9. The Effect of Bulky Ester Alkyl Substituents on Rate Constants of Radical Polymerization of Dialkyl Fumarates

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Abstract: The radical polymerization of dialkyl fumarates bearing various ester alkyl groups was investigated to evaluate the propagation and termination rate constants \((k_p\) and \(k_t\)) by means of electron spin resonance spectroscopy. It was revealed that the introduction of tert-butyl ester group promoted the polymerization reactivity not only the retardation of the termination, but also by the acceleration of the propagation despite of steric repulsion by the bulky substituents. The latter was interpreted by the stereospecific propagation leading to the diisotactic polymer formation.

Key words: 1,2-Disubstituted ethylene; dialkyl fumarate; propagation; termination; rate constants; tacticity.

Introduction. In the course of studies on the polymerization of dialkyl fumarates (DRF), it has been revealed that DRF bearing a bulky ester alkyl group homopolymerizes readily to give a high molecular weight polymer. The polymerization reactivity, deduced from polymerization rates and molecular weights of the resulting polymers, varies sensitively with the structure of the ester alkyl groups. It increases with the increasing bulkiness of the alkyl groups, e.g. di-tert-butyl fumarate (DtBF) has the highest polymerization reactivity, being conflicting with ordinary steric hindrance in organic chemistry that a reactivity decreases as steric bulkiness of the substituents increases. It has been interpreted by a balance of elementary reactions consisting of initiation, propagation, termination, and chain transfer. In a recent decade, electron spin resonance (ESR) spectroscopy has been applied for the determination of propagation and termination rate constants \((k_p\) and \(k_t\)) during the radical polymerizations of several vinyl monomers. The polymerization and termination rates are defined as follows;

\[
R_p = -d[M]/dt = k_p [P•][M] \tag{1}
\]

\[
R_t = -d[P•]/dt = k_t [P•]^2 \tag{2}
\]

where \(M\) and \(P•\) are the monomer and the polymer radical.

In the radical polymerization of DRF, the propagating radicals are observed at a considerably high concentration under ordinary polymerization conditions because bimolecular termination is suppressed on account of less mobility of the segments of semiflexible polymer chain due to the sterically hindered substituted polymethylene structure. We have found that the enhancement of the polymerization reactivity by the introduction of tert-butyl group as the ester alkyl substituents is due to not only the suppressed termination, but also acceleration of propagation from the kinetic study by ESR spectroscopy. This communication deals with the kinetic study of the polymerization...
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of DRF bearing various alkyl ester groups (Scheme 1) and the determination of $k_p$ and $k_t$ by the ESR method. The effects of the ester alkyl groups on $k_p$ are discussed in relation with the stereochemistry of the polymer produced.

**Experimental.** DRF were prepared by acid-catalyzed esterification of maleic anhydride with respective alcohol and subsequent isomerization with morpholine except for the tert-butyl esters, which was from maleic acid and isobutene. They were purified by distillation under reduced pressure or recrystallization from methanol. Dimethyl 2,2'-azobis(isobutyrate) (MAIB) and 2,2'-azobis(2,4,4-trimethylpentane) (ATMP) were recrystallized from hexane.

Polymerization was carried out in a degassed glass tube in the presence of an initiator in benzene at 60°C. After polymerization, the contents of tube were poured into a large amount of precipitant to isolate the polymer. The polymer yield was determined gravimetrically.

ESR measurement was carried out at 60°C in a degassed sealed ESR tube (5-mm diameter) by using a Bruker ESP-300 spectrometer. Sensitivity of the spectrometer changing along with conversion during polymerization was corrected with Mn²⁺. UV-vis spectra were recorded on a Shimadzu UV-160 photometer at 60°C.

