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Opening and Addition Modes in Propagation During Radical Polymerization of Fumaric and Maleic Derivatives

Akikazu Matsumoto[a]; Keiichi Shimizu[a]; Takayuki Otsu[b]
[a] Department of Applied Chemistry, Faculty of Engineering Osaka City University Sugimoto, Osaka, Japan [b] Faculty of Biology-Oriented Science and Technology Kinki University Uchita-cho, Wakayama, Japan

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OPENING AND ADDITION MODES IN PROPAGATION DURING RADICAL POLYMERIZATION OF FUMARIC AND MALEIC DERIVATIVES

AKIKAZU MATSUMOTO* and KEIICHI SHIMIZU

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

TAKAYUKI OTSU

Faculty of Biology-Oriented Science and Technology
Kinki University
Uchita-cho, Naga-gun, Wakayama 649-64, Japan

ABSTRACT

Polymers of bis(trimethylsilyl) fumarate, di-*tert*-amyl fumarate, and methyl *tert*-amyl fumarate were prepared by radical polymerization at 60 or 120°C. The polymers were converted into poly(dimethyl fumarate) via thermolysis or hydrolysis and subsequent methylation to determine the tacticity using ^{13}C-NMR spectroscopy. The probabilities of meso addition (P_m) were revealed to be 0.66 (60°C) for the bis(trimethylsilyl) ester, 0.60 (60°C) and 0.52 (120°C) for the di-*tert*-amyl ester, and 0.54 (60 and 120°C) for the methyl *tert*-amyl ester. From the temperature dependence of the P_m values, the differences in activation enthalpies and entropies for the meso and racemo additions were evaluated. The microstructure of poly(dimethyl fumarate) derived from poly(maleic anhydride) was also examined. The opening and addition modes in propagation of the fumaric and maleic derivatives were discussed based on the results obtained in the present and previous work.

INTRODUCTION

The microtacticity of vinyl polymers has been intensively investigated by NMR spectroscopy to reveal not only the effects on thermal, mechanical, and other properties of the polymers but also the polymerization mechanism. ^{13}C-NMR spectroscopy is the most powerful and reliable method to determine the sequence distribution regarding the higher sequences such as pentads and heptads [1, 2]. In the polymerization of 1,2-disubstituted ethylenes including dialkyl fumarates (DRF), the direction of monomer addition and the opening mode of the double bond are discriminated from each other, whereas in the polymerization of monosubstituted and 1,1-disubstituted ethylenes they are not separable because the stereochemical relation at the propagating chain end is not determined until the addition of the next monomer to the propagating radical [3]. Thus, clarification of the tacticity of substituted polymethylenes, which are obtained by the polymerization of 1,2-disubstituted ethylenes, enables us to discuss both the addition and opening modes. In previous work [4–9] we determined the values of the probability of the meso additions (P_m) for several poly(DRF)s. It has been revealed that di-*tert*-butyl fumarate (DtBF) shows the highest P_m value, e.g., $P_m = 0.80$ at 0°C [6]. The polymerization temperature dependency of the tacticity was also found to vary according to the monomers; the difference in the activation enthalpies for the meso addition to the racemo addition was positive for dimethyl fumarate (DMF) but negative for DtBF [6]. The opening mode of the double bond was also investigated in the copolymerization of DRF with dialkyl maleate (DRM) [8].

During the determination of the tacticity of poly(DRF), transformation of poly(DRF) to poly(methoxycarbonylmethylene) [poly(MCM)] is an important step because poly(MCM) provides a well-resolved ^{13}C-NMR spectrum whereas poly(DRF), with a bulky ester alkyl group such as *tert*-butyl, gave a broad one [5]. In the course of our study the poly(DRF)s with tertiary alkyl esters were converted quantitatively into poly(fumaric acid) by thermolysis, and then methylation with diazomethane provided poly(MCM) [10]. On the contrary, poly(DRF)s with secondary alkyl ester groups were subjected to determination of the tacticity without transformation because of the difficulty of thermolysis and hydrolysis [11].

For this work we selected several DRFs bearing *tert*-amyl esters or trialkylsilyl esters and maleic anhydride (MAn) as monomers and polymerized them in the presence of a radical initiator. These functional groups in the polymers can readily be converted into the methyl ester by thermolysis or hydrolysis followed by methylation. We investigated the microstructure of the polymers obtained from the radical polymerization of bis(trimethylsilyl) fumarate (BTMSF), di-*tert*-amyl fumarate (DtAF), methyl *tert*-amyl fumarate (MtAF), and MAn (Chart 1). The radical polymerization of bis(*tert*-butyldimethylsilyl) fumarate (BBDSF) was also attempted. The results obtained in this work are compared with the previous results for DMF, DtBF, and methyl *tert*-butyl fumarate (MtBF). The opening and addition modes during the polymerization of the fumaric and maleic derivatives are discussed in combination with the structures of the monomers.

