation of the primary radical from the initiator to termination, due to a low reactivity of DRF toward a bulky radical(10). To determine the k_t value for DiPF, the polymerization sensitized with 1,1'-azobiscyclohexane-1-carbonitrile (ACN) was initiated with UV irradiation, and a decrease in the radical concentration after interception of the irradiation was monitored by scavenge with 1,3,5-triphenylverdazyl (TPV)(11) or ESR spectroscopy. Since ACN used as a sensitizer thermally decomposes quite slowly at 30°C(12), we were able to determine the rate constant for solely the bimolecular reaction of poly(DiPF) radical in the dark. Probably a considerable difference in the k_t values for DEF and DiPF, 164 and 0.84 L/mol•s, could involve contribution of primary radical termination (PRT).

In the present work to estimate the role of PRT in DEF polymerization, we carried out determination of the k_p and k_t values for DEF based on the quantitative scavenge of the propagating radical with TPV. Comparison of the k_t values determined by the different methods could reveal participation of the primary radical to the termination in DEF polymerization.

Experimental

Commercial DEF was distilled under reduced pressure. ACN was recrystallized from methanol. TPV was prepared and purified as described in the literature(11). Polymerization was initiated with irradiation of a 100 W high pressure mercury lamp (Toshiba SHL 100) in bulk, and the overall rate of the polymerization (R_p) was calculated from the weight of the polymer isolated.

The quantitative scavenge of the polymer radical was performed using a H-shaped sealed ampoule equipped with a stop-cock with a Teflon plug. The polymerization mixture in an arm was irradiated with UV light and after a certain period, a benzene solution of TPV in another arm was added to the polymerization mixture through the stop-cock. The concentration of the active radical was calculated from a decrease in the absorbance of TPV at 720 nm after normalization for an increase in volume.

Results and Discussion

Polymerizations of DEF under different conditions were already reported, and the kinetic order with respect to DEF was found to be 1.66-1.72(5). The kinetic order higher than unity was considered to arise from a relatively slow addition of the primary radical to DEF and/or a decrease in k_t value with increasing chain length of the polymer radical. However, the kinetic order with respect to the initiator, 2,2'-azobisisobutyronitrile (AIBN), was found to decrease from 0.5 for the bulk polymerization at 30 and 60 °C to less than 0.5 by a decrease in DEF concentration and by raising the temperature from 60 to 70 °C(5). These changes in the experimental conditions seemed to facilitate PRT resulting in the deviation from the standard kinetic orders with respect to AIBN(13).

Propagation of DEF involves addition of poly(DEF) radical to monomeric DEF, and k_p is calculated from R_p and the radical concentration ([DEF•]):

$$k_p = R_p/([\mathrm{DEF}][\mathrm{DEF}\bullet]) \qquad [1]$$

If the radical concentration was determined, evaluation of k_p could be done irrespective of initiation and termination processes. Fig. 1 shows a linear relation between conversion and polymerization time for R_p determination. TPV has been used to quantitative scavenge of poly(DiPF) radical(6), and the same scavenger was employed for DEF polymerization. A benzene solution of an appropriate amount of TPV was added to the equal volume of the polymerization mixture containing the active polymer radical under vacuum

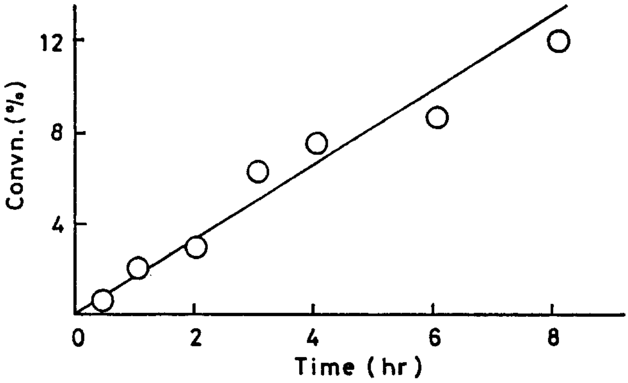
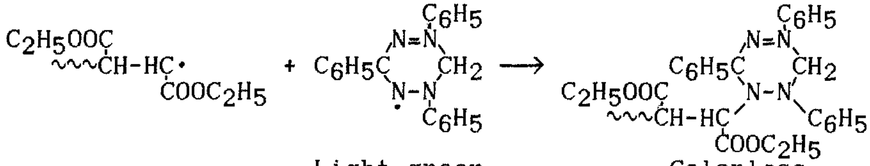


