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Opening Mode in the Propagation of Dialkyl Fumarates and Maleates as 1,2-Disubstituted Ethylenes in Radical Polymerization

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ABSTRACT: Opening mode of the carbon-to-carbon double bond of dialkyl fumarates and maleates as trans and cis 1,2-disubstituted ethylenes was investigated. In radical copolymerization of di-*tert*-butyl fumarate (DtBF) with dimethyl maleate (DMM), monomer reactivity ratios of the comonomers supported the occurrence of successive propagation of DMM, which does not give a high polymer in radical homopolymerization. From studies on the stereochemical microstructure of copoly(DtBF–DMM)s by means of ^{13}C NMR spectroscopy, it was revealed that no racemo–racemo triad sequence existed in the copolymers and that a meso diad is produced by the cis opening of the DMM double bond, whereas dimethyl fumarate (DMF) gives a meso diad by its trans opening. The conformations of propagating radicals in both copolymerization systems of DtBF–DMM and DtBF–DMF were very similar as studied by ESR spectroscopy. It has been concluded from these results that the terminal σ bond of the propagating radical rotates and the propagating radical has a favorable conformation, leading to a meso diad formation in the propagation of both fumarates and maleates.

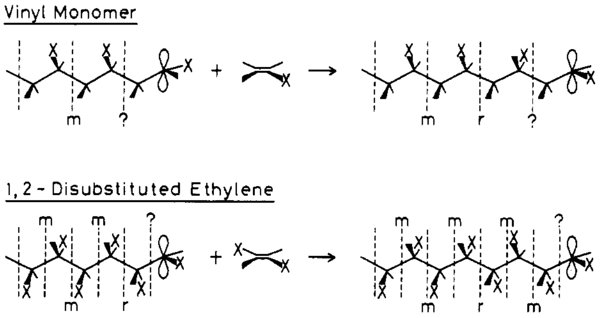
Introduction

We have reported that dialkyl fumarates (DRF), sterically hindered 1,2-disubstituted ethylenes, with bulky alkyl groups as an ester substituent homopolymerize readily with a radical initiator to give high molecular weight substituted polymethylenes.[1] The polymerization reactivity of DRF deduced from the yield and the molecular weight of the resulting polymers has been found to increase with an increase in the bulkiness of the ester substituents.[1] It has been revealed that the flexibility of the substituted polymethylene chains also depends on the structure of the substituents.[1,2] In the polymerization of DRF, absolute rate constants for propagation and termination (k_p and k_t, respectively) were determined to be much lower than those of ordinary vinyl monomers.[3] Such low k_t values permit the direct observation of the propagating poly(DRF) radical by ESR spectroscopy without any special technique and apparatus.[1,3]

The stereochemical structure of polymers obtained from 1,2-disubstituted ethylenes has been investigated by many workers[4-15] since the discovery of stereoregular polymers by Natta et al.,[16] because it gives us great information on polymerization mechanisms. That is, in the radical polymerization of ordinary vinyl monomers, since the stereochemical relation of a penultimate unit at the propagating chain end is not determined until the addition of an attacking monomer to a propagating radical, the direction of monomer addition and the opening mode of the carbon-to-carbon double bond cannot be discriminated from each other (Scheme I). On the other hand, in the case of the polymerization of 1,2-disubstituted ethylenes like DRF, the direction of monomer addition dominates the configuration of two carbons as shown in Scheme I. This means that the determination of the microstructure of substituted polymethylenes enables us to discuss the direction of monomer addition and the opening mode independently.

We have studied the tacticity of poly(DRF)s by ^{13}C NMR spectroscopy in order to clarify the propagation mechanism of DRF in radical polymerization.[15,17] The tacticity of poly(DRF)s, i.e., poly[(alkoxycarbonyl)methylene]s, should be considered on the basis of a methylene repeating unit, and it is dominated by both the opening mode of a carbon-to-carbon double bond and the direction of monomer addition to the propagating radical. However, when an opening of the double bond is restricted to either mode, the tacticity of poly(DRF) can be determined solely by the direction of addition, i.e., P_m and P_r, which represent the probability of meso and racemo additions, respectively. Thus, we determined P_m values for some DRFs by means of the restriction of the trans opening,[15,17] and revealed that the polymerization temperature dependence of P_m is drastically changed with the structure of ester alkyl groups; i.e., the difference in the activation enthalpies for meso and racemo additions is positive for dimethyl fumarate (DMF) but negative for di-*tert*-butyl fumarate (DtBF).[17b] Moreover, the absolute rate constants for meso and racemo additions were evaluated by the use of P_m and k_p.[3c]

