^{13}C nuclear magnetic resonance study of stereoregularity in poly(dialkyl fumarate)s bearing t-butyl ester groups

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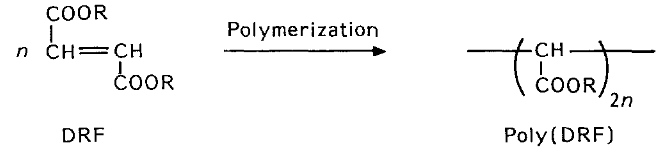
The stereochemical configuration of poly(dialkyl fumarate)s (poly(DRF)) bearing t-butyl groups, i.e. poly(di-t-butyl fumarate) (poly(DtBF)) and poly(methyl t-butyl fumarate) (poly(MtBF)), was investigated by means of ^{13}C nuclear magnetic resonance spectroscopy at 100 MHz. The microstructures of the polymers prepared by radical polymerization at 120°C were examined after they were transformed into poly(dimethyl fumarate) (poly(DMF)) by quantitative thermolysis and esterification in order to facilitate analysis of the spectra. The simulation of the spectra was carried out with the aid of modified Bernoullian statistics. It was revealed that the probability of *meso* addition in the propagation increased as a bulky ester group was introduced into DRF, i.e. in the order DtBF > MtBF > DMF. The average fraction of *meso* diads in poly(DtBF) increased when the polymerization temperature decreased.

(Keywords: poly(di-t-butyl fumarate); radical polymerization; tacticity; ^{13}C nuclear magnetic resonance; *meso* addition; poly(substituted methylene))

INTRODUCTION

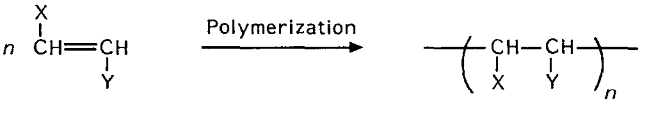
We have reported that dialkyl fumarates (DRF) bearing bulky alkyl esters such as t-butyl undergo radical polymerization to give a high-molecular-weight poly(substituted methylene):



$$n\,\underset{\text{COOR}}{\overset{\text{COOR}}{\text{CH}=\text{CH}}} \xrightarrow{\text{Polymerization}} \left(\underset{\text{COOR}}{\text{CH}}\right)_{2n}$$

(1)

The latter has a less flexible structure because it contains a defect in the form of a methylene group as a spacer in the main chain[1–5]. These poly(substituted methylene)s have different properties from ordinary flexible vinyl polymers. However, very few examples of poly(substituted methylene)s have ever been reported, except for some cyclic compounds and fluoro-substituted ethylenes, because 1,2-disubstituted ethylenes generally do not homopolymerize owing to steric hindrance of the substituent in a radical mechanism. On the other hand, in cationic and anionic polymerizations some polymers can be obtained from *cis*- or *trans*-1,2-disubstituted ethylenes, e.g. β-substituted vinyl ethers[6–8] and alkyl crotonates[9–11]. In the cases of these polymerizations, the two substituents on the ethylene are different from each other as represented below:



$$n\,\underset{\text{Y}}{\overset{\text{X}}{\text{CH}=\text{CH}}} \xrightarrow{\text{Polymerization}} \left(\underset{\text{X}}{\text{CH}}-\underset{\text{Y}}{\text{CH}}\right)_{n}$$

(2)

The stereochemistry of the polymers obtained from 1,2-disubstituted ethylenes has always attracted great attention since the discovery of stereoregular polymers by Natta *et al.*[12], because it gives us great information on the mechanism of polymerization, i.e. not only the direction of an attacking monomer but also the manner of opening of the double bond. It has been well established that n.m.r. spectroscopy is the most reliable method for elucidation of tacticity of polymers[13–16]. The stereochemical configurations of the polymers in equation (2) were clarified by analysis of their n.m.r. spectra[7–9,17,18]. In contrast, very few studies have been reported on the polymers represented in equation (1), except for poly(hydroxymethylene)[19] and poly(fluoromethylene)[20,21]. Recently, Ando and coworkers determined the configuration of poly(DRF) bearing secondary alkyl esters by means of 125 MHz ^{13}C n.m.r. spectroscopy[22].

