

Reaction Control in Radical Polymerization of Di-*n*-butyl Itaconate Utilizing a Hydrogen-Bonding Interaction

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Running Head: Hydrogen-Bonding Interaction in DBI Polymerization

ABSTRACT: We have reported that intramolecular chain-transfer reaction takes place in radical polymerization of itaconates at high temperatures and/or at low monomer concentrations. In this paper, radical polymerizations of di-*n*-butyl itaconate (DBI) were carried out in toluene at 60°C in the presence of amide compounds. The ¹³C NMR spectra of the obtained poly(DBI)s indicated that the intramolecular chain-transfer reaction was suppressed as compared with in the absence of amide compounds. The NMR analysis of DBI and *N*-ethylacetamide demonstrated both 1:1 complex and 1:2 complex were formed at 60°C through a hydrogen-bonding interaction. The ESR analysis of radical polymerization of diisopropyl itaconate (DiPI) was conducted in addition to the NMR analysis of the obtained poly(DiPI). It was suggested that the suppression of the intramolecular chain-transfer reaction with the hydrogen-bonding interaction was achieved by controlling the conformation of the side chain at the penultimate monomeric unit of the propagating radical with an isotactic

stereosequence.

Keywords: di-*n*-butyl itaconate; ^{13}C NMR; chain-transfer reaction; radical polymerization; hydrogen bond; tacticity;

INTRODUCTION

Itaconate is one of 1,1-disubstituted vinyl monomers, which gives high polymers through a free-radical polymerization despite its bulkiness. Its propagating polymer radical is easily observed by electron spin resonance (ESR) spectroscopy under the actual polymerization conditions. Therefore, we have investigated kinetically polymerizations of itaconates by means of ESR.¹⁻⁵ We have conducted ^{13}C NMR analysis of poly(di-*n*-butyl itaconate) [poly(DBI)] in detail as well as ESR analysis and found that intramolecular chain-transfer reaction takes place at high temperatures and/or at low feed monomer concentrations in radical polymerizations of itaconates.^{6,7}

In our previous reports,⁷⁻⁹ we have revealed interesting findings on the intramolecular chain-transfer reaction as follows: (1) a propagating radical with a syndiotactic stereosequence near the chain-end favors the intramolecular chain-transfer reaction more than that with an isotactic stereosequence; (2) the intramolecular chain transfer reaction takes place more frequently in polymerizations of bulkier itaconates; (3) two kinds of propagating radicals with different conformations exist in radical polymerization of itaconates and the intramolecular chain-transfer reaction depends on the conformation near the propagating chain-end; (4) a catalytic amount of Lewis acid such as scandium trifluoromethanesulfonate [$\text{Sc}(\text{OTf})_3$] significantly suppressed the intramolecular chain-transfer reaction.

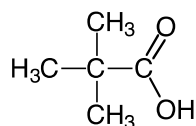
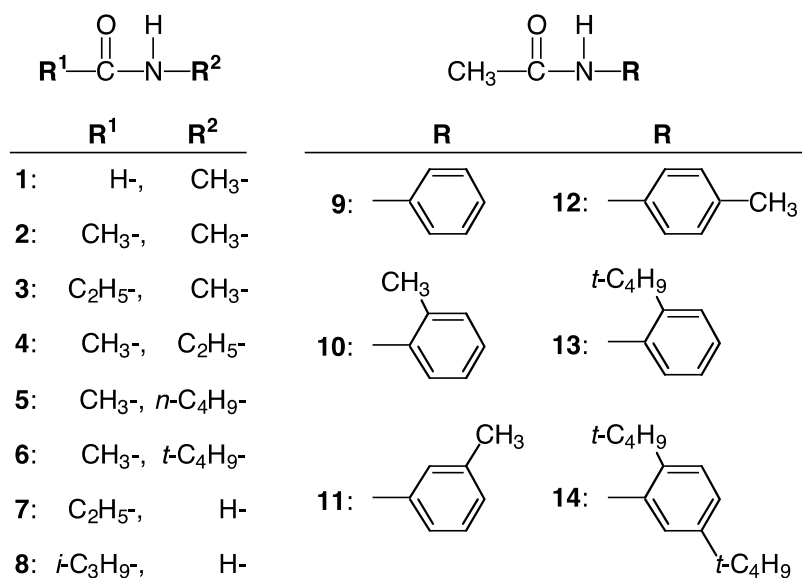
Recently, we found that the use of amide compound as a solvent also significantly suppressed the intramolecular chain-transfer reaction.¹⁰ This result indicates that even a weak hydrogen-bonding interaction is available for the control of

radical polymerization. Furthermore, we obtained a result implying that a hydrogen-bonding interaction plays an important role not only for suppression of the intramolecular chain-transfer reaction but for stereospecificity of itaconate polymerizations. Thus, in this paper, we investigated the role of a hydrogen-bonding interaction in itaconate polymerizations in more detail and discussed the mechanism of the suppression of the intramolecular chain-transfer reaction with a hydrogen-bonding interaction.