Scheme I



However, the nature of the restricted trans mode opening of the double bond of DRFs in polymerization has not been yet clear. If dialkyl maleates (DRM) as a cis isomer of DRF gave a homopolymer radically, much information about the opening mode could be obtained from analysis of the microstructure. DRM does not homopolymerize at all in the absence of an isomerization catalyst,[18] but it is expected to copolymerize with DRF. Although there have been many studies on the relative reactivities of cis and trans 1,2-disubstituted ethylenes including DRF and DRM toward some radicals, e.g., polystyryl,[19,20] methyl,[21] cyclohexyl,[22] and phenylthiyl radicals,[23] the reactivities of DRF and DRM in the direct copolymerization have not been examined. Therefore, in this study, DtBF and dimethyl maleate (DMM) were

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Table I
Results of the Copolymerization of DtBF (M_1) with DMF and DMM (M_2)

M_2	$[M_2]$ in feed, mol %	time, h	convn, %	$[M_2]$ in copolym, mol %	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$	P_m
DMF[a]	95.0	15	13.4	95.6	*b*	*b*	0.52
	80.4	10	29.4	61.6	*b*	*b*	0.53
	60.0	6	28.9	39.0	1.43	1.8	0.59
	40.0	3	25.9	24.5	1.57	2.0	
	20.1	0.75	8.4	13.6	1.80	2.1	0.62
DMM[c]	95.0	20	1.9	40.8	1.18	1.4	0.55
	90.0	15	9.2	32.3	1.28	1.5	
	80.0	6	11.3	17.5	1.81	2.0	0.60
	50.0	2.1	8.6	~0	3.63	2.2	

[a] [DTBPO] = 0.02 mol/L, at 120 °C. [b] Insoluble in tetrahydrofuran. [c] [ACN] = 0.02 mol/L, at 80 °C.

copolymerized, and the tacticity of the copolymers was examined by ^{13}C NMR spectroscopy in comparison with the copolymers of DtBF and DMF to discuss the trans opening of the carbon-to-carbon double bond. The conformation of the propagating radicals for the copolymerization systems was also examined by ESR spectroscopy.

Experimental Section

Materials. DtBF (mp 71 °C) was prepared as reported in the previous paper. Commercial DMM and DMF were used after distillation under reduced pressure and recrystallization from methanol, respectively: DMM, bp 60 °C (5 mmHg); DMF, mp 102 °C. Commercially available vinyl acetate (VAc) was distilled under reduced pressure. Di-*tert*-butyl peroxide (DTBPO), 1,1′-azobiscyclohexane-1-carbonitrile (ACN), and dimethyl 2,2′-azobisisobutyrate (MAIB) were used as radical initiators.

Copolymerization Procedures. Copolymerizations were carried out in a sealed glass tube. The copolymerization of DtBF with DMF was performed in the presence of a small amount of toluene ([comonomers] = 4.06–5.79 mol/L) with DTBPO (0.02 mol/L) at 120 °C, which is above the melting points of both the monomers. The copolymerization of DtBF with DMM was carried out in bulk with ACN (0.02 mol/L) at a lower temperature (80 °C) to avoid isomerization of DMM. DMM and DtBM were copolymerized with VAc in bulk and in benzene ([comonomers] = 1.61–8.76 mol/L), respectively, with MAIB as an initiator at 60 °C. After copolymerization for a given time, the copolymerization mixture was poured into a large amount of precipitant to isolate the copolymer. The composition of the copolymers was determined by the intensity ratios of the peaks in ^{1}H NMR spectra as follows: methyl protons in the DtBF unit (1.2–1.8 ppm) and other protons (2.5–4.2 ppm) were used for copoly(DtBF–DMF) and copoly(DtBF–DMM). In the cases of copoly(VAc–DMM) and copoly(VAc–DtBM), 4.4–5.3 ppm for main-chain methine protons of the VAc unit was used in combination with 3.3–4.0 ppm for methyl protons of the DMM unit and 1.2–3.0 ppm for other protons of the VAc and DtBF units, respectively. Monomer reactivity ratios (r_1 and r_2) were calculated by a nonlinear least-squares method.[24]

Transformation of *tert*-Butyl Ester to Methyl Ester. The *tert*-butyl esters in the copolymer were quantitatively transformed to methyl esters via isobutene elimination by thermolysis without any catalyst and subsequent methylation. The procedures with respect to this transformation were the same as described in the previous papers.[17]

Measurements. The number- and weight-average molecular weights ($\bar{M}_n$ and $\bar{M}_w$) of the resulting copolymers were determined by gel permeation chromatography (GPC) at 38 °C in tetrahydrofuran as the eluent and calibrated with standard polystyrenes. GPC was performed with Tosoh 8000 series GPC systems.