In this paper, therefore, the configuration of the polymer chain of poly(DRF) bearing a bulky t-butyl group is revealed from the ^{13}C n.m.r. spectra, and the relationship between the bulkiness of the ester substituents and the stereoregularity of the polymer is discussed.

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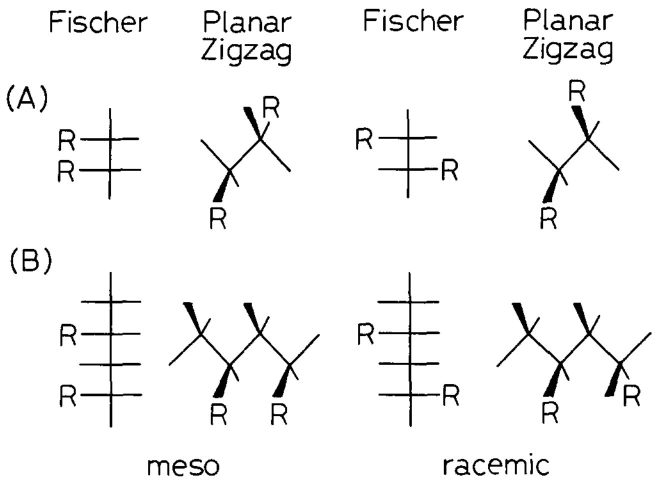

Figure 1 Fischer and planar zigzag projections of *meso* and *racemic* diads: (A) poly(substituted methylene); (B) vinyl polymer

EXPERIMENTAL

Preparation of poly(DRF)

DRF was prepared as reported in the previous papers. Polymerization was carried out in a sealed glass tube in the presence of a radical initiator. The polymerization mixture was poured into a large amount of precipitant to isolate the resulting poly(di-t-butyl fumarate) (poly(DtBF)), poly(methyl t-butyl fumarate) (poly(MtBF)) and poly(dimethyl fumarate) (poly(DMF)). The polymers were purified by repeated precipitations.

The number-average molecular weights of the polymers were determined by gel permeation chromatography calibrated with polystyrene standards.

Transformation of poly(DRF) to poly(DMF)

Poly(DtBF) and poly(MtBF) were heated at 180°C for 2 h in vacuum, followed by methylation, i.e. they were refluxed in methanol for 25 h, and then reacted with excess diazomethane[2,3]. The poly(DMF) obtained was reprecipitated from chloroform and diethyl ether. The quantitative transformation was confirmed by i.r. and n.m.r. spectra.

^{13}C n.m.r. measurements

The ^{13}C n.m.r. spectra were recorded on a JEOL GX-400 n.m.r. spectrometer at a ^{13}C frequency of 100 MHz in deuterochloroform or deuterobenzene as the solvent ($\sim$10% polymer concentration) at room temperature (27°C). The peaks of the solvent used ($\delta = 77.03$ and 128 ppm) were adopted as an internal standard for chemical shifts from tetramethylsilane. The acquisition time and delay time between pulses were 0.682 and 1.00 s, respectively, and 2000–4000 scans were accumulated for each sample.

Simulation of the spectra

A spectrum was simulated as an accumulation of Lorentzian curves for eight peaks corresponding to heptad sequences (see later). The chemical shift, height, linewidth at half-height of each peak and P_m values (as stated later) were determined as optimum values. The chemical shift for each heptad was determined with reference to those for pentads reported previously[22].

RESULTS AND DISCUSSION

Stereochemistry of poly(substituted methylene)

The stereochemistry of poly(DRF) should be considered on the basis of a methylene repeat unit, because each carbon atom in the main chain of poly(DRF) is pseudo-asymmetric. In the vicinal carbon atoms, two stereochemical configurations, i.e. *meso* and *racemic* diads, exist as shown in *Figure 1A*, which are represented by two kinds of projection, Fischer and planar zigzag. In the latter, the two substituents on consecutive methylene units are located on different sides when the configuration is *meso*. This is opposite to that for a vinyl polymer (*Figure 1B*).

