

# Effect of the Substituents on Radical Copolymerization of Dialkyl Fumarates with Some Vinyl Monomers

TAKAYUKI OTSU,\* AKIKAZU MATSUMOTO,\* KOHEI SHIRAISHI,<sup>†</sup>  
NAOYUKI AMAYA,<sup>‡</sup> and YASUMI KOINUMA<sup>‡</sup>

Department of Applied Chemistry, Faculty of Engineering, Osaka City University,  
Sugimoto, Sumiyoshi-ku, Osaka 558, Japan

## SYNOPSIS

Radical copolymerization of dialkyl fumarates (DRF) with various vinyl monomers was carried out in benzene at 60°C. The monomer reactivity ratios,  $r_1$  and  $r_2$ , were determined from the comonomer–copolymer composition curves. The relative reactivity of DRFs with various ester substituents toward a polystyryl radical was revealed to depend on both steric and polar effects of the ester groups. It has also been clarified that  $\alpha$ -substituents of the polymer radical have a significant role in addition of DRF, from the comparison of the monomer reactivity ratios determined in copolymerizations with monosubstituted and 1,1-disubstituted ethylenes. The absolute cross-propagation rate constants were also evaluated and discussed. © 1992 John Wiley & Sons, Inc.

**Keywords:** radical copolymerization • dialkyl fumarate • substituent effect • monomer reactivity ratio • steric effect • polar effect

## INTRODUCTION

The structure–reactivity relationships of vinyl monomers in radical polymerization have been investigated on the basis of substitution effects, i.e., polar, resonance, and steric effects.<sup>1,2</sup> Radical copolymerization of 1,2-disubstituted ethylenes is useful for evaluation of monomer reactivity because of a defect of the homopolymerization ability in many cases. Radical copolymerization of dialkyl fumarates (DRF) has been studied by many workers,<sup>3</sup> since Marvel et al. reported that fumarate had higher reactivity than maleate,<sup>4</sup> and Lewis and Mayo et al. discussed the difference of reactivities between the two isomers, i.e., fumarate and maleate, in their systematic copolymerization studies.<sup>5</sup>

We have reported since 1981 that DRF homopolymerizes with a radical initiator to yield high

molecular weight polymers consisting of a substituted polymethylene structure.<sup>6–11</sup> Moreover, it was found that DRF with isopropyl and *tert*-butyl groups had high polymerization reactivity despite the bulky ester alkyl groups because of the decrease in bimolecular termination rate between polymer radicals bearing bulky substituents. The propagation rate constants were also found to be smaller than those for ordinary vinyl monomers on account of the steric hindrance between substituted polymethylenes and sterically hindered DRF monomers.<sup>9–11</sup>

In this article radical copolymerization of DRF with some monosubstituted and 1,1-disubstituted ethylenes were carried out, and the effect of the substituents on monomer reactivity ratios is discussed.

## EXPERIMENTAL

### Materials

Dialkyl maleates were prepared, as described in the previous studies,<sup>6</sup> from maleic anhydride and corresponding alcohols in the presence of an acidic catalyst, and followed by isomerization to DRF with morpholine as an isomerization catalyst, except *tert*-

\* To whom all correspondence should be addressed.

<sup>†</sup> Present address: Department of Industrial Chemistry, Faculty of Engineering, Kinki University, Takaya, Higashi-Hirashima, 729-17, Japan.

<sup>‡</sup> Present address: Tsukuba Research Laboratory, Nippon Oil and Fats Co., Ltd. Tokodai, Tsukuba, Ibaragi, 300-26, Japan.

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alkyl esters which were prepared from fumaroyl dichloride and potassium alkoxides. They were purified by distillation or sublimation. Other monomers and solvents were distilled after ordinary purifications.

### Copolymerization Procedures

Copolymerization was carried out in a sealed glass tube in the presence of 2,2'-azobisisobutyronitrile (AIBN) or 1,1'-azobiscyclohexane-1-carbonitrile (ACN) as a radical initiator. After copolymerization was stopped at a low conversion (<10%), copolymerization mixture in the tube was poured into a large amount of appropriate precipitant to isolate copolymers. The copolymers obtained were purified by repeating reprecipitations. Elemental analysis and  $^1\text{H}$ -NMR spectroscopy were taken for determination of the composition in copolymers. Monomer reactivity ratios were calculated by nonlinear least-squares procedure.<sup>12</sup>

## RESULTS AND DISCUSSION

### Copolymerization Reactivity of DRF

Radical copolymerizations of diisopropyl fumarate (DiPF,  $M_2$ ) with various monosubstituted and 1,1-disubstituted ethylenes ( $M_1$ ) were carried out in benzene at 60°C. The comonomer-copolymer composition curves obtained are depicted in Figure 1(a)–(f); therefrom the monomer reactivity ratios,  $r_1$  and  $r_2$ , were determined and listed in Table I.