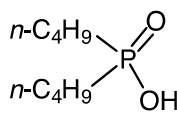
EXPERIMENTAL

Materials

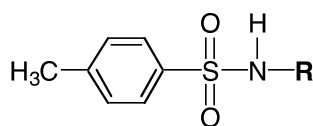
Commercially obtained DBI was purified by fractional distillation under reduced pressure. Diisopropyl itaconate (DiPI) was prepared as previously reported.⁵ Dimethyl 2,2'-azobisisobutyrate (MAIB) was recrystallized from methanol. Toluene and benzene were treated with sulfuric acid and then fractionally distilled. Tri-*n*-butylborane (*n*-Bu₃B) as a tetrahydrofuran (THF) solution (1.0 mol/L), *N*-methylformamide (**1**), *N*-methylacetamide (**2**), *N*-methylpropionamide (**3**), *N*-ethylacetamide (**4**), *N*-*n*-butylacetamide (**5**), *N*-*t*-butylacetamide (**6**), propionamide (**7**), isobutyramide (**8**), acetanilide (**9**), 2'-methylacetanilide (**10**), 3'-methylacetanilide (**11**), 4'-methylacetanilide (**12**), pivalic acid (**15**), di-*n*-butyl phosphate (**16**), *N*-methyl-*p*-toluenesulfonamide (**17**), and *N*-ethyl-*p*-toluenesulfonamide (**18**) were commercially obtained and used without further purification for polymerization reactions. Both 2'-*t*-butylacetanilide (**13**) and 2',5'-di-*t*-butylacetanilide (**14**) were prepared according to the literature.¹¹



15



16



R	
17:	CH ₃ -
18:	C ₂ H ₅ -

Polymerizations

In a typical procedure, MAIB (87 mg, 3.8×10^{-1} mmol) and **4** (0.89g, 10.2 mmol) were dissolved in toluene to prepare the 5ml solution of $[\text{MAIB}] = 7.5 \times 10^{-2}$ mol/L and $[\mathbf{4}] = 2.03$ mol/L. Four milliliter of the solution and DBI (2mL) were transferred to the glass ampoule and cooled at -50°C . The glass ampoule was degassed and filled with nitrogen repeatedly three times, and sealed *in vacuo*. The polymerization was initiated by the sealed tube being placed at 60°C . After 15h, the sealed tube was cooled, and a small amount of CHCl₃ solution of 4-*t*-butylcatecol was added to the polymerization mixture. The polymerization mixture was poured into a large amount of methanol/H₂O mixture (9:1 vol:vol). The precipitated polymer was purified three times by being dissolved in benzene and poured into a large amount of methanol/H₂O

mixture, and dried *in vacuo*. The polymer yield was determined from the weight ratio of the obtained polymer and the feed monomer.

Measurement

The ^{13}C NMR spectra of polymers were measured on a JEOL EX-400 spectrometer operated at 100MHz in CDCl_3 at 55°C. The tacticities of the polymers were determined from ^{13}C NMR signals due to carbonyl carbons. The ^{13}C NMR spectra of DBI-4 mixtures were recorded in toluene- d_8 at 0°C, 30°C, and 60°C. The molecular weights and molecular weight distributions of the polymers were determined by size exclusion chromatography {SEC; TOSO-HLC 8220 instrument ; Toso TSK gel SuperH2M-M x 2; [polymer] = 1.0 mg/mL, flow rate = 0.35 mL/min } at 40°C with THF as an eluent. The SEC chromatogram was calibrated with standard polystyrene samples.

RESULTS AND DISCUSSION

Radical Polymerization of DBI in Toluene in the Presence of Alkylamides

Table 1 summarizes the results of radical polymerization of DBI in toluene at 60°C in the presence of alkylamides. The addition of an equimolar amount of amide compound with DBI monomer increased both polymer yield and number-average molecular weight (\overline{M}_n). Figure 1 displays 100MHz ^{13}C NMR spectra of carbonyl carbons of the obtained poly(DBI)s. In all the spectra, the C resonances assigned to the structures derived from the intramolecular chain-transfer reaction (Scheme 1) were observed, as previously reported.⁷ However, the fraction of the C resonances in the whole carbonyl resonances (I_c) decreased by adding equimolar amounts of amide compounds as compared with by adding nothing. This result indicates that equimolar amounts of amide compounds to DBI monomer significantly suppressed the

intramolecular chain-transfer reaction as well as amide compounds used as solvents.

Table 1. Polymerization of DBI with MAIB in Toluene at 60°C for 15h in the Absence or Presence of Amide Compounds^a

Added amide	Yield %	\overline{M}_n^b 10 ³	\overline{M}_w^b \overline{M}_n	Tacticity ^c				I _C %
				<i>mm</i>	<i>mr</i>	<i>rr</i>	<i>r</i> ^d	
None	40	8.3	1.5	34.3	46.1	19.6	42.7	12
1	60	12.8	1.6	28.1	46.8	25.1	48.5	7
2	59	13.3	1.6	28.5	48.5	23.0	47.3	6
3	55	13.2	1.7	26.1	48.5	25.4	49.6	7
4	62	11.6	1.8	24.7	48.1	27.2	51.3	7
5	54	12.7	1.8	26.8	46.9	26.3	49.6	7
6	47	14.8	1.7	28.1	46.4	25.5	48.7	8
7	50	14.6	1.7	28.6	47.8	23.6	47.5	8
8	51	17.0	1.9	27.4	48.0	24.6	48.6	8

a. [DBI]₀ = 1.35 mol/L, [Amide]₀ = 1.35 mol/L, [MAIB]₀ = 5.0 × 10⁻² mol/L.

b. Determined by SEC (polystyrene standards).

c. Determined by ¹³C NMR signals due to carbonyl carbon A.

d. Calculated with $r = rr + 1/2mr$.