EXPERIMENTAL

Monomers

BTMSF was synthesized according to the following procedure. To fumaric acid (20 g, 0.17 mol) and triethylamine (36 g, 0.35 mol) in THF (150 mL), trimethyl-

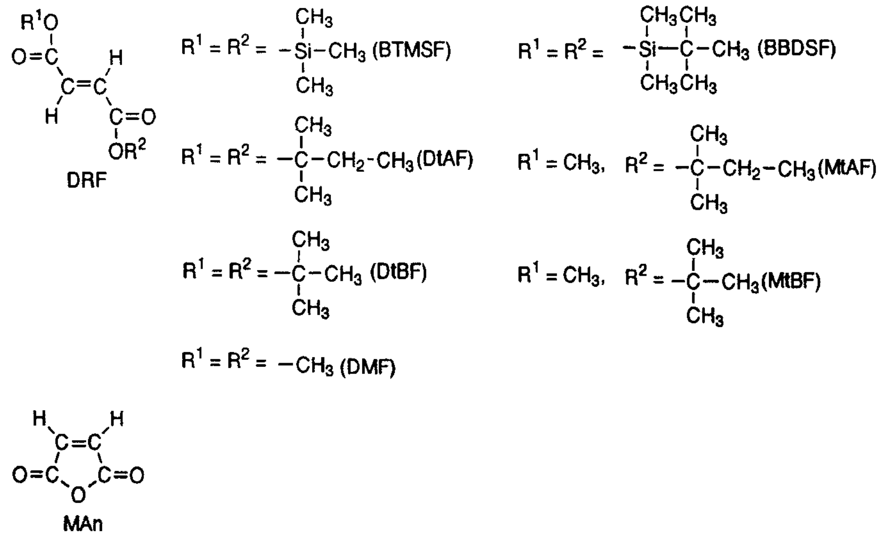


CHART 1.

silyl chloride (40 g, 0.37 mol) in 100 mL of THF was added dropwise at −78°C in a nitrogen atmosphere and stirred further at −78°C for 18 hours. After evaporation of the solvent, benzene was added to the residual mixture. The filtrate was passed through a short alumina column and then dried in vacuo. The sublimation provided a pure BTMSF. Yield: 31.4 g (70%), mp 60°C (Lit. 60°C [12]). ^{1}H NMR (C_6D_6, 60 MHz) δ 6.88 (s, 2H, CH=), 0.43 (s, 18H, CH_3).

BBDSF was prepared as follows. Fumaric acid (15g, 0.13 mol), *tert*-butyldimethylsilyl chloride (58.5 g, 0.39 mol), imidazole (52.8 g, 0.77 mol), and dimethylformamide (50 mL) in 180 mL of THF were stirred in a nitrogen atmosphere at room temperature for 68 hours. The reaction mixture separated into two layers. The lower layer was concentrated, then extracted twice with 100 mL of benzene, and combined with the upper layer. After the solvents were removed in vacuo, crude BBDSF was extracted with hexane. Passage through an alumina column with hexane and subsequent recrystallization from hexane provided BBDSF. Yield: 7.5 g (17%), mp 73-76°C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.73 (s, 2H, CH=), 0.97 (s, 18H, $(CH_3)_3C$), 0.31 (s, 12H, $(CH_3)_2Si$). IR(KBr) $\nu_{C=O}$ 1695, $\nu_{C=C}$ 1665 cm^{-1}.

Other monomers were prepared by the method described in previous papers [13, 14]. Dimethyl azobis(isobutyrate) (MAIB) was recrystallized from methanol. Benzoyl peroxide (BPO) was recrystallized from a chloroform and methanol mixture. Di-*tert*-butyl peroxide (DtBPO) was used as received without further purification. Solvents were distilled before use.

Polymerization Procedure and Isolation of the Polymers

The polymerization was carried out in a sealed glass tube in the presence of a radical initiator. The polymers produced from MtAF and DtAF were isolated by precipitation with a mixture of methanol/H_2O (3/1 in volume). Poly(MAn) was precipitated with diethyl ether. The polymer yield was determined gravimetrically.