In the polymerization of DRF, two pseudo-asymmetric centres are generated simultaneously in each propagation step, so that the Bernoullian probability of a *meso* diad must be represented as P_m and P'_m, which refer to the probabilities of *meso* addition and opening, respectively. Similarly, P_r and P'_r indicate those probabilities for a *racemic* diad. If opening of the carbon-to-carbon double bond is restricted to the *trans* mode (*meso*), i.e. the rate of rotation around the terminal sigma bond is much slower than the propagating rate because of steric hindrance of the bulky substituents[23]*, the P'_m value is equal to unity ($P'_r = 0$). As a result of this, stereoregularity of poly(DRF) can be represented solely by P_m, which is evaluated from a simulation of the n.m.r. spectra as mentioned later. Moreover, since P_m and P'_m appear alternatively along the polymer chain (*Figure 2*), the variety of real sequences decreases drastically when P'_r is zero, e.g. from 36 to 8 for a heptad as shown in *Table 1*. Thus we can analyse higher sequences such as heptads if some restrictions on the configuration of the chain are introduced[22,24]. In addition, we actually observe only odd-ads because of all the pseudo-asymmetric carbons in the main chain of poly(substituted methylene)s, and the probability for even-ads should be calculated[22].

^{13}C n.m.r. spectra of poly(DRF)

The poly(DRF)s were prepared by radical polymerization initiated with di-t-butyl peroxide (DtBPO) in toluene or in bulk at 120°C. The results of the polymerization are summarized in *Table 2*.

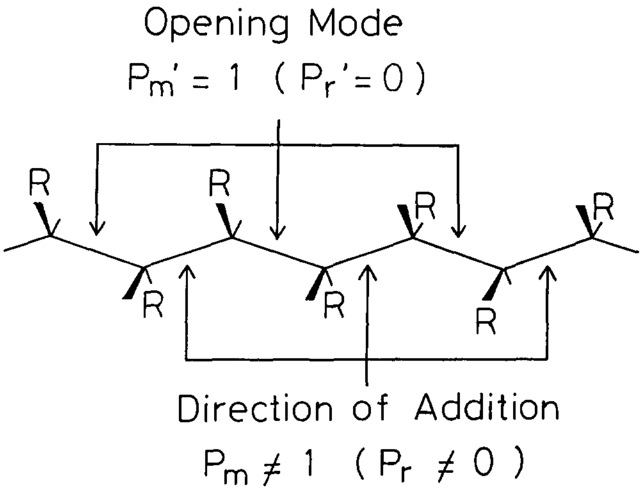

Figure 2 Probabilities of diad for poly(DRF); P_m and P'_m indicate probability of formation of *meso* diad by addition and opening, respectively