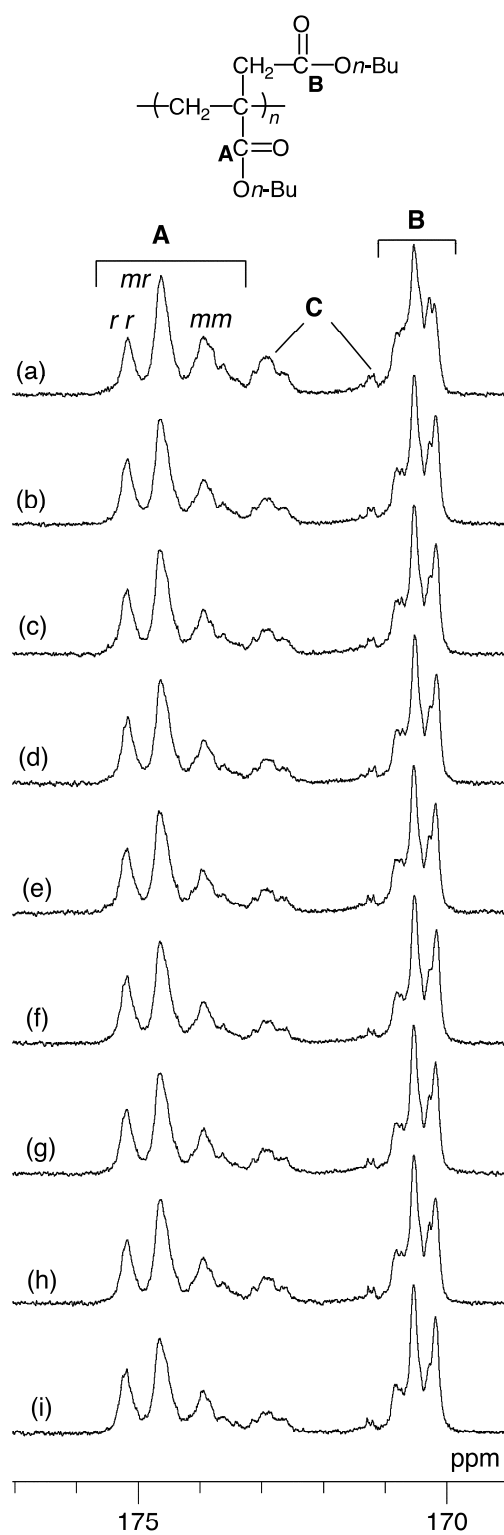
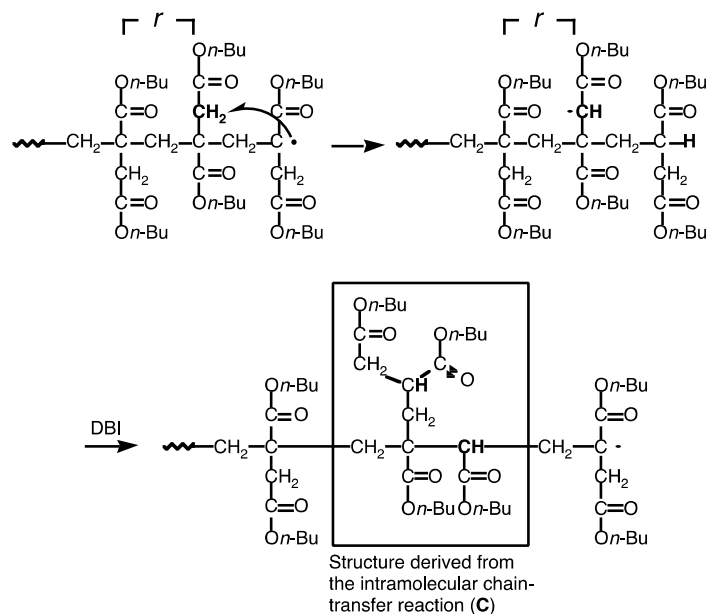


Figure 1. 100MHz ^{13}C NMR spectra of carbonyl carbons of poly(DBI)s prepared in toluene at 60°C in the presence of amide compounds; (a) None, (b) **1**, (c) **2**, (d) **3**, (e) **4**, (f) **5**, (g) **6**, (h) **7**, and (i) **8**, respectively.



Scheme 1. Proposed mechanism of the intramolecular chain-transfer reaction in DBI polymerization.

Carbonyl carbon A still exhibited the splittings due to triad tacticities despite the occurrence of the intramolecular chain-transfer reaction. The tacticities were determined by the resonances due to carbonyl carbon A, although accuracy of the assignment and precision of the determined tacticities are not enough.¹² The syndiotacticities of the obtained poly(DBI)s increased by adding an equimolar amount of each amide compound, whereas no obvious influence of the bulkiness of both carboxylic acid fragment and *N*-substituent was observed

Figure 2 portrays the relationship between the I_C value and r diad in the poly(DBI)s formed in the presence of amide compounds. The relation for poly(DBI)s obtained in common solvents, such as toluene, acetone, and chloroform, are also plotted, which demonstrate a rough linear dependence regardless of the kind of solvents.¹⁰ The relation for poly(DBI)s obtained in the presence of amide compounds were plotted under the linear dependence of poly(DBI)s prepared in common solvents. This result

also corresponds to the result when amide compound were used as a solvent.¹⁰

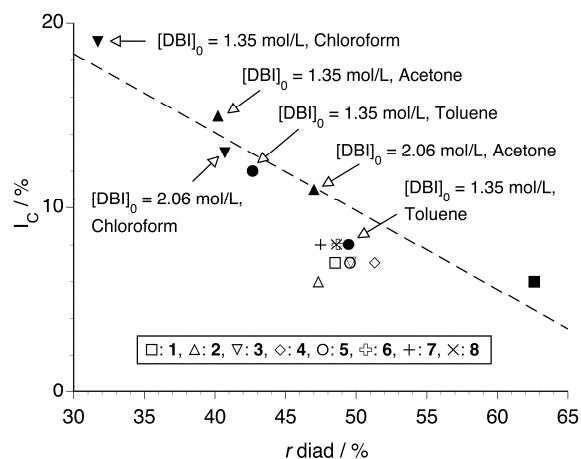


Figure 2. The relationship between the I_c value and r diad in poly(DBI)s prepared in the presence of amide compound.