**Results and discussions.** The radical polymerizations of DRF with various ester alkyl groups were carried out with MAIB in benzene at 60°C. In Table I, the polymerization rates ($R_p$) are listed, which were determined from an initial slope of the time-conversion relationship. DRF has $R_p$ depending on the structure of the ester alkyl groups in a wide range of $(0.1-5) \times 10^{-5}$ mol/L·s. The concentration of the propagating radical ([P·]) was

![Scheme 1](attachment:image.png)

Table I. Determination of propagation and termination rate constants for radical polymerization of DRF in benzene at 60°C

<table>
<thead>
<tr>
<th>DRF</th>
<th>Alkyl substituent</th>
<th>$R_p \times 10^5$ (mol/L·s)</th>
<th>$[P·] \times 10^5$ (mol/L)</th>
<th>$k_p$ (L/mol·s)</th>
<th>$R_t \times 10^7$ (L/mol·s)</th>
<th>$k_t$ (L/mol·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMF</td>
<td>Methyl</td>
<td>0.14</td>
<td>2.39</td>
<td>0.058</td>
<td>2.46</td>
<td>430</td>
</tr>
<tr>
<td>DEF</td>
<td>Ethyl</td>
<td>0.41</td>
<td>1.93</td>
<td>0.21</td>
<td>2.07</td>
<td>560(510)</td>
</tr>
<tr>
<td>DNPF</td>
<td>Neopentyl</td>
<td>0.18</td>
<td>6.32</td>
<td>0.028</td>
<td>1.76</td>
<td>44</td>
</tr>
<tr>
<td>DMOEF</td>
<td>2-Methoxyethyl</td>
<td>0.41</td>
<td>2.23</td>
<td>0.19</td>
<td>1.92</td>
<td>330</td>
</tr>
<tr>
<td>DCIEF</td>
<td>2-Chloroethyl</td>
<td>0.62</td>
<td>2.40</td>
<td>0.26</td>
<td>1.86</td>
<td>320</td>
</tr>
<tr>
<td>DiPF</td>
<td>Isopropyl</td>
<td>2.21</td>
<td>4.78</td>
<td>0.46</td>
<td>2.30</td>
<td>100(80)</td>
</tr>
<tr>
<td>DCHF</td>
<td>Cyclohexyl</td>
<td>4.17</td>
<td>6.91</td>
<td>0.60</td>
<td>1.90</td>
<td>40</td>
</tr>
<tr>
<td>DBF</td>
<td>tert-Butyl</td>
<td>5.14</td>
<td>8.49</td>
<td>0.61</td>
<td>2.13</td>
<td>30</td>
</tr>
<tr>
<td>MtBF</td>
<td>Methyl tert-Butyl</td>
<td>0.95</td>
<td>4.06</td>
<td>0.23</td>
<td>2.53</td>
<td>150</td>
</tr>
<tr>
<td>iPBF</td>
<td>Isopropyl tert-Butyl</td>
<td>4.63</td>
<td>9.07</td>
<td>0.51</td>
<td>2.11</td>
<td>26</td>
</tr>
</tbody>
</table>

a [DRF]=1 mol/L, [MAIB]=0.02 mol/L.
b Determined with $k_p=R_p/([P·][M]).$
c Determined with $k_t=(2k_p[MAB])/[P·]^2$. The values in parentheses indicate those which were determined with $-d[P·]/dt=k_t[<P·>^2$ by analysis of after-effect.
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determined by comparing an integral of the spectrum of the poly(DRF) radical with that of a solution of known concentration of 1,3,5-triphenylverdazyl (TPV) as a stable radical, followed by the correction with a sensitivity of the spectrometer which increases along with the conversion\(^6\) during the polymerization of DiPF, iPtBF, DtBF and DCHF. The \([P•]\) were not corrected for the other polymerizations because of the small \(R_p\).

The change of \([P•]\) in the course of the polymerization is shown in Fig. 1. The \([P•]\) increased with the time in an initial period of the polymerization and reached a steady-state concentration \([2\times 10^{-5} \text{ mol/L}]\) after a certain time. The period of the pre-effect observed for the DRF polymerization was considerably long as about ten or much more minutes, being different from that within a few minutes for ordinary polymerizations.\(^14\) Thus, in the DRF polymerization, the non-steady state polymerization can directly be observed without any special techniques such as a rotating sector and any assumptions because of its long time scale of the pre-effect.