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* See note added in proof

Table 1 Sequence probabilities in modified Bernoullian model

Sequence	Probability $P'_m \neq 1$ $(P'_r \neq 0)$	 $P'_m = 1$ $(P'_r = 0)$
Triad		
mm	$P_m P'_m$	P_m
mr	$P_m P'_r + P'_m P_r$	P_r
rr	$P_r P'_r$	0
Pentad		
mmmm	$P_m^2 P_m'^2$	P_m^2
mmmr	$P_m P'_m (P_m P'_r + P'_m P_r)$	$P_m P_r$
rmmr	$P_m P'_m P_r P'_r$	0
mmrm	$P_m P'_m (P_m P'_r + P'_m P_r)$	$P_m P_r$
mmrr	$2P_m P'_m P_r P'_r$	0
rmrm	$P_m^2 P_r'^2 + P_m'^2 P_r^2$	P_r^2
rmrr	$P_r P'_r (P_m P'_r + P'_m P_r)$	0
mrrm	$P_m P'_m P_r P'_r$	0
rrrm	$P_r P'_r (P_m P'_r + P'_m P_r)$	0
rrrr	$P_r^2 P_r'^2$	0
Heptad		
mmmmmm	$P_m^3 P_m'^3$	P_m^3
mmmmmr	$P_m^2 P_m'^2 (P_m P'_r + P'_m P_r)$	$P_m^2 P_r$
rmmmmr	$P_m^2 P_m'^2 P_r P'_r$	0
mmmmrm	$P_m^2 P_m'^2 (P_m P'_r + P'_m P_r)$	$P_m P_r$
mmmmrr	$2P_m^2 P_m'^2 P_r P'_r$	0
rmmmrm	$P_m P'_m (P_m^2 P_r'^2 + P_m'^2 P_r^2)$	$P_m P_r^2$
rmmmrr	$P_m P'_m P_r P'_r (P_m P'_r + P'_m P_r)$	0
mrmmrm	$P_m^2 P_m'^2 P_r P'_r$	0
mrmmrr	$P_m P'_m P_r P'_r (P_m P'_r + P'_m P_r)$	0
rrmmrr	$P_m P'_m P_r^2 P_r'^2$	0
mmmrmm	$P_m^2 P_m'^2 (P_m P'_r + P'_m P_r)$	$P_m^2 P_r$
mmmrmr	$P_m P'_m (P_m^2 P_r'^2 + P_m'^2 P_r^2)$	$P_m P_r^2$
rmmrmm	$2P_m^2 P_m'^2 P_r P'_r$	0
rmmrmr	$P_m P'_m P_r P'_r (P_m P'_r + P'_m P_r)$	0
mmmrrm	$2P_m^2 P_m'^2 P_r P'_r$	0
mmmrrr	$P_m P'_m P_r P'_r (P_m P'_r + P'_m P_r)$	0
rmmrrm	$P_m P'_m P_r P'_r (P_m P'_r + P'_m P_r)$	0
rmmrrr	$2P_m P'_m P_r^2 P_r'^2$	0
mrmrmm	$P_m P'_m (P_m^2 P_r'^2 + P_m'^2 P_r^2)$	$P_m P_r^2$
mrmrmr	$P_m^3 P_r'^3 + P_m'^3 P_r^3$	P_r^3
rrmrmm	$P_m P'_m P_r P'_r (P_m P'_r + P'_m P_r)$	0
rrmrmr	$P_r P'_r (P_m^2 P_r'^2 + P_m'^2 P_r^2)$	0
mrmrrm	$P_m P'_m P_r P'_r (P_m P'_r + P'_m P_r)$	0
mrmrrr	$P_r P'_r (P_m^2 P_r'^2 + P_m'^2 P_r^2)$	0
rrmrrm	$2P_m P'_m P_r^2 P_r'^2$	0
rrmrrr	$P_r^2 P_r'^2 (P_m P'_r + P'_m P_r)$	0
mmrrmm	$P_m^2 P_m'^2 P_r P'_r$	0
mmrrmr	$P_m P'_m P_r P'_r (P_m P'_r + P'_m P_r)$	0
rmrrmr	$P_m P'_m P_r^2 P_r'^2$	0
mmrrrm	$P_m P'_m P_r P'_r (P_m P'_r + P'_m P_r)$	0
mmrrrr	$2P_m P'_m P_r^2 P_r'^2$	0
rmrrrm	$P_r P'_r (P_m^2 P_r'^2 + P_m'^2 P_r^2)$	0
rmrrrr	$P_r^2 P_r'^2 (P_m P'_r + P'_m P_r)$	0
mrrrrm	$P_m P'_m P_r^2 P_r'^2$	0
mrrrrr	$P_r^2 P_r'^2 (P_m P'_r + P'_m P_r)$	0
rrrrrr	$P_r^3 P_r'^3$	0

The ^{13}C n.m.r. spectra of poly(DtBF) and poly(MtBF) obtained were taken in C_6D_6 and $CDCl_3$, respectively. The whole and expanded spectra were depicted in *Figures 3* and *4*, respectively. The spectra obtained were too broad to evaluate the stereoregularity precisely, because of the stiffness of the poly(DRF) chains bearing bulky t-butyl groups in the side-chains. Furthermore, in the case of poly(MtBF) the spectrum becomes more complicated owing to the two different ester alkyl groups. Therefore, these polymers were converted quantitatively into poly(DMF) via thermolysis and esterification[2,3]. The poly(DMF) obtained from polymerization of DMF monomer was also investigated for comparison.