Radical Polymerization of DBI in Toluene in the Presence of Acetanilide Derivatives

To investigate the effect of bulkiness of amide compounds in more detail, acetanilide derivatives were added into the radical polymerization of DBI (Table 2), although hydrogen-bonding abilities of acetanilide derivatives are weaker than those of alkylamides. The addition of acetanilide derivatives increased polymer yield as well as alkylamides, but decreased \overline{M}_n except for bulkier derivatives such as **13** and **14**.

Acetanilide exhibited significant suppression comparable to alkylamides in spite of its weaker hydrogen-bonding-ability. Although an introduction of an alkyl group decreases the hydrogen-bonding-ability of acetanilide in addition, *ortho*-substituted derivatives such as **13** and **14** exhibited slightly better suppression of the intramolecular chain-transfer reaction, whereas an introduction of methyl group at *meta*- or *para*-position reduced the ability of the suppression ability of acetanilide. It

is suggested that bulkiness is also one of the important factors for the control with a hydrogen-bonding interaction.

Table 2. Polymerization of DBI with MAIB in Toluene at 60°C for 15h in the Absence or Presence of Acetanilide Derivatives^a

Added amide	Yield %	\overline{M}_n^b 10 ³	\overline{M}_w^b \overline{M}_n	Tacticity ^c				I _C %
				<i>mm</i>	<i>mr</i>	<i>rr</i>	<i>r</i> ^d	
9	65	6.3	1.5	30.3	45.8	23.9	46.8	8
10	54	5.6	1.7	30.2	45.5	24.3	47.1	8
11	57	7.5	1.5	30.0	46.3	23.7	46.9	9
12	58	7.7	1.6	28.8	46.4	24.8	48.0	9
13	54	9.2	1.5	27.3	48.2	24.5	48.6	7
14	53	10.1	1.8	27.8	47.8	24.4	48.3	7

a. [DBI]₀ = 1.35 mol/L, [Amide]₀ = 1.35 mol/L, [MAIB]₀ = 5.0 × 10⁻² mol/L.

b. Determined by SEC (polystyrene standards).

c. Determined by ¹³C NMR signals due to carbonyl carbon A.

d. Calculated with $r = rr + 1/2mr$.

Radical Polymerization of DBI in Toluene in the Presence of Organic Acids or *p*-Toluenesulfonamide Derivatives

To investigate the effect of acidity of added compounds, radical polymerizations were carried out in the presence of organic acids or *p*-toluenesulfonamide derivatives (Table 3). As with alkylamides, both polymer yield and \overline{M}_n increased and the I_C values decreased with the addition of more acidic compounds. It is considered that both organic acids and *p*-toluenesulfonamide derivatives are also effective in suppressing the intramolecular chain-transfer reaction. However, the abilities for the suppression of organic acids and *p*-toluenesulfonamide derivatives were almost the same as those of alkylamides or acetanilide derivatives, although a hydrogen-bonding interaction should be strengthened.

Table 3. Polymerization of DBI with MAIB in Toluene at 60°C for 15h in the Absence or Presence of Organic Acids or *p*-Toluenesulfonamide Derivatives^a

Added compound	Yield %	\overline{M}_n^b 10 ³	\overline{M}_w^b \overline{M}_n	Tacticity ^c				I _C %
				<i>mm</i>	<i>mr</i>	<i>rr</i>	<i>r</i> ^d	
15	53	13.5	1.9	26.8	47.6	25.6	49.4	7
16	46	15.4	1.8	25.8	47.3	26.9	50.6	8
17	68	10.1	1.7	29.7	47.4	22.9	46.6	8
18	64	9.1	1.9	29.0	49.1	21.9	46.8	8

a. [DBI]₀ = 1.35 mol/L, [Added compound]₀ = 1.35 mol/L, [MAIB]₀ = 5.0 × 10⁻² mol/L.

b. Determined by SEC (polystyrene standards).

c. Determined by ¹³C NMR signals due to carbonyl carbon A.

d. Calculated with $r = rr + 1/2mr$.

Tacticities of Poly(DBI)s Prepared at Low Temperature

In the relationship between the I_C value and *r* diad in the obtained poly(DBI)s, the plots for poly(DBI)s prepared in common solvents obeyed a rough linear dependence regardless of the kind of solvents (cf. Figure 2). Thus, it appears that the kind of solvents influences not the stereospecificity of polymerization but the intramolecular chain-transfer reaction. However, the plot obtained in the presence of amide compounds deviated below from the linear dependence. This result implies that a hydrogen-bonding interaction affected the stereospecificity of polymerization and hence the intramolecular chain-transfer reaction was suppressed. Thus, we conducted DBI polymerization at 0°C where the intramolecular chain-transfer reaction does not occur (Table 4). However, both the kind of solvents and the monomer concentration hardly affected tacticity of the obtained poly(DBI) even at 0°C. Therefore, it is difficult to say that a hydrogen-bonding interaction significantly affects the stereospecificity of DBI polymerization at 60°C.