^{1}H and ^{13}C NMR spectra were recorded on JEOL GX-400 or Hitachi R-24B spectrometers with deuteriochloroform as the solvent. The operation conditions of ^{13}C NMR measurements and the procedures for simulation of the spectra for determination of P_m were similar to those in the previous paper.[17]

The measurement of ESR spectra for copolymerization systems was carried out in a degassed ESR tube by means of a Bruker ESP-300 spectrometer at 60 °C. The typical operation conditions were as follows: microwave frequency, 9.49 GHz; modulation frequency, 100 kHz; modulation amplitude, 0.096 G; time constant, 655.36 ms.

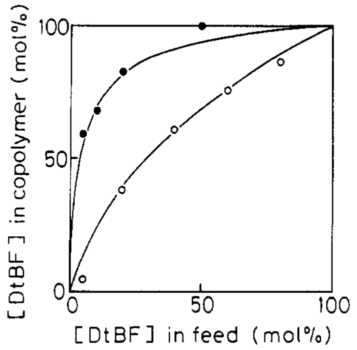


Figure 1. Comonomer–copolymer composition curves for the copolymerization of DtBF (M_1) with DMF (○) and DMM (●) (M_2).

Results and Discussion

Reactivity of DRF and DRM in Copolymerization. The results of copolymerizations of DtBF (M_1) with DMF and DMM (M_2) and the comonomer–copolymer composition curves are shown in Table I and Figure 1, respectively. In the copolymerization of DtBF and DMF, the monomer reactivity ratio of DtBF was higher than that of DMF, $r_1 = 1.88$, $r_2 = 0.36$, indicating that DtBF has a higher reactivity as a monomer in the copolymerization despite its bulkier ester substituent. Similar copolymerization behaviors have also been obtained for the copolymerization of diisopropyl fumarate (DiPF) (M_1) and dioctadecyl fumarate (M_2) ($r_1 = 1.07$, $r_2 = 0.33$),[25] which have secondary and primary alkyl esters, respectively. Recently, we revealed that k_p of DRF increases with an increase in the bulkiness of the ester substituents, and it may be interpreted by the difference in the propagation rates between meso and racemo additions.[3c] The enhancement of the monomer reactivity by the introduction of bulkier alkyl groups might also be concerned with the any factors as to the stereochemical requirement.

The relative monomer reactivity of DtBF in the copolymerization with DMM was much higher as expected; i.e., $r_1 = 16$, $r_2 = 0.02$. Despite no homopolymerization ability of DMM, the monomer reactivity ratio of DMM was calculated to be not equal to zero, indicating the occurrence of the propagation between a poly(DMM) radical and DMM.

The copolymerization of DMM and di-*tert*-butyl maleate (DtBM) (M_2) with vinyl acetate (VAc) (M_1) was also performed (Table II and Figure 2). The monomer reactivity ratios in the copolymerization of VAc–DMM and VAc–DtBM are listed in Table III, indicating that the structure of the ester substituents hardly affects the monomer reactivity in these copolymerizations and that

Table II
Results of the Copolymerization of VAc (M_1) with DMM and DtBM (M_2) at 60 °C[a]

M_2	$[M_2]$ in feed, mol %	time, h	convn, %	$[M_2]$ in copolym, mol %
DMM	89.8	8	10.2	52.0
	68.8	1.25	9.57	45.9
	42.4	0.25	5.03	42.4
	32.9	0.25	6.12	36.4
	12.8	0.17	4.94	31.2
DtBM	90.0	20	5.75	53.3
	80.0	6	14.5	48.1
	59.9	2.5	17.4	47.1
	40.1	1	4.98	43.5
	30.1	0.5	24.4	41.3
	10.0	0.5	21.6	22.5

[a] [MAIB] = 0.02 mol/L.

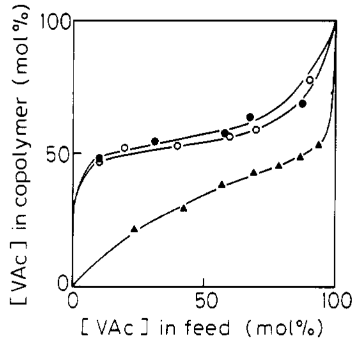


Figure 2. Comonomer–copolymer composition curves for the copolymerization of VAc (M_1) with DMM (●), DtBM (○), and DiPF (▲) (M_2).