The expanded spectra of carbonyl and methine carbons of the three poly(DMF) samples, i.e. poly(DMF) prepared by polymerization of DMF and poly(DMF)s derived from poly(MtBF) or poly(DtBF) by polymer reactions, are shown in *Figures 5A–C*. It has already been reported that the peak due to an *mm* triad is observed at a higher field than that due to an *mr* triad for the carbonyl carbon, and oppositely at a lower field for the methine carbon for poly(DRF)s[22]. It is clear, as seen in *Figure 5*, that

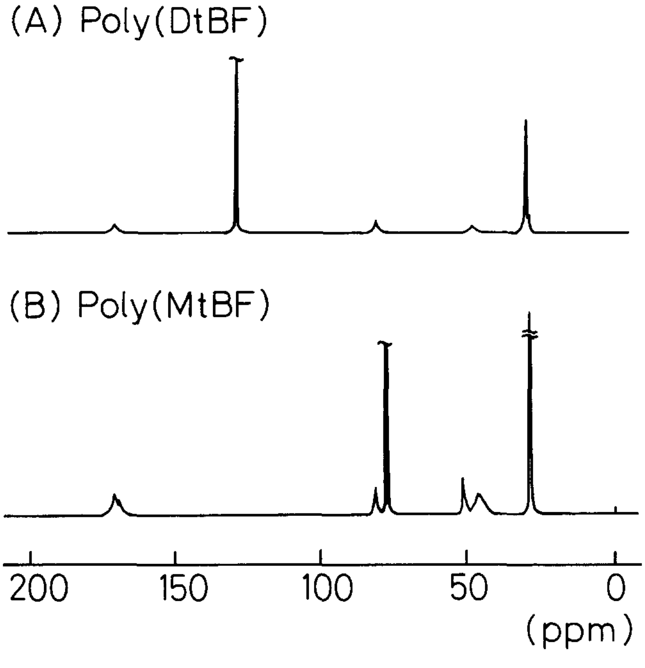

Figure 3 ^{13}C n.m.r. spectra of (A) poly(DtBF) in C_6D_6 and (B) poly(MtBF) in $CDCl_3$

Table 2 Results of radical polymerization of DRF

DRF (mol l^{-1})	Initiator[a] (mmol l^{-1})	Solvent	Temp. (°C)	Time (h)	Conversion (%)	$\bar{M}_n$[b] $\times 10^{-4}$	$\bar{M}_w/\bar{M}_n$[b]
DtBF (3.8)	DtBPO (38)	Toluene	120	3	38.9	1.3	2.0
DtBF (2.0)	AIBN (20)	Benzene	40	30	22.1	1.2	2.3
MtBF (5.6)	DtBPO (20)	None	120	5	44.0	1.8	1.8
DMF (6.2)	DtBPO (62)	Toluene	120	12	25.5	–	–

[a] DtBPO, di-t-butyl peroxide; AIBN, 2,2′-azobisisobutyronitrile
[b] Determined by gel permeation chromatography in tetrahydrofuran