The polymerization mixture of BTMSF was poured into methanol containing a small amount of HCl to precipitate the polymer and was further refluxed for 3 hours. The polymer yield was determined after methylation with diazomethane.

Transformation of Poly(DRF) to Poly(MCM)

Poly(DtAF) and poly(MtAF) were thermolyzed at 180°C for 2 hours in vacuo and then refluxed in methanol for 10 hours. Subsequently they were methylated with diazomethane. Poly(MAn) was refluxed in methanol for 10 hours and then methylated. Poly(BTMSF) were converted into poly(MCM) by the procedure described above. The poly(MCM) thus obtained was purified by reprecipitation with methanol and diethyl ether, followed by passage through an alumina column with chloroform.

^{13}C-NMR Measurement

100 MHz ^{13}C-NMR spectra were recorded on a Jeol GX-400 spectrometer with deuteriochloroform as solvent at ambient temperature. The concentration of the polymers was 10–20 wt%.

Determination of Tacticity by Simulation

Simulation of the NMR spectra was carried out as an accumulation of Lorentian curves for eight peaks corresponding to heptad sequences using a personal computer PC-9800. The chemical shift, height, linewidth at half-height of each peak, and P_m values were determined. Poly(MCM) derived from poly(BTMSF) (60 and 80°C): P_m, 0.66; linewidth, 0.40 ppm (for carbonyl carbon) and 0.45 ppm (for methine carbon). Poly(MCM) derived from poly(DtAF) (60°C); P_m, 0.60; linewidth, 0.40 ppm (for carbonyl carbon). Poly(MCM) derived from poly(DtAF) (120°C): P_m, 0.52; linewidth, 0.55 ppm (for carbonyl carbon). Poly(MCM) derived from poly(MtAF) (60 and 120°C): P_m, 0.54; linewidth, 0.55 ppm (for carbonyl carbon) and 0.85 ppm (for methine carbon).

Other Measurements

Gel permeation chromatography was performed with a Tosoh 8000 series GPC system equipped with TSK-gel columns using tetrahydrofuran as eluent. Number-average molecular weight (M_n) and weight-average molecular weight (M_w) were calibrated with standard polystyrenes. IR spectra were recorded on a Jasco A-202 spectrometer.

RESULTS AND DISCUSSION

Preparation of Poly(DRF)

Table 1 shows the results of radical polymerization of DRF in bulk or in benzene. The polymerization of BTMSF in benzene in the presence of MAIB at 60°C proceeded inhomogeneously to give a polymer in 50% yield. The polymeriza-

TABLE 1. Radical Polymerization of DRF in Bulk

DRF	Initiator	Temperature, °C	Time, hours	Yield, %	$M_n \times 10^{-4}$	M_w/M_n
BTMSF[a]	MAIB (0.7 mol%)	60	16	49.6[c]	–	–
BTMSF	BPO (0.7 mol%)	80	10	90.4[c]	–	–
BBDSF[b]	MAIB (1.7 mol%)	60	52	0	–	–
BBDSF	BPO (0.7 mol%)	80	48	0	–	–
DtAF	MAIB (0.02 mol/L)	60	20	16.1	1.03	2.2
DtAF	DtBPO (0.03 mol/L)	120	16.5	27.3	–	–
MtAF	MAIB (0.02 mol/L)	60	63	20.0	1.67	2.0
MtAF	DtBPO (0.06 mol/L)	120	20.5	68.5	0.56	1.6
MAn	BPO (2 mol%)	80	28	1.7	–	–

[a] Solution polymerization. BTMSF 3 g, benzene 0.5 mL.
[b] Solution polymerization. BBDSF 2 g, benzene 3 mL.
[c] Determined after transformation of poly(BTMSF) to poly (MCM).

tion reactivity of BTMSF is likely to be lower than that of DtBF despite similar structures of the ester substituents [12, 13]. Because poly(BTMSF) was partly hydrolyzed during the polymerization, the resulting polymer was isolated as poly(fumaric acid) by precipitation with methanol containing a small amount of HCl. The BTMSF monomer was also hydrolyzed during polymerization, but the resulting fumaric acid would hardly participate in polymerization because of its extremely low solubility in the monomer and benzene. Hydrolysis occurred more rapidly during polymerization at a higher temperature.