Table III
Monomer Reactivity Ratios for the Copolymerization of DRM and DRF (M_2) with VAc (M_1) at 60 °C

M_2	r_1	r_2	$1/r_1$	ref
DMM	0.27	0.010	3.7	this work
DtBM	0.22	0.014	4.5	this work
DiPF	0.012	0.90	83	26

the reactivities of DRM are much less than those of DRF: e.g., r_1 = 0.012, r_2 = 0.90 for VAc (M_1)–DiPF (M_2) copolymerization.[26] The relative reactivity of DiPF ($1/r_1$) toward a poly(VAc) radical was found to be about 20 times higher than that of DMM and DtBM. This result is consistent with previous reports,[20-23] which dealt with the difference in the reactivities of DRF and DRM toward some radicals, where the ratio of the reactivities of DRF to DRM was determined to be 6–40 depending on the structure of the attacking radicals used.

Estimation of the Opening Mode in the Propagation. In order to estimate the opening mode in the propagation for the radical polymerization of DRF and DRM, the stereochemical microstructure of copoly(DtBF–DMF) and copoly(DtBF–DMM) was investigated by ^{13}C NMR spectroscopy after transformation of the *tert*-butyl esters in the copolymers to methyl esters, i.e., poly[(methoxycarbonyl)methylene]. In the polymerization of DRF, it is considered that opening of the carbon-to-carbon double bond gives a meso diad in the following two cases: (i) a rate of rotation around the terminal σ bond is much smaller than a propagation rate, and (ii) a terminal σ bond rotates rapidly, but the propagating radical has a thermodynamically favorable conformation that results in the production of a meso diad in the propagation. In the former case, the DMM unit in the copolymers in this work would yield a racemo diad by opening of its double bond, and the copolymers would contain an rr triad sequence (Figure 3) which is absent in poly(DRF)s.[17] On the other hand, a meso diad would be formed similarly to DRF in the latter case.

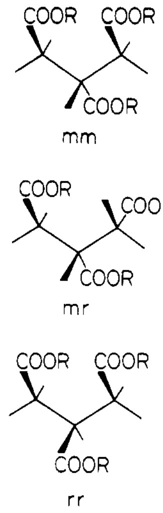


Figure 3. Three possible configurations for triad sequences of poly[(alkoxycarbonyl)methylene].

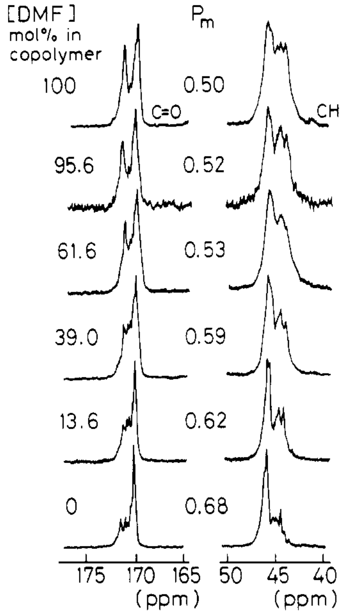


Figure 4. ^{13}C NMR spectra for methine and carbonyl carbons for poly[(methoxycarbonyl)methylene]s derived from copoly(DtBF–DMF)s. Copolymerization temperature, 120 °C. The spectra for poly(DMF) and the polymethylene derived from poly(DtBF)[17] were also included.

Figures 4 and 5 show the main-chain methine and carbonyl carbon regions of ^{13}C NMR spectra of the poly[(methoxycarbonyl)methylene]s derived from copoly(DtBF–DMF) and copoly(DtBF–DMM), respectively, in which the spectra of the polymethylenes derived from the homopolymerization of DtBF and DMF[17] are also included.

