

***meso* and *racemo* Additions in Propagation for Radical Polymerization of Dialkyl Fumarates I. Stereoregularity of Poly(dialkyl fumarate)s**

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(Received March 14, 1991)

ABSTRACT: The polymerization temperature dependence of the stereochemical configuration of some poly(dialkyl fumarate)s as poly(substituted methylene) was investigated by the use of ^{13}C NMR spectroscopy in order to clarify the propagation process in radical polymerization of dialkyl fumarates. The probability of *meso* addition (P_m) for polymerization of di-*tert*-butyl fumarate increased from 0.68 to 0.80, when the polymerization temperature decreased from 120°C to 0°C. On the other hand, it was revealed that P_m for dimethyl fumarate and diisopropyl fumarate decreased by the decreasing polymerization temperature, and that it was almost independent of the temperature for methyl *tert*-butyl fumarate. From the differences in activation enthalpies and entropies for *meso* and *racemo* additions, the effect of the ester alkyl groups on the propagation manner was discussed.

KEY WORDS Dialkyl Fumarate / Radical Polymerization / Poly(substituted methylene) / ^{13}C Nuclear Magnetic Resonance / Stereoregularity / Activation Enthalpy / Activation Entropy /

It has been reported that dialkyl fumarates (DRF) with bulky ester alkyl groups homopolymerize readily to give high molecular weight polymers in a radical mechanism despite of the 1,2-disubstituted ethylene structure, and that the resulting poly(DRF)s consist of a semiflexible poly(substituted methylene) structure.¹⁻⁵ The polymerization reactivity (polymerization rate and molecular weight of the polymer) and the flexibility of poly(DRF)s depend intensively upon the structure (bulkiness) of the ester substituents, indicating that the polymerization of DRF shows unique characteristics different from ordinary vinyl polymerizations. It has been also revealed that stereochemical structure of poly(DRF)s is dependent of the structure of the ester alkyl groups.^{6,7}

The tacticity of poly(DRF)s is dominated by both opening mode of carbon-to-carbon double bond and direction of monomer addition to the propagating polymer radical.

As each carbon atom in the main chain of poly(DRF) as poly(substituted methylene) is pseudo-asymmetric, the stereochemistry based on the methylene unit should be considered as is shown in Figure 1. When Bernoullian probability is applied to the stereochemistry of poly(DRF)s, two parameters, P_m (P_r) and P'_m (P'_r) are required, which represent the probability of *meso* (*racemo*) addition and opening, respectively. However, because the opening of double bond is restricted to *trans* mode for polymerization of DRF, *i.e.*, $P'_m = 1$ and $P'_r = 0$, the stereoregularity of poly(DRF) can be determined with solely P_m .^{6,7}

In the previous paper,⁷ we investigated the P_m values for polymerization of di-*tert*-butyl fumarate (DtBF), methyl *tert*-butyl fumarate (MtBF) and dimethyl fumarate (DMF) by the use of ^{13}C NMR spectroscopy, and confirmed that *meso* addition was preferable in the propagation of DRF having a *tert*-butyl group as is shown in Figure 2. Furthermore, pre-

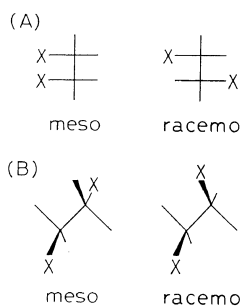


Figure 1. (A) Fischer and (B) planar zigzag projections of *meso* and *racemo* diads for poly(substituted methylene).

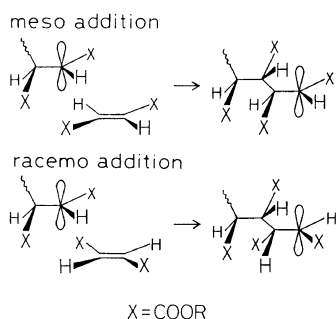


Figure 2. *meso* and *racemo* additions of DRF to a poly(DRF) radical, where the opening mode of double bond is restricted to *trans* (*meso*) mode (see the text).

liminary results indicated that *meso* addition was favored for polymerization of DtBF as the polymerization temperature decreased. Recently, we have found that temperature dependence of P_m for other DRFs is different utterly from that for DtBF.

The purpose in this study is to examine the temperature dependence of P_m for polymerization of various DRFs with the aid of ^{13}C NMR spectra of poly(DRF)s as a step for clarification of the addition manner of the monomer in propagation.