Table 4. Polymerization of DBI with *n*-Bu₃B at 0°C for 48h ^a

Solvent	Yield %	\overline{M}_n^b 10 ³	\overline{M}_w^b \overline{M}_n	Tacticity ^c				I _c %
				<i>mm</i>	<i>mr</i>	<i>rr</i>	<i>r</i> ^d	
Bulk ^e	32	20.9	4.9	1.6	35.4	63.0	80.7	0
Toluene	17	17.2	2.4	1.7	34.1	64.2	80.5	0
4	7	46.8	3.4	2.2	37.0	60.8	79.3	0

a. [DBI]₀ = 2.03 mol/L, [*n*-Bu₃B]₀ = 5.0 × 10⁻² mol/L.

b. Determined by SEC (polystyrene standards).

c. Determined by ¹³C NMR signals due to carbonyl carbon A.

d. Calculated with $r = rr + 1/2mr$.

e. [DBI]₀ = 4.06 mol/L.

Complex Formation between DBI and Amide Compound with Hydrogen-Bonding Interaction

In our previous report,¹⁰ we pointed out that DBI and **4** formed a complex through a hydrogen-bonding interaction between ester group (-CO-O-) of DBI and amide group (-CO-NH-) of **4**, based on the result of NMR analysis. Thus, to investigate the stoichiometry of the DBI-**4** complex in more detail, we conducted ¹³C NMR analysis under the conditions as follows; [-CO-O-]₀ + [CO-NH-]₀ = 0.5 mol/L, in toluene-*d*₈ at 0, 30, and 60°C. Figure 3 shows changes in the chemical shift of amide carbon of **4** when the fraction of [CO-NH-]₀ was varied. The plots roughly obeyed quadratic equations at any temperatures and became close to a linear dependence as the temperature was increased. Thus, the stoichiometry of the complex was evaluated by Job's method (Figure 4) with the following equation (1);¹³

$$[\text{DBI} - \mathbf{4}] = \frac{\delta(-\text{CONH-}) - \delta(-\text{CONH-})_f}{\delta(-\text{CONH-})_c - \delta(-\text{CONH-})_f} \times [\text{CO-NH-}]_0 \quad (1)$$

where $\delta(-\text{CONH-})$ and $\delta(-\text{CONH-})_f$ are the chemical shifts of amide carbon of the sample mixture and **4** alone, respectively. The chemical shift for the saturated mixture ($\delta(-\text{CONH-})_c$) was evaluated from the intercept in Figure 3.

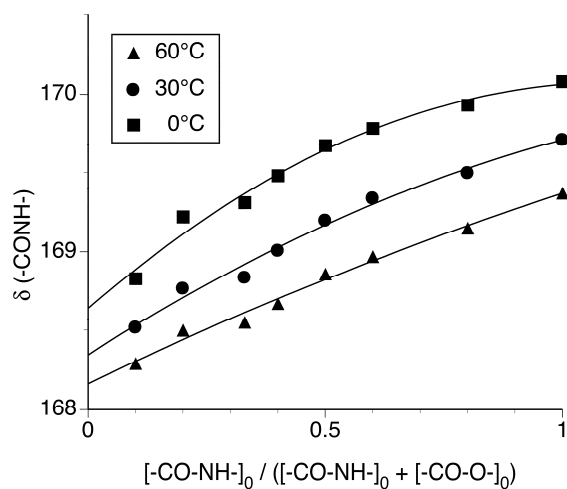


Figure 3. Changes in the amide carbon chemical shifts of **4** in the presence of DBI in toluene-*d*₈ at 0°C, 30°C, and 60°C.

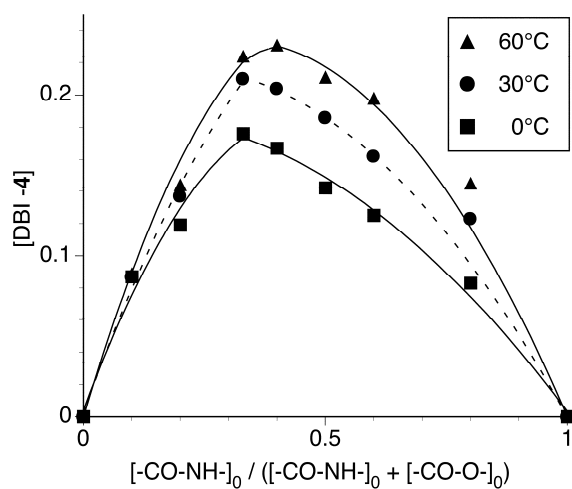
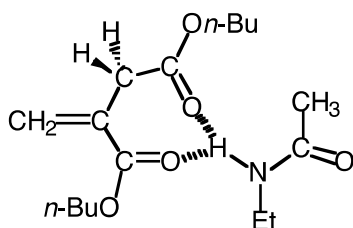


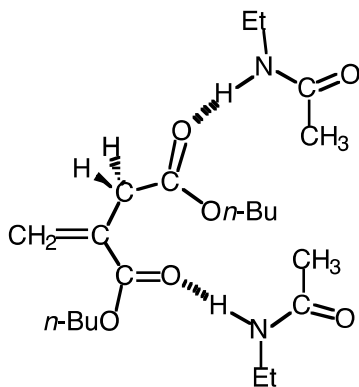
Figure 4. Job's plots for the association of DBI with **4** evaluated from the changes in the chemical shift of amide carbon of **4**.

At 0°C, the maximum was observed around 0.33 of the [-CO-NH-]₀ fraction, indicating that the complex consisted of one -CO-NH- group and two -CO-O- groups through a hydrogen-bonding interaction. Since DBI has two -CO-O- groups, it is assumed that DBI and **4** forms a chlate complex as shown below.