Fig. 1. Conversion-time plot for DEF polymerization initiated with UV irradiation in the presence of ACN at 30 °C: [DEF] = 6.19 mol/L and [ACN] = 0.05 mol/L

Table 1. Concentration of poly(DEF) radical and k_p value

Time (hr)	[DEF•] x 10^4 (mol/L)	k_p x 10^2 (L/mol•s)
0.50	1.24	3.4
0.50	1.55	2.7
0.75	1.58	2.6
1.00	1.33	3.1
Average	1.43 ± 0.08	2.9 ± 0.3

a) [DEF] = 6.07 mol/L, R_p = 2.54 x 10^{-5} mol/L•s, and [TPV] = 1.850 x 10^{-4} mol/L and TPV was allowed to react with poly(DEF) radical:



Concentration of the propagating radical was determined at different polymerization times and the results of the scavenge experiment are summarized in Table 1. The values of k_p evaluated from eq. [1] are shown in this table.

The scavenger method was also used to measure the radical concentration for k_t determination. After the polymerization with UV irradiation for a certain period, the polymerization ampoule was left in the dark for a prescribed time, and then the concentration of the radical remaining was determined. Fig. 2 shows the second order rate plot according to eq. [2]:

$$[DEF\cdot]_0/[DEF\cdot]_t = 1 + k_t t[DEF\cdot] \qquad [2]$$

where subscripts 0 and t are refer to the reaction times. A linear relation obtained by a plot of $[DEF\cdot]_0/[DEF\cdot]_t$ versus time evidences the fact that the polymer radical loses its activity solely by a bimolecular reaction.

Table 2 compares the k_p and k_t values determined by the different methods. The k_p value obtained in the present study agrees with that determined by the rotating

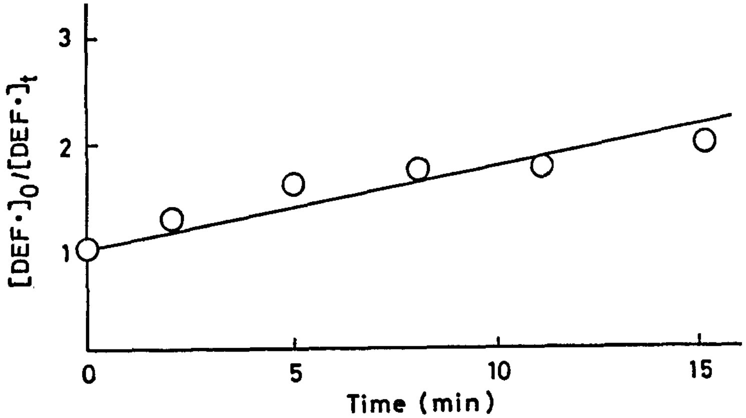


Fig. 2. Second order plot for mutual termination of poly(DEF) radical at 30 °C

Table 2. Absolute rate constants determined by rotating sector method and by quantitative scavenge at 30 °C

Method	Rate constants (L/mol•s) k_p	Rate constants (L/mol•s) k_t	Ref.
Sector	0.015	164	5
Scavenger	0.029	8.0	This work

sector method(5), and the k_t value evaluated by the scavenger method is 1/20 of that determined by the sector method(5).