EXPERIMENTAL

DRFs were prepared and purified as reported previously.¹⁻⁴ DtBF: mp 71°C, MtBF: bp 65°C (1 mmHg), DiPF: bp 93°C (7 mmHg), DMF: mp 102°C. 2,2'-Azobisisobutyronitrile (AIBN), dimethyl 2,2'-azobisisobu-

tyrate (MAIB), 1,1'-azobiscyclohexanecarbonitrile (ACN), di-*tert*-butyl peroxide (DTBPO) and *tert*-butyl hydroperoxide (TBHPO) were used as a radical initiator.

Polymerization was carried out in a degassed glass tube. The polymerization mixture was poured into a large amount of precipitant to isolate the polymer. Methanol, *n*-hexane, and diethyl ether were used as precipitant for poly(DtBF) or poly(DiPF), poly(MtBF), and poly(DMF), respectively. The polymer obtained was dried under vacuum. The purification of the polymers was performed by reprecipitation.

The number- and weight-average molecular weights (\bar{M}_n and \bar{M}_w , respectively) and polydispersity (\bar{M}_w/\bar{M}_n) of the resulting polymers were determined by gel permeation chromatography (GPC) at 38°C in tetrahydrofuran as an eluent by means of Tosoh 8000 series GPC system, and calibrated with standard polystyrenes.

The ^{13}C NMR spectra were recorded on a JEOL GX-400 spectrometer using deuteriochloroform as a solvent and an internal standard (δ 77.03) at an ambient temperature (*ca.* 27°C). The operating conditions were same as those in the previous paper.⁷ The spectra were simulated to determine the P_m according to the method previously reported.⁷ The typical examples of simulation parameters are as follows. Poly(DMF) derived from poly(MtBF) (120°C); P_m 0.57, for carbonyl carbon, chemical shifts 170.20 (*mmmmmm*), 170.20 (*mmmmmr*), 170.40 (*mmmmrm*), 170.75 (*rmmmrmm*), 171.00 (*mmmrmm*), 171.25 (*mmmrmr*), 171.50 (*mrmrmm*), and 171.60 ppm (*mrmrmr*), half width 0.5 ppm; for methine carbon, chemical shifts, 46.00 (*mmmmmm*), 46.45 (*mmmmmr*), 46.30 (*mmmmrm*), 45.90 (*rmmmrmm*), 44.50 (*mmmrmm*), 45.20 (*mmmrmr*), 45.00 (*mrmrmm*), and 44.15 ppm (*mrmrmr*), half width 1.0 ppm. Poly(DiPF) (120°C); P_m 0.55, for carbonyl carbon, chemical shifts 169.35 (*mmmmmm*), 169.35 (*mmmmmr*), 169.85 (*mmmmrm*), 170.00 (*rmmmrmm*), 170.10 (*mmmrmm*), 170.25 (*mm-*

rmr), 170.45 (*mrmrmm*), and 170.65 ppm (*mrmrmm*), half width 0.52 ppm; for methine carbon, chemical shifts, 46.20 (*mmmm*), 46.20 (*mmmr*), 44.85 (*mmrm*), and 44.70 ppm (*mrmr*), half width 1.2 ppm.

RESULTS AND DISCUSSION

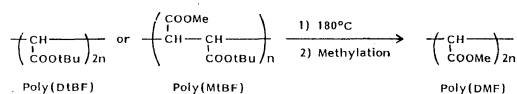
Preparation of Poly(DRF)s

To investigate the effect of polymerization temperature on P_m , poly(DRF)s were prepared at various temperatures. Table I summarizes the results of radical polymerization of DRFs in bulk or in solution in the presence of an appropriate initiator with or without UV irradiation in the temperature range of 0–160°C. The effect of initiator, solvent, and monomer concentration on tacticity of the resulting polymers are neglected in the present study. All polymerizations gave high molecular weight polymers ($\bar{M}_n > 10^4$) enough to be used for determination of tacticity. DtBF which has the highest polymerization reactivity among

the DRFs examined gave a polymer at 0°C, whereas DMF necessitated high polymerization temperature to obtain a polymer because of its lower reactivity. These results agree with the previous result that DRFs with bulkier substituents have a higher polymerization reactivity.⁴

Polymerization Temperature Dependence of P_m

In the previous paper,⁷ it was reported that the splitting due to the tacticity appeared in the signals for main-chain methine and carbonyl carbons in ¹³C NMR spectra of poly(DRF)s, but the both spectra for poly(DtBF) and poly(MtBF) were too broad to predict their stereoregularity precisely. Therefore, these polymers were converted quantitatively into poly(DMF) by pyrolysis without any catalyst



Scheme 1.