In contrast, no change was observed during the polymerizations of BBDSF in bulk at 80°C or in benzene at 60°C. The reaction mixture of BBDSF was poured into methanol, but no precipitation was observed. Furthermore, excess diazomethane was added to this solution and subsequently it was poured into a large amount of diethyl ether. However, no polymer was isolated. Therefore, we concluded that BBDSF yields no polymer under these conditions. The substituent is probably too large to homopolymerize as observed in the polymerizations of *tert*-amyl esters and neopentyl ester in previous work [9, 14].

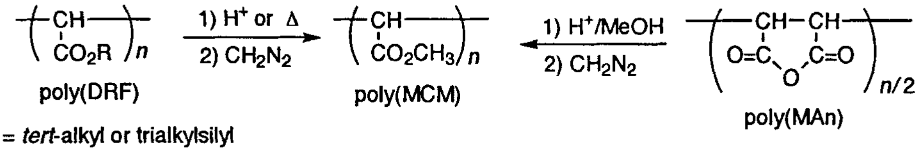
The *tert*-amyl esters, i.e., DtAF and MtAF, yielded the polymers in bulk polymerization, although the polymerization reactivities were lower than those of DtBF and MtBF [3]. This agrees well with the previous results [13, 14]. The poly(DtAF) prepared at 60°C was soluble in benzene and insoluble in methanol, whereas the poly(DtAF) prepared at 120°C was partly insoluble in benzene and soluble in methanol. Therefore, poly(DtAF) was isolated by precipitation with a methanol-H_2O mixture. Poly(MtAF) was also isolated similarly. Thus, the solubility depends on the monomer structure and the polymerization temperature, suggesting that the *tert*-amyl ester partly reacted to yield a carboxylic acid moiety during polymerization at a high temperature such as 120°C. MAn gave a polymer in low yield in the bulk polymerization because of its low reactivity [15].

Transformation of Polymers to Poly(MCM) and Determination of Tacticity

Poly(DRF) and poly(MAn) were converted to poly(MCM) via thermolysis or hydrolysis and subsequent methylation with diazomethane (Scheme 1) and provided determination of the tacticity. The quantitative transformation was confirmed by ^{1}H-NMR spectroscopy. Figure 1 shows the expanded spectra of the carbonyl and methine regions of the ^{13}C-NMR spectra of poly(MCM) derived from several kinds of poly(DRF)s. As has been described in previous papers [4–9], the tacticity of poly(DRF)s should be considered on the basis of the methylene repeating unit of poly(alkoxycarbonylmethylene)s, and it is determined by both the opening mode and the direction of monomer addition (Fig. 2). Here P_m and P_r are the probabilities of the meso and racemo additions, respectively, and P'_m and P'_r are of the opening modes. The fine-splittings in the spectra can be assigned to the eight kinds of heptad sequences as shown in a previous paper [5]. The P_m values were determined by simulation of the spectra. A typical example of the simulation is shown in Fig. 1(e). The chemical shifts of the heptad sequences are as follows: 170.20 (*mmmmmm*), 170.20 (*mmmmmr*), 170.40 (*mmmmrm*), 170.75 (*rmmrmm*), 171.60 (*mmmrmm*), 171.25 (*mmmrmr*), 171.50 (*mrmrmm*), 171.00 pm (*mrmrmr*) for carbonyl carbon; 46.00 (*mmmmmm*), 46.45 (*mmmmmr*), 46.30 (*mmmmrm*), 45.90 (*rmmrmm*), 44.50 (*mmmrmm*), 45.20 (*mmmrmr*), 45.00 (*mrmrmm*), 44.15 ppm (*mrmrmr*) for methine carbon. The P_m values determined are summarized in Table 2.

Opening Mode of Double Bond

Despite three possible configurations, i.e., *mm*, *mr*, and *rr*, for the triad sequences of poly(MCM) illustrated in Fig. 3, we can see only *mm* and *mr* triad-center sequences in the observed spectra of poly(MCM). This is due to the exclusive trans (meso) opening of the double bond of the monomer during polymerization. The opening mode is dominated by the conformation of the radical in the transition state, which is closely related to the stable conformation of the radical in the ground state. The preferred meso opening of DRF and DRM was confirmed by our previous results about the tacticity of poly(MCM) derived from poly(DRF) and the copolymers of DRF with DRM [6, 8]. The product ratio of the disastereomers in the reaction of DRF or DRM with bromotrichloromethane also supports the predominant meso opening of the double bond of DRF or DRM [16, 17]. Highly diastereoselective hydrogen abstractions have also been reported, and the high selectivity is interpreted as due to allylic strain effects which were proved by ESR observation and ab-initio calculation [18, 19]. In the polymerization of DRF, the propagation rate constants are remarkably small due to the lower reactivity of the sterically



SCHEME 1.