It was reported that an mm triad signal appeared at a lower magnetic field that an mr triad signal for the methine carbon and at a higher field for the carbonyl carbon in the ^{13}C NMR spectra of poly(DRF)s.[15,17] Figure 4 indicates clearly that the fraction of mr triad regions decreased along with the decrease in the molar fraction of DMF in copoly(DtBF–DMF) for both carbons. From simulation of the spectra, P_m, i.e., the probability of meso addition, was determined to be 0.52–0.62, depending on the fraction of DMF (Table I). These values are intermediate between the P_m values for DtBF and DMF.[17] The spectra with respect to the copoly(DtBF–DMM)s seemed

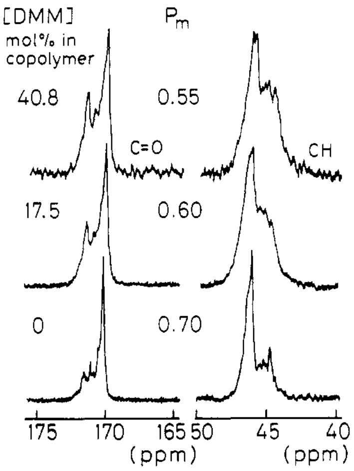


Figure 5. ^{13}C NMR spectra for methine and carbonyl carbons for poly[(methoxycarbonyl)methylene]s derived from copoly(DtBF-DMM)s. Copolymerization temperature, 80 °C. The spectra for the polymethylene derived from poly(DtBF)[17] were also included.

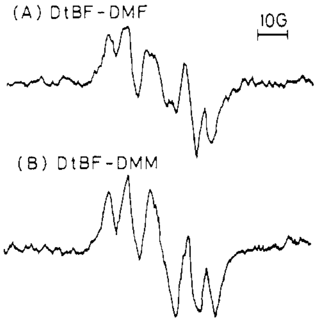


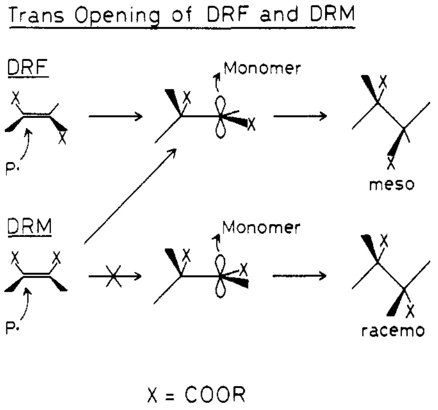
Figure 6. ESR spectra recorded during the copolymerization of (A) DtBF-DMF ([DtBF] = 79.7 mol % in the feed) and (B) DtBF-DMM ([DtBF] = 20.0 mol % in the feed) at 60 °C.

to have no rr triad signals (Figure 5), being very similar to the spectra of copoly(DtBF-DMF)s. It was possible to simulate these spectra in the same manner as poly(DRF)s. The obtained P_m values depended on the fraction of DMM and increased with a decrease in the DMM fraction (Table I). From these results, the DMM unit in the copoly(DtBF-DMM)s was revealed to give a meso diad by opening of its double bond.

These results of the tacticity of copoly(DtBF-DMM)s suggest that the meso formation by the opening of the double bond originates from case ii. In that case, the propagating radical bearing DMM as a terminal unit is expected to have a conformation similar to that of DMF because of a rotation around the terminal bond. Therefore, propagating radicals in the copolymerization systems in the present study were investigated by ESR spectroscopy. Because a comparison of ESR spectra of the two propagating radicals produced from homopolymerization systems of DMF and DMM would involve another essential problem as to the chain length dependence of the conformation,[27] ESR measurements were carried out for the copolymerization of DtBF-DMF and DtBF-DMM, which give high enough molecular weight polymers to discuss the conformation around the polymer radical.

Figure 6 shows the ESR spectra obtained for both copolymerization systems; DtBF are 79.7 and 20.0 mol % in the feed for the DtBF-DMF and DtBF-DMM copolymerizations, respectively, where the resulting copolymers have similar compositions. These spectra are utterly different from those obtained during homopolymerization of both DtBF and DMF,[3c] but the spectra for both copolymerization systems are very similar, suggesting that the propagating radicals for each copolymerization system have a similar conformation.

Scheme II



From these studies on the microstructure of the copolymers and the conformation of the propagating radicals, it has been concluded that the propagating radical having a DMM as an ultimate unit rotates and takes the same conformation as DMF before the addition to a next monomer, leading to the formation of a meso diad (Scheme II). In other words, the meso diad was formed by trans and cis openings of the double bonds of DMF and DMM, respectively, according to case ii, but not case i mentioned above. The propagating radical bearing DMM as a terminal unit is indistinguishable from that bearing DMF; i.e., DMF and DMM radicals have the same conformation, i.e., the same reactivity, leading to the successive propagation of DMM. The reason why DRMs give no high molecular weight polymer in the homopolymerization may be mainly a result of the less reactivity of DRM toward the radicals, but not less reactivity of the poly(DRM) radicals.

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