Table I. Results of radical polymerization of DRF

[DRF]	[Initiator]	Solvent ^a	Temp.	Time	Convsn.	\bar{M}_n	\bar{M}_w/\bar{M}_n
mol l ⁻¹	mol l ⁻¹		°C	h	%	$\times 10^{-4}$	
DtBF							
3.77	DTBPO (0.038)	Tol	120	3	38.9	1.32	2.0
Bulk	ACN (0.01)	None	80	8	56.9	6.82	2.9
2.0	AIBN (0.02)	Bz	40	30	22.1	11.6	2.3
0.95	DTBPO (0.02)	Tol	0 ^b	50	1.7	1.78	1.7
MtBF							
Bulk	DTBPO (0.02)	None	120	5	44.0	1.87	1.8
Bulk	ACN (0.02)	None	80	20	62.5	5.94	1.9
Bulk	AIBN (0.02)	None	40	55	11.7	13.9	1.9
DiPF							
Bulk	DTBPO (0.02)	None	120	3	29.6	4.41	1.4
3.46	MAIB (0.02)	Bz	60	1.5	15.7	13.8	1.6
2.69	DTBPO (0.1)	Tol	0 ^b	20	5.6	1.74	1.7
DMF							
5.78	TBHPO (0.02)	Xyl	160	10	14.0	—	—
6.18	DTBPO (0.062)	Tol	120	12	25.5	(0.05) ^c	—
2.78	ACN (0.02)	Bz	80	10	8.9	—	—

^a Tol, toluene; Bz, benzene; Xyl, *p*-xylene.

^b Polymerized under UV irradiation.

^c [η] in benzene at 30°C (in dl g⁻¹).

and subsequent methylation (Scheme 1),⁷ prior to determination of the tacticity.

Figures 3–6 show the expanded ¹³C NMR spectra for the methine and the carbonyl carbons of poly(DRF)s prepared under the conditions shown in Table I. It should be noted that the spectra in Figures 3 and 4 were observed as poly(DMF)s derived from poly-(DtBF) and poly(MtBF), respectively, but not as poly(DtBF) and poly(MtBF) themselves. Poly(DiPF) was measured directly without any derivation, because quantitative transformation to poly(DMF) was very difficult.⁸

Previous studies^{6,7} with respect to triad sequences for poly(DRF) indicated that an *mm* triad signal appeared at a higher magnetic field than an *mr* triad signal for the carbonyl carbon, and at a lower field for the methine carbon. The spectra of poly(DMF) derived from poly(DtBF) (Figure 3) clearly indicates that intensities of the *mm* triad regions of the both

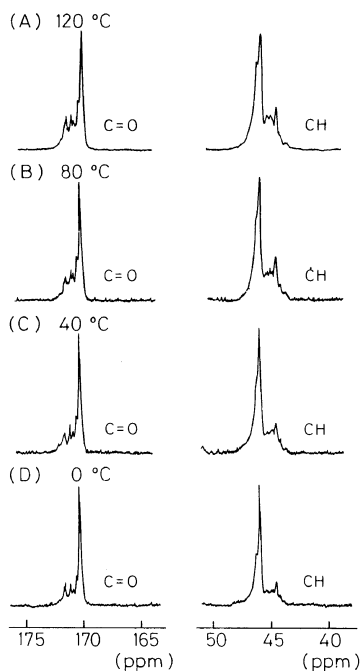


Figure 3. ¹³C NMR spectra of main-chain methine and carbonyl carbons for poly(DMF) derived from poly-(DtBF). Polymerization temperature: (A) 120°C; (B) 80°C; (C) 40°C; (D) 0°C.

carbons, *i.e.*, 169.5–170.6 ppm and 45.6–48.0 ppm for the carbonyl and methine carbons, respectively, increase with decreasing polymerization temperature. On the other hand, the peak intensities for the corresponding carbons of poly(DMF) derived from poly(MtBF) do