The value of k_t for DEF is smaller than that for DiPF by a factor of 9.5. Since DiPF polymerizes faster to higher moleculer weight than DEF, the smaller k_t for DiPF might be ascribed to dpendence of k_t on the chain length of the polymer radical. A large difference in the k_t values in Table 2 is considered to ascertain a contribution of PRT. The greater k_t value determined by the sector method could involve the contribution of PRT. However, we experimentally confirmed the apparent dependency of R_p on the square root of AIBN concentration, and the k_p and k_t were evaluated according to the standard kinetic equation of radical polymerization(5):

$$R_p = (R_i/k_t)^{0.5}k_p[\mathrm{DEF}] \qquad [3]$$

A change in R_p under intermittent irradiation of UV light was observed from 0.50 to 0.25 of R_p under continuous irradiation depending on flash time in the rotating sector experiment(5), indicating that R_p was proportional to the square root of the initiation rate, R_i. Thus except the difference in the k_t values in Table 2, the results of the sector and related experiments did not exhibit the contribution of PRT(5).

The following reactions are considered as termination in DEF polymerization:

$$\mathrm{DEF}\bullet + \mathrm{DEF}\bullet \xrightarrow{k_t} \mathrm{Polymer}$$

$$\mathrm{DEF}\bullet + \mathrm{R}\bullet \xrightarrow{k_{PRT}} \mathrm{Polymer}$$

The rates of the respective reactions are

$$R_t = k_t[\mathrm{DEF}\bullet]^2$$

and

$$R_{PRT} = k_{PRT}[\mathrm{DEF}\bullet][\mathrm{R}\bullet]$$

where DEF• and R• are poly(DEF) radical and the 1-cyano-1-cyclohexyl radical, respectively.

Although termination consists of the bimoleuclar reaction of poly(DEF) radical and PRT, the k_t value determined by the sector method was approximated by the rate constant for solely the bimolecular termination:

$$R_t = k_{APP}[\mathrm{DEF}\bullet]^2 \fallingdotseq k_t[\mathrm{DEF}\bullet]^2 + k_{PRT}[\mathrm{DEF}\bullet][\mathrm{R}\bullet] \qquad [4]$$

and

$$k_{APP} \fallingdotseq k_t + k_p k_{PRT}[\mathrm{DEF}][\mathrm{R}\bullet]/R_p \qquad [5]$$

where k_{app} corresponds to the termination rate constant determined by the sector method. Substituting the numerical values already given into eq. [5], we obtained $k_{PRT} = 2.3 \times 10^{-3}/[\mathrm{R}\bullet]$ L/mol•s. In conventional vinyl polymerization, the rate dermining step of initiation is decomposition of the initiatior, and the second term of eq. [4] is not considered. Since the primary radical was not detected by ESR spectroscopy, concentration of the cyclohexyl radical could be of the order of 10^{-8} mol/L or below. Accordingly the estimate of k_{PRT} is not less than 2.3×10^5 L/mol•s, which is close to the avearage of k_t and the rate constant of bimolecular reaction of the 1-cyano-1-cyclohexyl radical, 3.6×10^9 L/mol•s(14). The large difference between the k_t

and k_{PRT} values is considered to suggest chain length dependencey of the rate constants for the reactions involving poly(DRF) radical.

When PRT contributes to DEF polymerization, an increase in the initiator concentration brings about increases in the concentrations of poly(DEF) radical and of the primary radical to different extents. Accordingly $[R\cdot]/R_p$ could be remained constant depending on the concentration range of the initiator. In such a case, R_p appeares to be proportional to the square root of the initiator concentration.

Since k_{APP} = 164 L/mol•s, the first and second terms of eq. [4] are estimated to be 1.6×10^{-7} and 3.3×10^{-7} mol/L, respectively, at $[DEF\cdot] = 1.43 \times 10^{-4}$ mol/L which is the average of the concentrations of poly(DEF) radical in Table 1. Although a considerable contribution of PRT is predicted in DEF polymerization, the termination rate was found to balance with the propagation rate leading to poly(DEF) formation.

Acknowledgment

A part of this work was supported by a Grant-in-Aid of Scientific Research on Priority Areas from The Ministry of Education, Science, and Culture.

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Accepted May 10, 1991 S