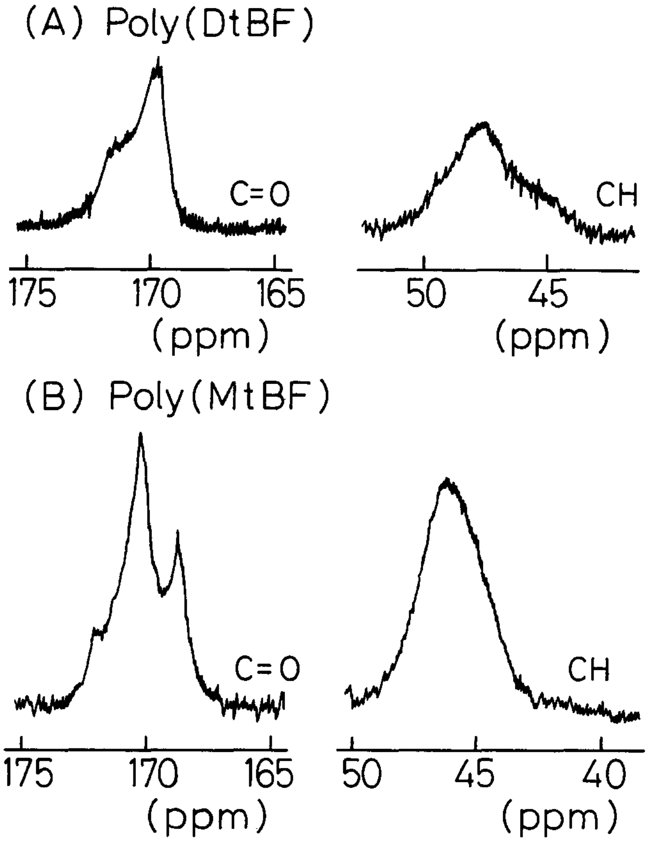

Figure 4 Expanded ^{13}C n.m.r. spectra of (A) poly(DtBF) and (B) poly(MtBF)

the intensity ratio of peaks of the *mm* and *mr* triads changes according to the ester alkyl groups. *Table 3* shows the ratio of peak areas of both triads, which was approximated by division at 45.6 ppm for the methine carbon, and at 170.6 ppm for the carbonyl carbon. These results indicate that the fraction of the *mm* triad increased in the order poly(DtBF) > poly(MtBF) > poly(DMF), agreeing well with the bulkiness of the substituents. However, the ratios obtained in this way do not reflect an accurate P_m value because the peaks are overlapped. Therefore we judged that the determination of P_m necessitated the aid of simulation.

It should be noteworthy that a slight splitting in the OCH_3 region was also observed, although the resolution of the peaks was not sufficient as for the methine or carbonyl carbons. This might be attributed to the poly(substituted methylene) structure.

Simulation of the spectra

The spectra of the methine and carbonyl carbons were simulated in order to determine P_m values (probability of *meso* addition). Since our preliminary simulation for triad or pentad sequences did not provide appropriate spectra, we carried out a simulation with respect to heptad sequences. A typical example of a simulated spectrum and the simulation parameters for poly(DMF) from poly(DtBF) are shown in *Figure 6* and *Table 4*, respectively. The spectra (observed and simulated) were in good agreement with each other. The spectra of the poly(DMF)s from poly(MtBF) and DMF were also simulated similarly. As shown in the results of the simulations in *Table 5*, the P_m values were determined to be 0.68, 0.57 and 0.50 for poly(DtBF), poly(MtBF)