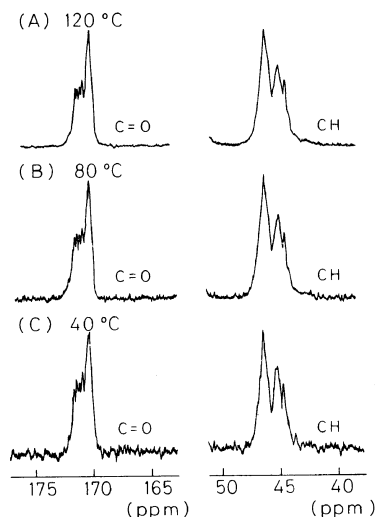


Figure 4. ¹³C NMR spectra of main-chain methine and carbonyl carbons for poly(DMF) derived from poly-(MtBF). Polymerization temperature: (A) 120°C; (B) 80°C; (C) 40°C.

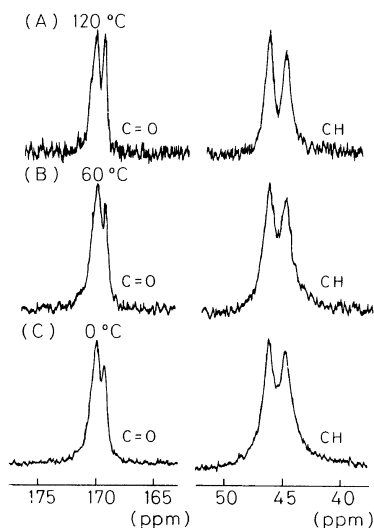


Figure 5. ¹³C NMR spectra of main-chain methine and carbonyl carbons for poly(DiPF). Polymerization temperature: (A) 120°C; (B) 60°C; (C) 0°C.

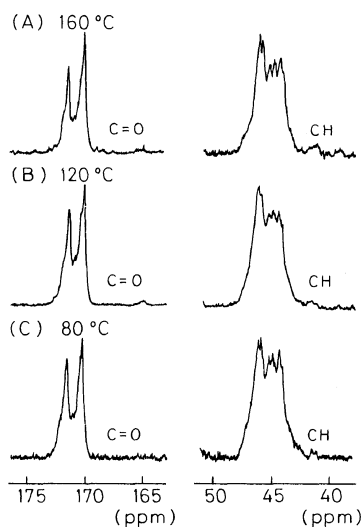


Figure 6. ^{13}C NMR spectra of main-chain methine and carbonyl carbons for poly(DMF). Polymerization temperature: (A) 160°C; (B) 120°C; (C) 80°C.

not observed to change with the temperature as shown in Figure 4. In the cases of poly(DiPF) (Figure 5) and poly(DMF) (Figure 6), the *mm* triad regions slightly decrease with decreasing polymerization temperature.

In order to determine P_m (probability of *meso* addition), the spectra of the methine and the carbonyl carbons of poly(DRF)s were simulated. The simulation was carried out with respect to heptad sequences except for the spectra for the methine carbon of poly(DiPF), which was simulated with pentad sequences because of their broad signals.⁶

Table II shows the P_m determined by the simulation of the spectra in Figures 3—6. The P_m values obtained were in the following order; DtBF > MtBF > DiPF > DMF, agreeing with the results in the previous report.⁷ The P_m for poly(DtBF) increased with the decrease in the polymerization temperature, *i.e.*, it reached 0.80 at 0°C, where an average fraction of the *meso* diad for the polymer was as high as 0.90 (Table II). On the other hand, the P_m values for DiPF and DMF showed the opposite temperature dependence to DtBF, *i.e.*, the P_m decreases with decreasing temperature. No

Table II. P_m values for polymerization of DRF and the probability of *meso* diad ($[m]$) in poly(DRF)

DRF	Polymerization Temperature		P_m	$[m]$
	°C			
DtBF	120		0.68	0.84
	80		0.70	0.85
	40		0.75	0.88
MtBF	0		0.80	0.90
	120		0.57	0.79
	80		0.57	0.79
DiPF	40		0.57	0.79
	120		0.55	0.78
	60		0.54	0.77
DMF	0		0.53	0.77
	160		0.52	0.76
	120		0.50	0.75
	80		0.48	0.74

dependence of the P_m value was observed for polymerization of MtBF.