Alternating copolymerization of DiPF was observed with electron-donating monomers ( $r_1 \ll 1$ ,  $r_2 \ll 1$ ), e.g., styrene (St) and *N*-vinylcarbazole (VCZ),<sup>13</sup> but DiPF showed a low reactivity toward electron-accepting monomers, methyl acrylate (MA), phenyl acrylate (PhA), and acrylonitrile (AN) ( $r_1 \gg r_2$ ). It has been already reported that dimethyl fumarate (DMF) and diethyl fumarate (DEF) show alternating copolymerization with isobutyl vinyl ether and St.<sup>14</sup> DiPF also copolymerized easily with isobutene (IB), vinyl acetate (VAc), and vinyl chloride (VCl) as a nonconjugative monomer.

Similar copolymerization tendency was also observed in copolymerization with 1,1-disubstituted ethylenes, but the relative reactivity of DiPF was decreased by the existence of the  $\alpha$ -substituents. The detailed discussions on monomer reactivity ratios will appear later.

**Table I.** Monomer Reactivity Ratios for Radical Copolymerization of DiPF ( $M_2$ ) with Vinyl Monomers ( $M_1$ ) in Benzene at 60°C

$M_1$	$Q_1^a$	$e_1^a$	$r_1$	$r_2$
<i>Monosubstituted</i>				
<i>Ethylenes</i>				
VCZ	0.41	1.40	$\sim 0$	$\sim 0$
St	1.0	-0.8	0.40	0.055
MA	0.42	0.60	1.9	0.091
PhA	0.90	0.61	3.4	0.070
AN	1.78	1.20	16	0.20
IB	0.033	-0.96	$\sim 0$	0.42
VAc	0.026	-0.22	0.012	0.90
VCl	0.044	0.20	0.29	0.49
<i>1,1-Disubstituted</i>				
<i>Ethylenes</i>				
MMA	0.74	0.40	23	0.17
MAN <sup>b</sup>	1.12	0.81	85	$\sim 0$
IPAc	0.045	-0.50	0.011	0.67
VDCI	0.36	0.22	48	0.095

<sup>a</sup> Data from Reference 3.