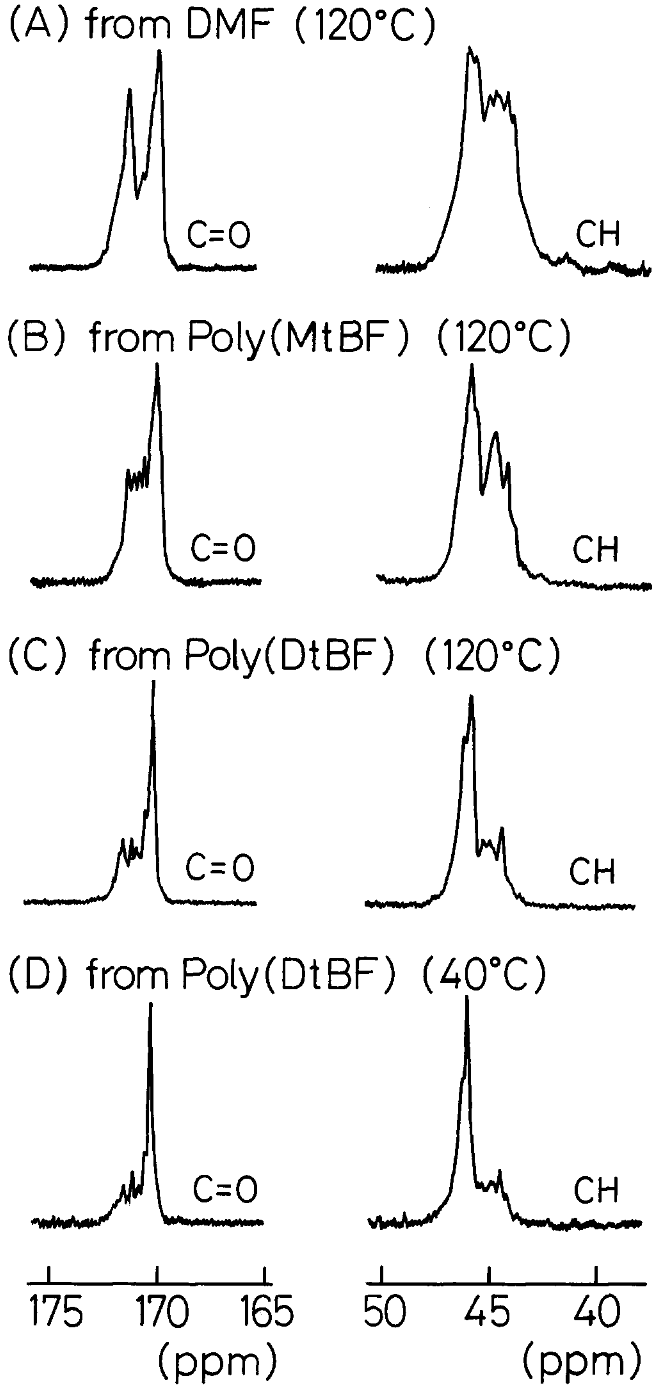

Figure 5 Expanded ^{13}C n.m.r. spectra of poly(DMF) in $CDCl_3$: (A) from polymerization of DMF at 120°C; (B) derived from poly(MtBF) (polymerized at 120°C); (C) derived from poly(DtBF) (polymerized at 120°C); (D) derived from poly(DtBF) (polymerized at 40°C)

Table 3 Peak intensity ratio of *mm* and *mr* triads for poly(DRF)[a]

	Fraction of triads, *mm*/*mr*	
Poly(DRF)	Methine	Carbonyl
Poly(DMF)	0.45/0.55	0.40/0.60
Poly(MtBF)	0.53/0.47	0.53/0.47
Poly(DtBF)	0.64/0.36	0.57/0.43

[a] Fraction of *rr* is equal to zero (see text)

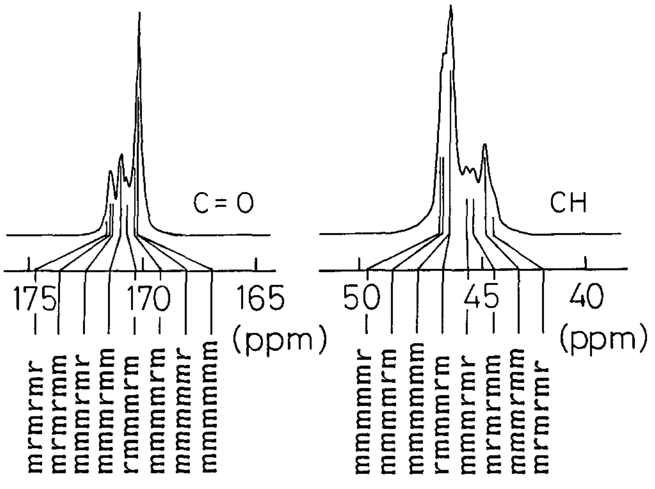

Figure 6 Simulated ^{13}C n.m.r. spectra of poly(DMF) derived from poly(DtBF); see also *Table 4*

Table 4 Typical simulation parameters for heptad of poly(DMF) derived from poly(DtBF)[a]