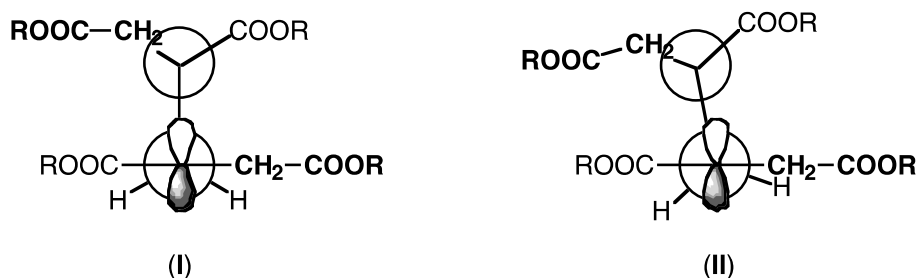
This structure corresponds to that of the complex of DBI with Lewis acid, $\text{Sc}(\text{OTf})_3$. The addition of $\text{Sc}(\text{OTf})_3$ exhibited no influence in stereospecificity of DBI polymerization,⁹ although $\text{Sc}(\text{OTf})_3$ increases isotactic-specificity in polymerization of other acrylate-type monomers such as methyl methacrylate.¹⁴ As mentioned above, no influence was observed in tacticities of poly(DBI)s prepared in bulk, toluene, and **4**, respectively, at 0°C. This result also corresponds to that of DBI polymerization in the presence of $\text{Sc}(\text{OTf})_3$.

However, the maximum was shifted to higher $[-\text{CO}-\text{NH}-]_0$ fraction and was observed around 0.4 of the $[-\text{CO}-\text{NH}-]_0$ fraction at 60°C. Thus, it is suggested that, at higher temperatures, DBI and **4** form a mixture of 1:1 complex and 1:2 complex, since the maximum at 0.5 of the $[-\text{CO}-\text{NH}-]_0$ fraction means 1:2 complex formation.



ESR Analysis of Radical Polymerization of DiPI in the Presence of a Hydrogen-Bonding Interaction

It is known that two kinds of radicals (**I** and **II**) with different conformations near the propagating chain-end exist in radical polymerization system of itaconates.



In ESR spectra of radical polymerizations of DiPI, the conformer **I** gives a five-line signal and the conformer **II** gives another signal which have not been precisely assigned because of the overlap with the signal due to **I** (cf. Figure 5(a)). In our previous paper,⁸ we concluded that the radicals with a syndiotactic sequence should favor the conformation **I** and those with an isotactic sequence the conformer **II**, since both the relative intensity ratio of the five-line signal in ESR spectra of DiPI polymerization and syndiotacticity of the obtained poly(DiPI)s decreased as the intramolecular chain-transfer reaction increased. Therefore, we examined DiPI polymerization in the presence of a hydrogen-bonding interaction to investigate the relationship between the intramolecular chain-transfer reaction and the conformation near the propagating chain-end.

Figure 5 shows ¹³C NMR spectra of poly(DiPI) prepared at 50°C for 24h in benzene and **4**, respectively. The resonances of carbonyl carbon A showed the splitting due to triad tacticity, but the signals of *mm* and *mr* triads overlapped so that tacticities were calculated as *mm* + *mr* : *rr*, as summarized in Table 5. The intramolecular chain-transfer reaction was suppressed and syndiotacticity increased in **4** as compared with those in benzene, although the magnitudes of both changes were small (Table 5). This tendency corresponds to the results observed for DBI polymerizations in toluene and **4**.¹⁰

Table 5. Polymerization of DiPI with MAIB at 50°C for 24h^a

Solvent	$\frac{[\text{MAIB}]_0}{\text{mol/L}}$	Yield %	$\frac{\overline{M}_n^b}{10^3}$	$\frac{\overline{M}_w^b}{\overline{M}_n}$	Tacticity ^c		I _c %
					<i>mm + mr</i>	<i>rr</i>	
Benzene	5.0×10^{-2}	30	23.7	1.5	69.7	30.3	16
4	2.0×10^{-1}	52	8.7	1.4	68.6	31.4	14

a. $[\text{DBI}]_0 = 2.0 \text{ mol/L}$.

b. Determined by SEC (polystyrene standards).

c. Determined by ¹³C NMR signals due to carbonyl carbon A.

Figure 6 displays ESR spectra of DiPI polymerizations under the same conditions as the polymerizations mentioned above. For the polymerization in **4**, the concentration of the propagating radical drastically decreased as compared with that in benzene, although a 4-fold amount of MAIB was added for the polymerization in **4**. This result suggests that a hydrogen-bonding interaction affect also the kinetics of elementary reactions in DiPI polymerization. Furthermore, the relative intensity ratio of the signal marked with arrows decreased in ESR spectrum measured in **4** as compared with that in benzene. Thus, it is considered that an abundance of the conformer **I** was enhanced in **4** more than in benzene. As mentioned above, however, ¹³C NMR spectra exhibited smaller I_c value in **4** than in benzene. Consequently, it can be presumed that, in the presence of the hydrogen-bonding interaction, the intramolecular chain-transfer reaction was suppressed, although the relative existent ratio of the conformer **I** increased, which favors the intramolecular chain-transfer reaction more than the conformer **II**.