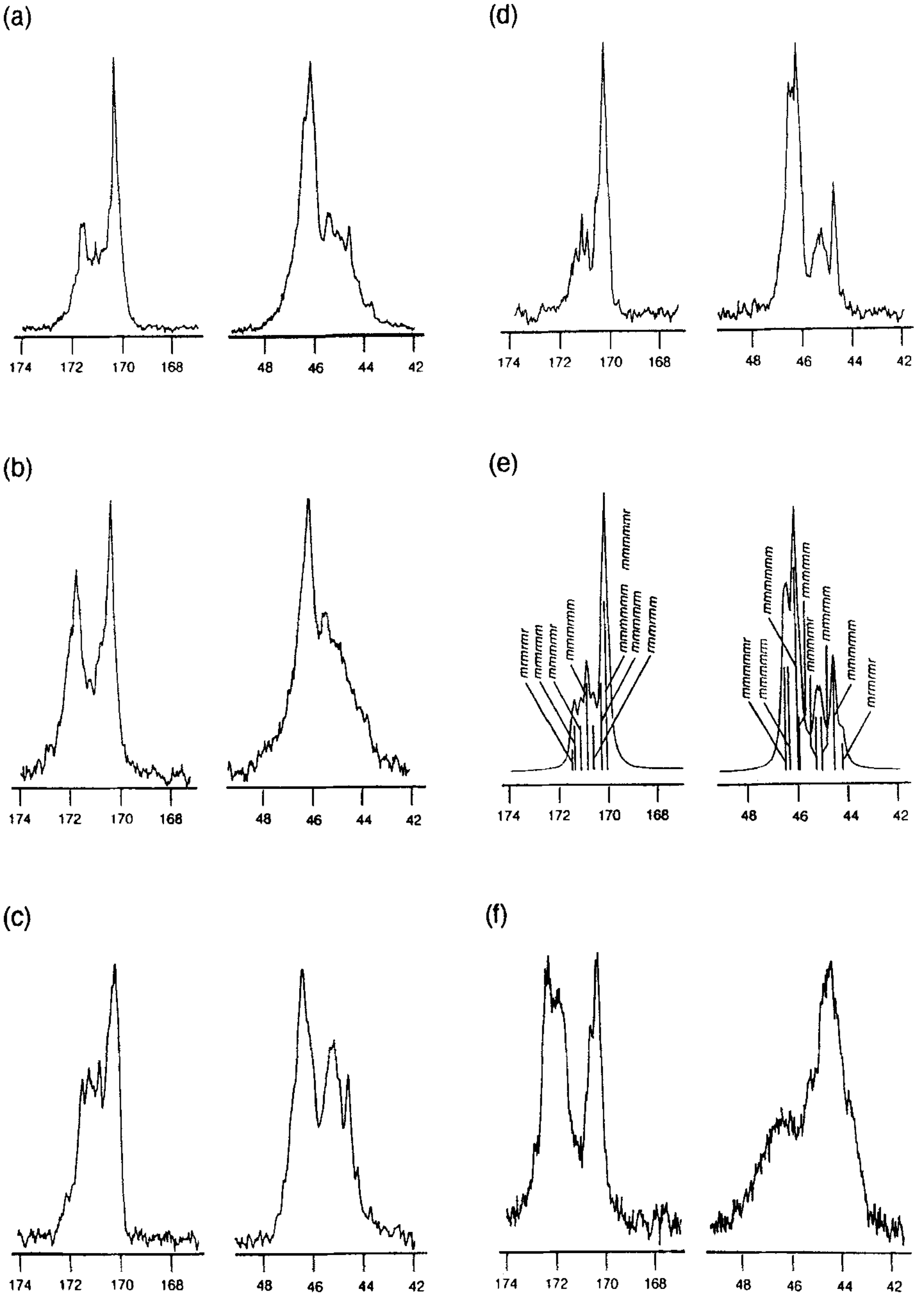


FIG. 1. Expanded ^{13}C-NMR spectra of poly(DMF) measured in $CDCl_3$ at ambient temperature. (a) Derived from poly(DtAF) (60°C); (b) derived from poly(DtAF) (120°C); (c) derived from poly(MtAF) (60°C); (d) derived from poly(BTMSF) (60°C); (e) simulation for the spectrum of (d); (f) derived from poly(MAn) (80°C).