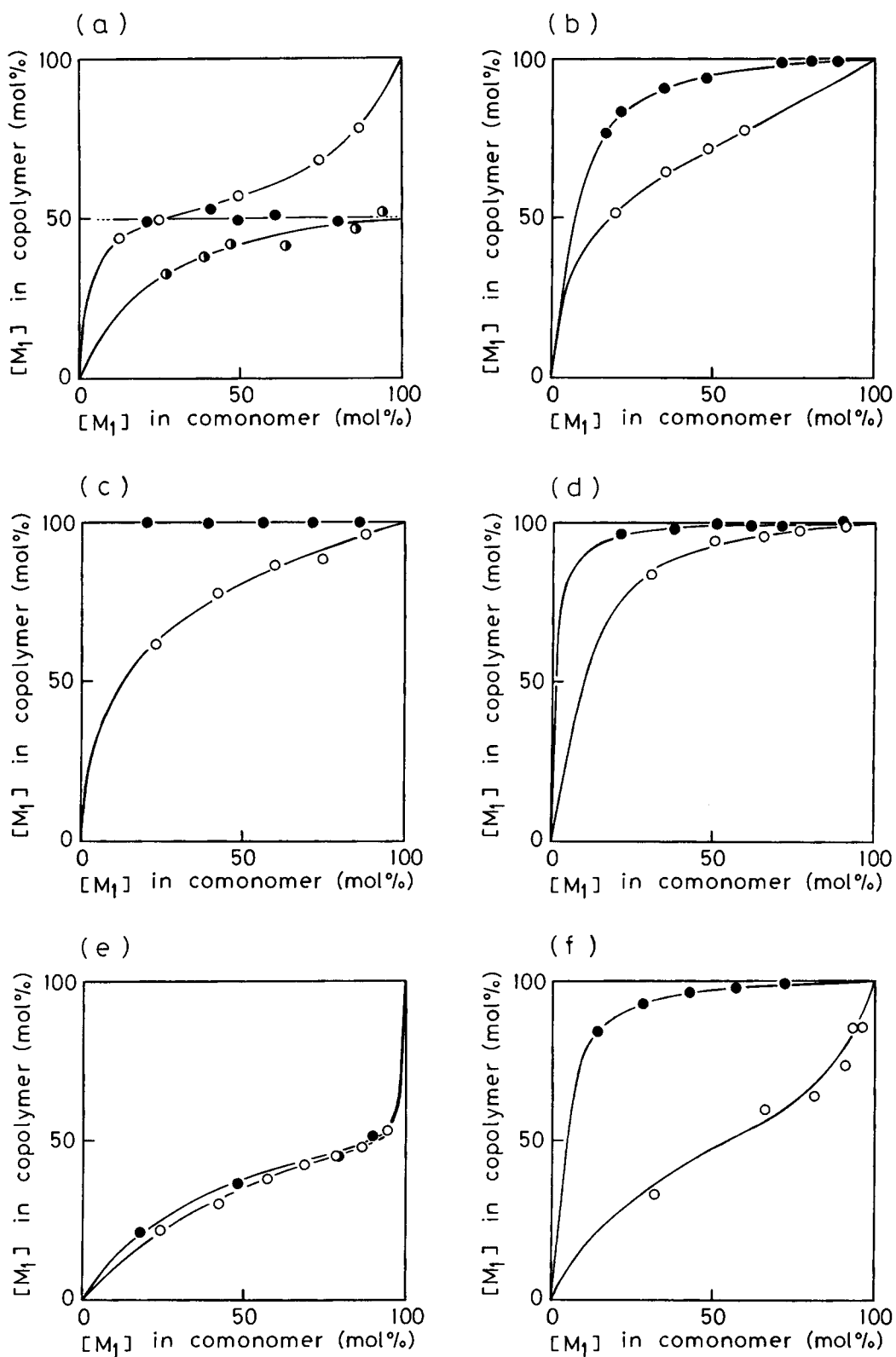
<sup>b</sup> Copolymerized in bulk at 80°C.

### Effect of the Ester Substituents of DRF

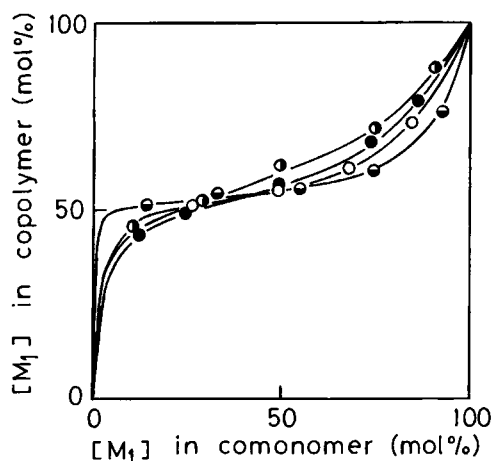
To evaluate the substitution effect of the ester groups in DRF, radical copolymerization of 16 kinds of DRF ( $M_2$ ) with St ( $M_1$ ) was carried out in benzene at 60°C. Typical copolymerization composition curves are shown in Figure 2, and the monomer reactivity ratios and the  $Q_2$  and  $e_2$  values determined are listed in Table II.

All DRF copolymerized alternately with St to yield small  $r_1r_2$  products similarly to copolymerization with DiPF. The relative reactivity of DRF toward a poly(St) radical [ $\log(1/r_1)$ ] was found to decrease by the introduction of bulky substituents, e.g., isopropyl, cyclohexyl, *tert*-butyl, and *tert*-amyl esters, and increased with an electron-withdrawing group such as 2-cyanoethyl or 2-chloroethyl group. Figure 3 shows that the relationships between  $\log(1/r_1)$  and Taft's steric and polar substitution constants,  $\sigma^*$  and  $E_s$ , respectively.<sup>15</sup> The reaction constants  $\rho^*$  and  $\delta$  were estimated to be 0.8 and 0.2, respectively, indicating that the reactivity of addition of DRF to a poly(St) radical is affected by both polar and steric factors of the ester substituents.