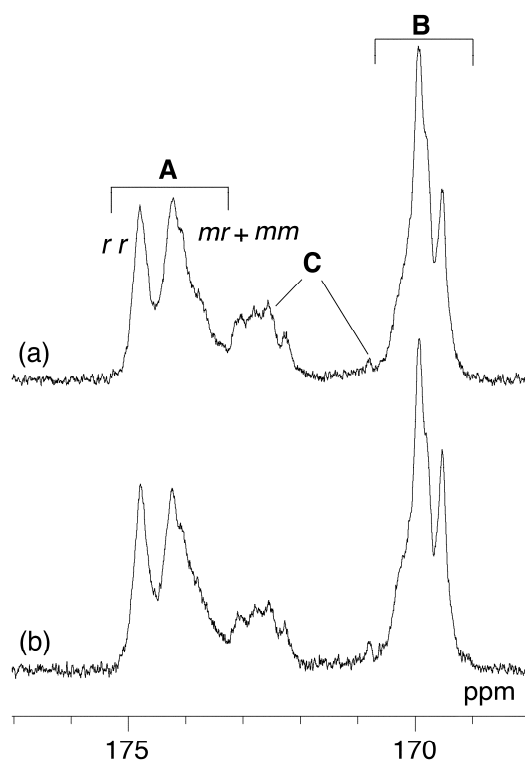


Figure 5. 100MHz ^{13}C NMR spectra of carbonyl carbons of poly(DiPI)s prepared with MAIB at 50°C (a) in benzene and (b) in **4**, respectively.

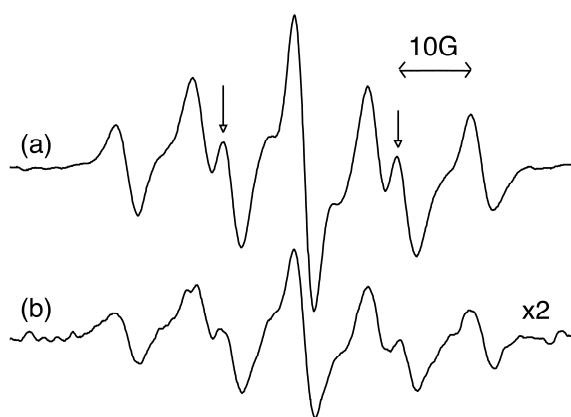
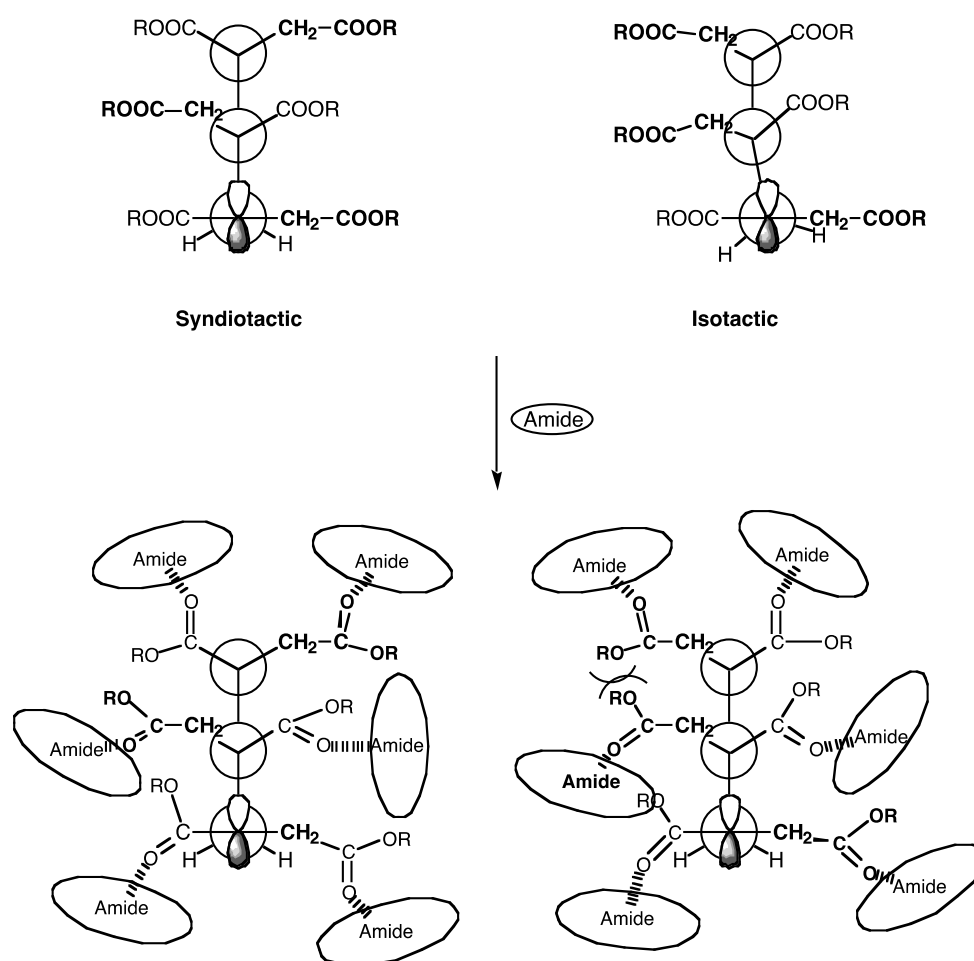


Figure 6. ESR spectra of DiPI polymerizations initiated with MAIB at 50°C (a) in benzene and (b) in **4**, respectively.