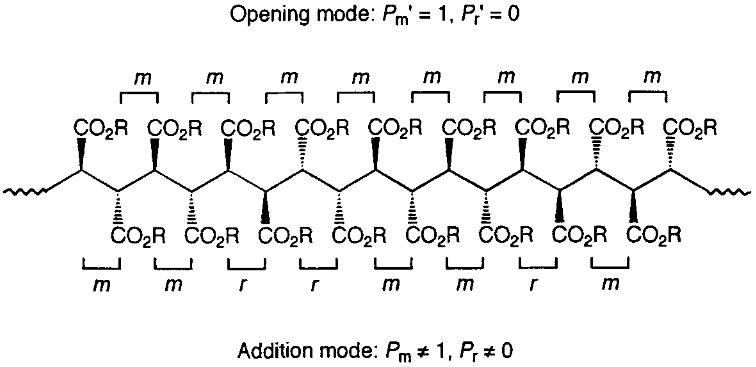


FIG. 2. Stereochemical structure of substituted polymethylene determined by both opening and addition modes during polymerization.

TABLE 2. Probability of Meso Addition in Radical Polymerization of DRF

DRF	Temperature, °C	P_m	$\Delta H^{\ddagger}_{m} - \Delta H^{\ddagger}_{r}$, $kJ \cdot mol^{-1}$	$\Delta S^{\ddagger}_{m} - \Delta S^{\ddagger}_{r}$, $J \cdot mol^{-1} \cdot K^{-1}$
BTMSF	60	0.66	—	—
DtAF	60	0.60	−5.9	−14
	120	0.52		
MtAF	60	0.54	0	1.3
	120	0.54		
DtBF[a]	120	0.68	−4.9	−6.4
MtBF[a]	120	0.57	0	2.3
DMF[a]	120	0.50	2.6	6.5

[a] From Ref. 6.

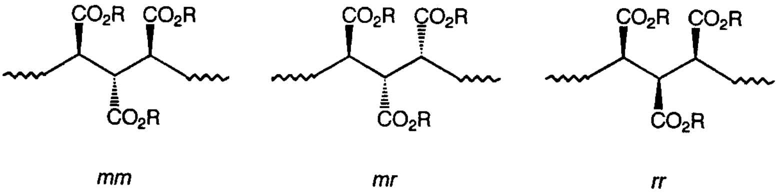


FIG. 3. Three possible triad sequences for poly(alkoxycarbonylmethylene).

hindered poly(DRF) radicals [9, 20]. The selectivity of the opening mode during the polymerization of DRF would increase, and P'_m can be regarded as equal to unity.

To the contrary, poly(MCM) derived from poly(MAn) provided an NMR spectrum different from those of poly(DMF) derived from poly(DRF), as is shown in Fig. 1(f). In this spectrum the additional peaks around 172–173 ppm were observed for the carbonyl carbons. For the methine carbons, the peaks around 44 ppm had a greater intensity than the peak at a lower magnetic field. The *rr* triad may exist in poly(MCM) derived from poly(MAn), as expected from the restricted ring structure of the monomer. The opening mechanism of DRF or DRM as acyclic monomers and MAn as a cyclic monomer is illustrated in Fig. 4, where P· represents the polymer radical. Whereas both DRF and DRM provided an identical polymer radical that yields the meso structure by the subsequent reaction [8], the opening of the double bond of MAn results in the racemo structure. That is, P'_m is equal to unity for the polymers of DRF and DRM, but not for MAn. Bacskai et al. [21], Rätzsch et al. [22], and Komber [23] reported the analysis of the microstructure of the alternating copolymers of MAn and olefins. They found that the racemo opening of MAn occurs predominantly. However, it is not clear whether or not P'_m is equal to zero in the homopolymerization of MAn. When both the meso and racemo openings occur, the statistics of the tacticity become very complicated [5]. We could not determine the P_m value for MAn because of the difficulty of assignment of the chemical shifts for the *rr*-center heptad sequences and uncertainty of the opening mode.