A linear relationship of the monomer reactivities with  $E_s$  was first indicated by Tsuruta et al. for copolymerization of methyl  $\alpha$ -alkylacrylates.<sup>16</sup> It has been also reported that the polar effect of ester alkyl groups is significant for the reactivities of alkyl



**Figure 1.** The comonomer-copolymer composition curves for copolymerization of DiPF ( $M_2$ ) in benzene at 60°C with: (a) St (○), VCZ (●), and IB (◐); (b) MA (○) and MMA (●); (c) PhA (○) and PhMA (●); (d) AN (○) and MAN (●) (in bulk at 80°C); (e) VAc (○) and IPAc (●); (f) VCl (○) and VDCI (●).



**Figure 2.** Typical comonomer-copolymer composition curves for copolymerization of DRF ( $M_2$ ) with St ( $M_1$ ) in benzene at 60°C: (○) DEF, (●) DiPF, (●) DtBF, (○) DCIEF.

acrylates<sup>17</sup> and methacrylates<sup>18</sup> toward a poly(St) radical ( $\rho^* = 0.56$  and  $0.33$ , respectively), but the reactivity does not depend on the steric factor ( $\delta = 0$ ). The polar reaction constant for DRF obtained in this work was larger than those for acrylates and methacrylates. It may be interpreted with the fact that DRF has two ester groups. It is concluded that the steric effect also has a significant role in addition to the polar effect in the case of DRF because of the bulky  $\beta$ -alkoxycarbonyl substituents. Recently a similar steric effect was also observed in copolymerization of dialkyl itaconates, which are one of

1,1-disubstituted ethylene bearing bulky substituents.<sup>19</sup>

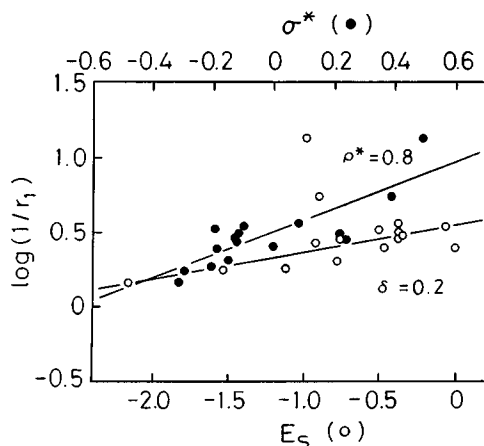
The  $e_2$  and  $Q_2$  values calculated for DRF were 1.0–1.5 and 0.4–0.6, respectively, indicating that all DRFs are electron-accepting conjugative monomers. The  $e_2$  values of DRFs are about twice of those for acrylic esters, and comparable to those expected from the additivity of the substitution effects as to  $e$  values, which is well-established in 1,1-disubstituted ethylenes, especially those of  $\alpha$ -substituted acrylates and  $\alpha$ -substituted acrylonitriles.<sup>20</sup>

The  $Q_2$  values were much smaller than those expected from the 1,2-di(alkoxycarbonyl)ethylene structure, and were almost equal to those of the acrylic esters, being different from the fact that 1,1-di(alkoxycarbonyl)ethylenes have large  $Q$  values.<sup>20</sup> However, the wavelength of UV absorption of the carbon-to-carbon double bond of DRF in ethanol were found to be longer rather than those of corresponding acrylic esters,<sup>21</sup> suggesting that the low  $Q_2$  values of DRF are not due to the prohibition of resonance in the monomer, but due to the reduced reactivity by the steric effect. Similar diminishing  $Q$  values were reported for other 1,2-disubstituted ethylenes, e.g., diphenylethylenes,<sup>4</sup> 2-butenes,<sup>22</sup> diphenylthioethylenes,<sup>23</sup> and propenyl chlorides.<sup>24</sup> The additivity as to  $Q$  values, which was proposed for 1,1-disubstituted ethylenes,<sup>20</sup> can not apply to 1,2-disubstituted ethylenes. There is significant difference in that the  $\beta$ -substituent contributes to stabilization by resonance in the monomer, but it is impossible in its corresponding polymer radical, in

**Table II.** Monomer Reactivity Ratios for Copolymerization of DRF ( $M_2$ ) with St ( $M_1$ ) and  $Q_2$  and  $e_2$  Values