By using of the \([P•]\) at a steady-state and \(R_p\), \(k_p\) was estimated according to eq. 3.

\[
k_p = R_p/([P•][M])
\]

As shown in Table I, DRF with a bulkier ester alkyl group has larger \(k_p\); e.g. DtBF (0.61 L/mol-s) > DiPF (0.46) > DEF (0.21) > DMF (0.058). For DRF with different alkyl groups in the same molecule, \(k_p\) is between those for two DRF which have same alkyl groups, e.g. \(k_p\) of iPtBF and MtBF (0.51 and 0.23 L/mol-s, respectively) are smaller than that of DtBF and larger than those of DMF or DiPF. This result is not consistent with the steric hindrance of the ester substituents in propagation. It has been found that \(k_p\) has no simple correlation with respect to steric and polar factors, Taft's steric and polar substituent constants, \(E_s\) and \(a^p\).

The \(k_p\) of DRF is significantly influenced with an addition manner, i.e. meso and racemo additions. The absolute rate constant for the meso and racemo additions (\(k_m\) and \(k_r\), respectively) for the radical polymerization of DRF is evaluated by the combination of \(k_p\) with the probability of meso (or racemo) addition (\(P_m\) or \(P_r\)), which is determined from the tactivity of poly(DRF), as follows\(^17\):

\[
k_p = P_m k_m + P_r k_r
\]

\[
P_m/P_r = k_m/k_r
\]
The tacticities of poly(DRF) have already been clarified for the methyl, isopropyl, and tert-butyl esters. The probability of the meso addition, \( P_m \), are 0.73, 0.57, 0.54, and 0.47 for the DtBF, MtBF, DiPF, and DMF polymerizations, respectively.\(^{10}\) The \( k_m \) for the DtBF polymerization was recalculated by using the \( k_p \) value determined in this work to be 0.74 L/mol-s, which is larger than those for the other DRF, i.e. 0.054, 0.23, and 0.46 L/mol-s for DMF, MtBF, and DiPF, respectively. It suggests an energetic preference at the transition state of the meso propagation in the DtBF polymerization on account of a certain particular conformation, probably a helical chain structure.\(^{18}\)

\( k_t \) was estimated from the following equation, which was derived from a steady state equation with respect to the radical concentration.

\[
kt = 2k_d/[\text{MAIB}]/[P^-]^2
\]  

(6)

where \( k_d \) and \( f \) are the decomposition rate and the efficiency of the initiator. The initiation rate (\( R_i = 2 k_d/[\text{MAIB}] \)) was determined by means of the primary radical trapping method with TPV.\(^{6}\) \( f \) were calculated to be 0.55-0.75 by using the \( k_d \) value reported (8.4×10\(^{-4}\) s\(^{-1}\)).\(^{19}\) These results indicate that \( k_t \) decreases as the bulkiness of the ester group increased in the following order: DtBF (30 L/mol-s) < DiPF (100) < DEF (560) = DMF (430), as was expected. An analysis of the after-effect in the photopolymerization after an interception of UV irradiation gave similar \( k_t \), where ATMP, which does not decompose at 60°C without UV irradiation was used as a photoinitiator.

Fig. 2 shows a plot of log \( k_p \) with log \( k_t^{0.5} \) for various acrylic monomers, which were determined by similar ESR methods.\(^{5-10}\) It was found that both \( k_p \) and \( k_t \) of DRF are smaller than those of other monomers; for example, \( k_p \) of DRF are about 10\(^2\) times smaller than that of alkyl methacrylate (RMA) including methyl methacrylate\(^{5-7}\) and \( k_t \) are 10\(^6\)-10\(^7\) times smaller, but the ratio for \( k_p/k_t^{0.5} \) is enough to homopolymerize to give a high polymer. It the cases of dialkyl itaconates (DRI)\(^{3,9}\) and N-substituted maleimides (RMI),\(^{10}\) when \( k_p \) decreases by the steric effects of the alkyl substituents, \( k_t \) also decreases in a similar fashion. However, in the DRF polymerization the steric bulkiness assists the promotion of polymerization reactivity by both the increase in \( k_p \) and the decrease in \( k_t \), as shown in the tert-butyl substitution, resulting in the polymerization reactivity sensitive to the structure of the ester alkyl substituents.

Fig. 2. Relationship between log \( k_p \) and log \( k_t^{0.5} \) for various acrylic monomers in benzene at 60°C; DRF (○), DRI (□), RMI (△), RMA (●).
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References