Meso and Racemo Additions

The P_m values determined were in the following order: DtBF (0.68) > MtBF (0.57) > MtAF (0.54) > DtAF (0.52) > DMF (0.50) at 120°C. The probability of the meso addition decreases with variation of the ester substituents from *tert*-butyl to *tert*-amyl and methyl. In the polymerization of MtAF, P_m was independent of the polymerization temperature and very similar to the previous results observed for MtBF [6]. That is, the difference in activation enthalpies for meso and racemo additions ($\Delta H^\ddagger_m - \Delta H^\ddagger_r$) is equal to zero in the polymerization of methyl alkyl fumarates (MRF), as shown in Fig. 5.

$$\ln(P_m/(1 - P_m)) = -(\Delta H^\ddagger_m - \Delta H^\ddagger_r)/RT + (\Delta S^\ddagger_m - \Delta S^\ddagger_r)/R \qquad (1)$$

Poly(DtAF) showed a negative temperature dependence of P_m. That is, as the polymerization temperature decreased, the P_m value increased, as observed in the polymerization of DtBF [6]. However, the magnitude of P_m for DtAF was smaller than that of DtBF because of the small $\Delta S^\ddagger_r - \Delta S^\ddagger_r$ value. The P_m value for BTMSF polymerization was intermediate between those of DtBF and DtAF (Fig. 5a).

In the addition of DRF, the selectivity of the meso and racemo additions is determined by the interaction between the substituents in the polymer chain and the monomer, i.e., the interactions between the ester substituents, E_α or E_β and E'_α, as shown in Fig. 6. Probably the interaction between E_α or E_β and E'_β would be less important. Table 3 summarizes the relationship between the size of the ester alkyl substituents and the preferred addition modes.

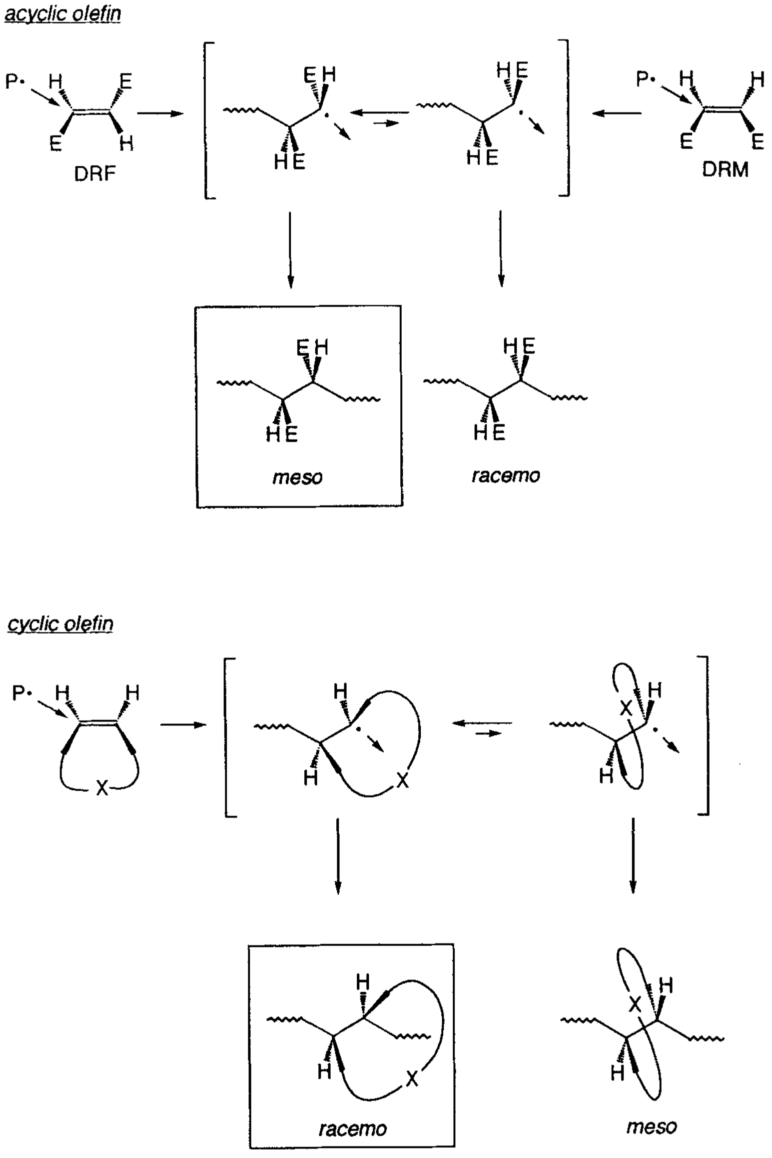


FIG. 4. Mechanism of meso and racemo opening for cyclic and acyclic monomers.