DRF	Substituent	$r_1$	$r_2$	$\log(1/r_1)$	$E_s^a$	$\sigma^{*a}$	$Q_2$	$e_2$
DMF	methyl	0.39	0.03	0.41	0	0	0.48	1.31
DEF	ethyl	0.29	0.02	0.54	-0.07	-0.1	0.56	1.47
DnPF	<i>n</i> -propyl	0.32	0.02	0.49	-0.36	-0.115	0.50	1.48
DiPF	isopropyl	0.40	0.06	0.40	-0.47	-0.190	0.52	1.15
DnBF	<i>n</i> -butyl	0.35	0.04	0.46	-0.39	-0.130	0.57	1.18
DiBF	isobutyl	0.37	0.05	0.43	-0.93	-0.125	0.54	1.21
DsBF	<i>sec</i> -butyl	0.55	0.04	0.26	-1.13	-0.210	0.42	1.03
DtBF	<i>tert</i> -butyl	0.57	0.04	0.24	-1.54	-0.300	0.37	1.14
DtAF	<i>tert</i> -amyl	0.69	0.08	0.16	-2.17	-0.315	0.37	0.92
DCPF	cyclopentyl	0.30	0.06	0.52	-0.51	-0.20	0.68	1.18
DCHF	cyclohexyl	0.49	0.06	0.31	-0.79	-0.15	0.45	1.08
DBzF	benzyl	0.32	< 0.01	0.50	-0.38	0.215	—	—
DPhEF	2-phenylethyl	0.27	< 0.01	0.57	-0.38	0.080	—	—
DMOEF	2-methoxyethyl	0.35	0.03	0.46	-0.77	0.24	0.50	1.37
DCIEF	2-chloroethyl	0.18	< 0.01	0.74	-0.90	0.385	—	—
DCNEF	2-cyanoethyl	0.07	0.09	1.13	-0.99	0.49	—	—

<sup>a</sup> Taft's steric and polar substituent constant<sup>15</sup> of the ester alkyl groups.



**Figure 3.** The plots of the relative reactivity of DRF toward a poly(St) radical at 60°C: (○) toward steric substitution constant ( $E_s$ ) of the ester alkyl groups, (●) toward polar substitution constant ( $\sigma^*$ ).

contrast to the fact that two substituents in 1,1-disubstituted ethylenes may participate in stabilization of both monomer and polymer radical.

### Copolymerization with 1,1-Disubstituted Ethylenes

Although DRF is less-reactive than MA and AN as an electron-accepting vinyl monomer, as mentioned above, this tendency was found to be more pronounced in the copolymerization with 1,1-disubstituted ethylenes, i.e.,  $\alpha$ -methyl vinyl monomers. As seen in the comparison of the comonomer–copolymer composition curves for DiPF with MA and methyl methacrylate (MMA) in Figure 1(b), DiPF showed very low reactivity to MMA. The calculated monomer reactivity ratios were  $r_1 = 23$  and  $r_2 = 0.17$  for the MMA ( $M_1$ )–DiPF ( $M_2$ ) system, similar to the results reported for MMA ( $M_1$ )–DEF ( $M_2$ ) system ( $r_1 = 40.4$ ,  $r_2 = 0.03$ ).<sup>25</sup> These values indicate that DiPF is less reactive in copolymerization with MMA compared to copolymerization with MA.

In copolymerization with phenyl esters, this tendency was more distinguishing as shown in Figure 1(c). It suggests that DiPF does not participate in polymerization of phenyl methacrylate (PhMA). It seems to result as difficulty of addition of DiPF to the tertiary poly(PhMA) radical consisting of a crowded structure at the polymer end, and promotion in monomer reactivity of PhMA itself with the presence of an  $\alpha$ -methyl group. It has been known that the introduction of an  $\alpha$ -methyl group into  $\alpha,\beta$ -unsaturated esters and nitriles enlarges the reactiv-

ity of the attack of a methyl radical<sup>26</sup> and a poly(St) radical.<sup>4</sup>

Figure 1(d) represents the composition curves for copolymerizations of DiPF with AN in benzene at 60°C and methacrylonitrile (MAN) in bulk at 80°C. The monomer reactivity ratios were as follows:  $r_1 = 16$  and  $r_2 = 0.20$  for DiPF ( $M_1$ )–AN ( $M_2$ );  $r_1 = 85$  and  $r_2 \sim 0$  for DiPF ( $M_1$ )–MAN ( $M_2$ ). Similarly to copolymerization with methacrylates, the reactivity of DiPF toward poly(MAN) radical was very low.