Activation Enthalpies and Entropies for *meso* and *racemo* Additions

The differences in activation enthalpies and entropies for *meso* and *racemo* additions ($\Delta H_m^\ddagger - \Delta H_r^\ddagger$ and $\Delta S_m^\ddagger - \Delta S_r^\ddagger$, respectively) can be determined from the Arrhenius plot of the P_m (eq 1), because P_m is generally determined by the differences in free energies of activation for *meso* and *racemo* additions ($\Delta G_m^\ddagger - \Delta G_r^\ddagger$).^{9,10}

$$\begin{aligned}
 \ln[P_m/(1-P_m)] &= \ln(k_m/k_r) \\
 &= -(\Delta G_m^\ddagger - \Delta G_r^\ddagger)/RT \\
 &= -(\Delta H_m^\ddagger - \Delta H_r^\ddagger)/RT + (\Delta S_m^\ddagger - \Delta S_r^\ddagger)/R
 \end{aligned} \quad (1)$$

Where, k_m and k_r represent the rate constants for *meso* and *racemo* additions, respectively, and R is the gas constant, and T is the absolute polymerization temperature.

The plots of $\ln[P_m/(1-P_m)]$ against $1/T$ gave a linear relation for each DRF (Figure 7). The

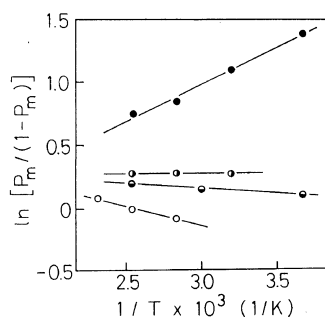


Figure 7. Arrhenius plots for the ratio of probabilities of *meso* addition to *racemo* addition for radical polymerization of DtBF (●), MtBF (●), DiPF (◐), and DMF (○).

Table III. Differences in activation enthalpies and entropies for *meso* and *racemo* additions in radical polymerization of DRF

DRF	$\Delta H_m^\ddagger - \Delta H_r^\ddagger$ kJ mol ⁻¹	$\Delta S_m^\ddagger - \Delta S_r^\ddagger$ J mol ⁻¹ K ⁻¹	$\Delta G_m^\ddagger - \Delta G_r^\ddagger$ (60°C) kJ mol ⁻¹
DtBF	-4.9	-6.4	-2.8
MtBF	0	2.3	-0.77
DiPF	0.6	3.2	-0.47
DMF	2.6	6.5	0.43

$\Delta H_m^\ddagger - \Delta H_r^\ddagger$ and $\Delta S_m^\ddagger - \Delta S_r^\ddagger$ determined are listed in Table III. The $\Delta H_m^\ddagger - \Delta H_r^\ddagger$ value indicates that *meso* addition is preferred by enthalpy for polymerization of DtBF. On the other hand, the $\Delta H_m^\ddagger - \Delta H_r^\ddagger$ value is positive for polymerization of DMF. For polymerization of DiPF and MtBF, the $\Delta H_m^\ddagger - \Delta H_r^\ddagger$ values are the intermediate between those of DtBF and DMF. These results indicate that the $\Delta H_m^\ddagger - \Delta H_r^\ddagger$ value depends remarkably on the structure of the ester substituents. The $\Delta S_m^\ddagger - \Delta S_r^\ddagger$ value is also dependent on the ester groups, *i.e.*, it decreases along with the bulkiness of the ester substituents, indicating that the *racemo* addition is advantageous by entropy on account of the steric hindrance.

The $\Delta G_m^\ddagger - \Delta G_r^\ddagger$ at 60°C were calculated from the $\Delta H_m^\ddagger - \Delta H_r^\ddagger$ and the $\Delta S_m^\ddagger - \Delta S_r^\ddagger$ values, and are included in Table III. The values indicate that ΔG_r^\ddagger is larger than ΔG_m^\ddagger for polymerization of DtBF, while ΔG_m^\ddagger value is

larger for polymerization of DMF. It is surprising characteristics because the dependence on the structure of ester groups was scarcely observed for polymerization of alkyl methacrylates¹¹ except for triphenylmethyl methacrylate,¹² which shows the different behaviors originated from the formation of stable helical conformation in the polymerization solution.¹³ In the polymerization of DRFs, the effect of the structure of the ester substituents on $\Delta G_m^\ddagger - \Delta G_r^\ddagger$ might be due to the steric factors peculiar to an attack of the 1,2-disubstituted ethylene toward the poly(substituted methylene) radical.

Furthermore, since the P_m/P_r values are correlated to the k_m/k_r values by using eq 1, it is possible to determine the absolute values of k_m and k_r when the propagation rate constant is obtained. The detailed results are described in the next paper.

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