Sequence	Chemical shift (ppm)		Probability[d]
	Methine[b]	Carbonyl[c]	
mmmmmm	46.00	170.20	0.314
mmmmmr	46.45	170.20	0.148
mmmmrm	46.30	170.40	0.148
rmmmrm	45.90	170.75	0.070
mmmrmm	44.50	171.00	0.148
mmmrmr	45.30	171.40	0.070
mrmrmm	45.00	171.50	0.070
mrmrmr	44.15	171.60	0.033

[a] Polymerized at 120°C in toluene
[b] Linewidth at half-height is 0.65 ppm
[c] Linewidth at half-height is 0.40 ppm
[d] Calculated with $P_m=0.68$ and $P'_m=1$

and poly(DMF), respectively. This indicates that *meso* addition is considerably favoured in the propagation of DtBF with a bulky ester group, but the addition of DMF is random.

In the spectra of poly(DMF) obtained from DMF, trivial disagreement was found between the observed spectrum and the simulated one around 172–173 and 42–44 ppm in the C=O and CH regions, respectively. This may suggest that the assumption of exclusive *meso* (*trans*) opening (i.e. $P'_m=1$) is inadequate in the strict sense in the case of polymerization of DMF; i.e. a rotation of the end-group of the propagating polymer chain might occur slightly in the polymerization of DMF at high temperature. Unfortunately, dialkyl maleate as a *cis* isomer of DRF does not homopolymerize at all in the absence of an isomerization catalyst[3,4], although it would be expected to give much information.

Temperature dependence of the spectra

The polymerization of DtBF was carried out at 40°C to investigate the temperature dependence of the stereoregularity of the polymer. The observed spectra of the poly(DMF) derived from poly(DtBF) prepared at 40°C is shown in *Figure 5D*. The P_m value was determined to be 0.75 by simulation, indicating that *meso* addition was more favoured as the polymerization temperature decreased. The average value of the *meso* diad for poly(DtBF) at 40°C was as high as 0.88 (*Table 5*). When the polymerization temperature decreased further, e.g. 0°C, it was confirmed that the *meso* content of poly(DtBF) further increased[25].

Table 5 Probabilities of *meso* addition (P_m) and *meso* opening (P'_m) and the average fraction of *meso* diads in poly(DRF)

Polymer	Temp. (°C)	P_m	P'_m	Fraction of *meso* diad
Poly(DMF)	120	0.50	1	0.75
Poly(MtBF)	120	0.57	1	0.79
Poly(DtBF)	120	0.68	1	0.84
Poly(DtBF)	40	0.75	1	0.88

This indicates that the differences in activation enthalpies ($\Delta H^{\ddagger}_{m}-\Delta H^{\ddagger}_{r}$) for *meso* and *racemic* propagations, which is given by the slope of the Arrhenius plot of the value of P_m to P_r, is negative (ca. $-5\,\mathrm{kJ\,mol^{-1}}$) for polymerization of DtBF. Recently, we have found that the differences in activation enthalpies are positive for polymerization of the primary alkyl esters of DRF including DMF[25]. This was surprising because the kind of ester groups does not essentially affect the kinetic parameters for *meso* and *racemic* propagations, as seen in the case of radical polymerization of alkyl methacrylates[26], except for triphenylmethyl methacrylate[27], which shows kinetic behaviour different from other esters because of the formation of a stable helical structure in the polymerization solution[28].

The intensive effect of the kind of ester alkyl group on the tacticity of poly(DRF) might presumably originate from their poly(substituted methylene) structure. Further investigations on the dependence of both polymerization temperature and structure of the alkyl groups on the configuration of poly(DRF) continue at the present time. We believe that elucidation of the stereochemical configuration of poly(DRF) opens up a new route not only for the relationship between polymer structure and properties but also for the mechanism of radical polymerization of DRF.

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Note added in proof

There is another possibility for the *meso* opening. When the polymer radical has a thermodynamically favourable comformation which results in a *meso* opening, opening is also restricted to the *trans* mode irrespective of rotation of the chain end. Recently we have investigated the opening mode of DRF and dialkyl maleates in copolymerization by means of n.m.r. and e.s.r. spectroscopies[23].