It is very interesting that the structure of poly(MAN) radical resembles a primary radical from AIBN. In homopolymerization of DRFs with AIBN as an initiator, initiation seems to be slow because of a low reactivity of the initiating primary radical toward DRF.<sup>27,28</sup>

Whereas DiPF copolymerizes alternately with St, no polymer was obtained throughout all comonomer compositions in copolymerization with  $\alpha$ -methylstyrene (MSt) in bulk at 80°C. It may be ascribed to the reason that DiPF could not add to a bulky poly(MSt) radical, and that the propagation reaction of MSt did not occur apparently above the ceiling temperature.<sup>4</sup> In fact, it was confirmed that the addition of a few drops of MSt was enough to inhibit polymerization of DRF.

The effect of introduction of a methyl group into the  $\alpha$ -position of nonconjugative VAc on copolymerization reactivities was also investigated. The difference in monomer reactivity was not almost observed for copolymerization of DiPF with VAc and isopropenyl acetate (IPAc) in benzene as shown in Figure 1(e). The monomer reactivity ratios were calculated to be  $r_1 = 0.012$ ,  $r_2 = 0.90$  and  $r_1 = 0.011$ ,  $r_2 = 0.67$  for copolymerization with VAc and IPAc, respectively. It indicates that the polymer radical from nonconjugative IPAc has high reactivity toward DiPF, even in the presence of the methyl group in its  $\alpha$ -position.

In copolymerization of vinylidene dichloride (VDCI), the relative reactivity of DiPF decreased compared with the case of VCl, i.e.,  $r_1 = 0.29$  and  $r_2 = 0.49$  for VCl, and  $r_1 = 48$  and  $r_2 = 0.095$  for VDCI, as shown in Figure 1(f). It seemed to disagree apparently with the results for VAc and IPAc, but it may be due to a strong electron-accepting nature of VDCI.

### Reactivities of DRF and Poly(DRF) Radical

The absolute rate constants of elementary propagation reactions for copolymerization of DiPF with some vinyl monomers were calculated from the

**Table III.** Absolute Rate Constants of Elementary Propagation Reactions for Copolymerization of DiPF ( $M_2$ )<sup>a</sup>

$M_1$	$k_{11}$ (Reference) (L/mol s)	$k_{12}$ (L/mol s)	$k_{21}$ (L/mol s)
St	106 (30)	270	5.6
MA	720 (33)	380	3.4
MMA	315 (34)	14	1.8
AN	1960 (35)	120	1.6
MAN	26 (36)	0.3	—
VAc	1012 (37)	170000	0.34

<sup>a</sup>  $k_{22} = 0.31$  L/mol s (Ref. 11),  $k_{12} = k_{11}/r_1$ ,  $k_{21} = k_{22}/r_2$ .

combination of the  $r_1$  and  $r_2$  values with propagation rate constants,  $k_p$  ( $= k_{22}$  and  $k_{11}$ ) for homopolymerizations of DiPF<sup>11</sup> and vinyl monomers. The results are shown in Table III.

From comparison of  $k_{12}$  values, it has been clarified that the rates of addition of DiPF to polymer radicals from the monosubstituted ethylenes are not slow despite steric hindrance of the  $\beta$ -substituent of DiPF. DiPF adds rapidly to not only an electron-donating polymer radical such as poly(St) radical and a reactive nonconjugative radical such as poly(VAc) radical, but also to electron-accepting polymer radicals, e.g., poly(MA) and poly(AN) radicals.

The rate of addition of MA toward poly(St) radical is assumed to be 140 L/mol/s, from its monomer reactivity ratios,  $r_1 = 0.75$  and  $r_2 = 0.18$  for St ( $M_1$ )–MA ( $M_2$ ),<sup>29</sup> and the  $k_{11}$  value (106 L/mol/s)<sup>30</sup> for St. It suggests that the addition rate of DiPF toward a poly(St) radical is about twice that of MA. It agrees well with the reactivities of several alkyl radicals to DRFs and acrylates.<sup>31</sup>

In the case of reaction with a poly(MMA) radical, steric hindrance of DRF and an  $\alpha$ -methyl group of the polymer radical became significant, i.e., the  $k_{12}$  value for MMA (14 L/mol s) decreased drastically compared with that for MA (380 L/mol s). Similar deceleration for the addition rate of DiPF was also observed for the reaction to a poly(MAN) radical. It has been demonstrated that steric effects become more significant in the reaction of a sterically hindered tertiary carbon radical with DRF.<sup>32</sup>

On the other hand, it has also been revealed that the addition rates of vinyl monomers toward the poly(DiPF) radical, i.e.,  $k_{21}$  were very small, indicating that the poly(DiPF) radical is less reactive due to steric effects of the substituents around the polymer radical center.

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