With regard to enthalpy, racemo addition would be preferred due to the interaction between the β-CO_2R substituent of the radical and the CO_2R group of the monomer, i.e., the E_β-E'_α interaction. However, as the ester alkyl group becomes larger, the polymer chain will propagate at the regulated chain-end structure like a helix, and consequently the energy in the transition state for the meso addition will decrease. The entropy effect induces a change from the meso addition to the racemo addition according to the increase in the steric hindrance of the substituents. That is, when R is small, a significant interaction between E_α and E'_α results in the

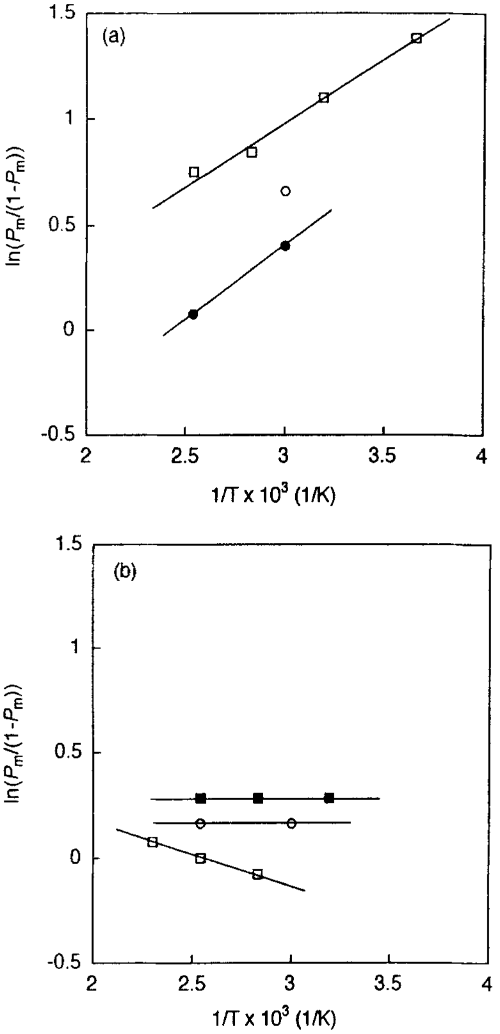


FIG. 5. Arrhenius plots for the ratio of probabilities of meso addition to racemo addition during radical polymerization of DRF. (a) Dialkyl fumarates: (○) BTMSF, (●) DtAF, (□) DtBF. (b) Methyl alkyl fumarates: (○) MtAF, (■) MtBF, (□) DMF.

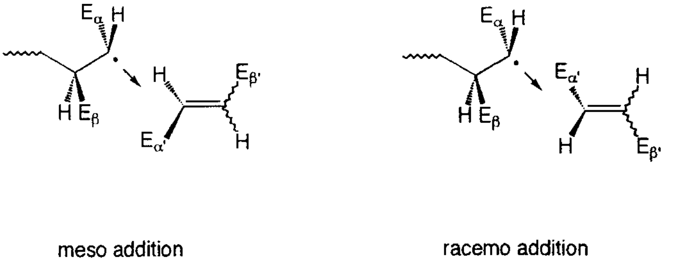


FIG. 6. Meso and racemo additions in propagation of DRF.

TABLE 3. Relationship between Monomer Structure and Preferred Addition Modes

Monomer	Size of substituent	Preferred addition mode	
		Enthalpy	Entropy
DRF	Large	Meso	Racemo
MRF	Medium	Meso/racemo	Meso
DMF	Small	Racemo	Meso

meso addition. In contrast, a large R group makes the E_β-E'_α interaction more important and so yields the racemo addition.

In the polymerization of MRF, the regioselectivity of the propagation, i.e., head-to-tail and head-to-head propagation, has not been fully clarified [7]. The intermediate enthalpy and entropy effects observed in this work suggest that regioselectivity is not high in the polymerization of MRF.

CONCLUSIONS

The microtacticities of the polymers from bis(trimethylsilyl) fumarate, di-*tert*-amyl fumarate, methyl *tert*-amyl fumarate, and maleic anhydride have been determined using ^{13}C-NMR spectroscopy. The opening and addition modes in propagation have been discussed based on the results obtained in the present and previous work. We confirmed the exclusive *trans* (meso) opening of the double bond of the fumarates during polymerization, while the racemo-racemo triad sequence due to the racemo opening was detected in the polymer of maleic anhydride as a cyclic *cis*-olefin. The probability of meso addition decreased with the variation of the ester substituents from *tert*-butyl to *tert*-amyl and methyl for the polymerization of the fumarates at 120°C. It has been revealed from the temperature dependence of the probability that the meso and racemo additions are favored in the aspect of enthalpy and entropy, respectively, as the size of the ester substituent becomes larger.

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