Proposed Mechanism for Suppression of the Intramolecular Chain-Transfer

Reaction with the Aid of a Hydrogen-Bonding Interaction

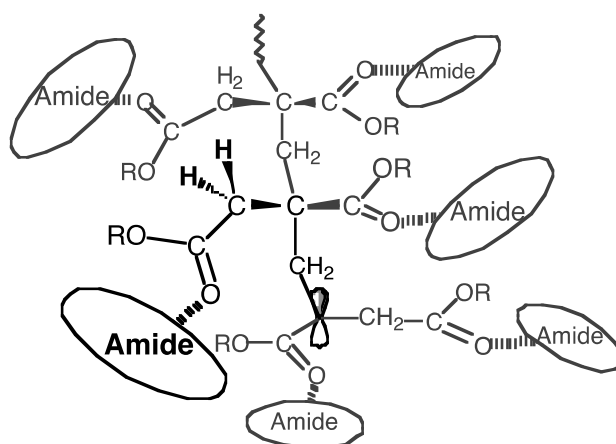
In a radical polymerization of itaconates in common solvents such as benzene, the radical with a syndiotactic sequence should favor the conformer **I** and that with an isotactic sequence should favor the conformer **II**, probably because of the steric interaction between bulkier substituents (-CH₂-COOR) at the penultimate and antepenultimate monomeric units of an *m*-ended (isotactic) propagating radical. However, the coordination by amide compounds to carbonyl group of the propagating radical makes the steric difference between -COOR and -CH₂-COOR groups small, that is, every side chains look like bulkier substituents. Thus, the steric interaction between less bulky substituents (-COOR) at the chain-end diad of the *m*-ended radical also would affect the conformation significantly, resulting in the predominance of the conformer **I** regardless of the stereoregularity near the propagating chain-end (Scheme 2).



Scheme 2. Expected transformation of conformers by changing the solvent from common solvents to amide compounds.

However, the disadvantage of steric repulsion between the bulkier substituents ($-\text{CH}_2\text{COOR}$) should remain, even after the coordination by amide compounds transforms the *m*-ended radical from the conformer **II** to the conformer **I**. Thus, it is assumed that the amide compound coordinating to the $-\text{CH}_2\text{COOR}$ at the penultimate monomeric unit is crowded out to the front free-space to reduce the steric repulsion. If so, the target hydrogen atoms of the abstraction in the intramolecular chain-transfer reaction, at the penultimate monomeric unit, would be far from the propagating radical center of the *m*-ended propagating radical (Scheme 3). As a result, the intramolecular chain-transfer reaction would be suppressed. In other words, the hydrogen-bonding

interaction would suppress the intramolecular chain-transfer reaction not by controlling the conformation near the propagating chain-end but by controlling the conformation of the side chain of the penultimate monomeric unit.



Scheme 3. Possible conformational structure near the propagating chain-end of the *m*-ended radical.

As mentioned above, DBI and amide compound form a mixture of 1:1 complex and 1:2 complex at 60°C. When 1:1 complex undergoes a propagating reaction, the corresponding radical should be formed. In this case, steric hindrance around the propagating chain-end would be somewhat reduced. However, it is assumed that the amide compound coordinating to ester groups at the penultimate monomeric unit is also crowded out to the front free-space as well as 1:2 complex, resulting in the suppression of the intramolecular chain-transfer reaction.

As previously reported,¹⁰ the intramolecular chain-transfer reaction increased and the syndiotacticity of the obtained polymers decreased, as the feed monomer concentration decreased. For instance, the I_C value increased from 8% to 12% and the *r* diad content decreased from 49.5 % to 42.7%, when $[DBI]_0$ was reduced from 2.03 mol/L to 1.35 mol/L for polymerization in toluene. However, when amide compounds were used as solvents, only the syndiotacticity significantly decreased, whereas the

change in the I_c was kept almost constant. For example, when $[DBI]_0$ was reduced from 2.03 mol/L to 1.35 mol/L for polymerization in **3**, the I_c value increased only 1% (from 7% to 8%), but the r diad content decreased 4.8% (from 50.3 % to 45.5%). Thus, it is suggested that the hydrogen-bonding interaction affected the stereospecificity of the intramolecular chain-transfer reaction, because no influence was observed in the stereospecificity of DBI polymerization. If the above-mentioned hypothesis is correct, the hydrogen-bonding interaction should suppress predominantly the intramolecular chain-transfer reaction by the propagating radical with an isotactic stereosequence. Furthermore, the decrease in the monomer concentration would increase the fraction of 1:2 complex which is expected to suppress the intramolecular chain-transfer reaction more than 1:1 complex. Thus, it is assumed that the intramolecular chain-transfer reaction by the propagating radical with an isotactic stereosequence is selectively suppressed and the selectivity increased with a decreased in the monomer concentration. As a result, only the syndiotacticity looked to decrease with a decrease in the monomer concentration.

CONCLUSIONS

The effect of hydrogen-bonding interaction on the intramolecular chain-transfer reaction in radical polymerizations of itaconates was examined. The addition of an equimolar amount of amide compound or organic acid significantly suppressed the intramolecular chain-transfer reaction as well as the use as solvents. The NMR analysis of DBI and **4** demonstrated that a mixture of 1:1 complex and 1:2 complex was formed at 60°C. The ESR analysis of DiPI polymerization and NMR analysis of the obtained poly(DiPI) revealed that the hydrogen-bonding interaction increased the relative existence ratio of the conformer **I**, which favor the intramolecular chain-transfer reaction more than the conformer **II**, but the intramolecular chain-transfer reaction was suppressed nevertheless. In conclusion, it was suggested that the

suppression of the intramolecular chain-transfer reaction with the hydrogen-bonding interaction was achieved by controlling the conformation of the side chain at the penultimate monomeric unit.

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