RAPID COMMUNICATION

Temperature Dependence of Stereospecificity in the Radical Polymerization of Di-*n*-butyl Itaconate in Bulk

TOMOHIRO HIRANO, SACHIKO TATEIWA, MAKIKO SENO, TSUNEYUKI SATO

Department of Chemical Science and Technology, Faculty of Engineering, Tokushima University, Minamijosanjima 2-1, Tokushima 770-8506, Japan

INTRODUCTION

The development of stereospecific radical polymerization has been approached by many researchers for a long time. However, efficient polymerization systems for stereospecific radical polymerization have hardly been observed because of the high activity of electrically neutral propagating species. There are few reports on stereospecific radical polymerization[1–7] except for the isotactic-specific radical polymerizations of acrylamides with chiral auxiliaries[1] and bulky triarylmethyl methacrylates such as triphenylmethyl methacrylate (TrMA)[2,3] and 1-phenyldibenzosuberyl methacrylate.[4] In these isospecific polymerizations, the stereoregulating efficiency depends on the structure of the monomer and, consequently, cannot be applied to common monomers. Recently, Okamoto et al.[5] found a large temperature dependence of the stereospecificity in the polymerization of vinyl esters in perfluoroalcohol and obtained stereoregular polymers by lowering the polymerization temperature: vinyl acetate, $r = 72.2\%$ at $-78\,°C$, and vinyl pivalate, $mr = 61.0\%$ at $-40\,°C$. In such polymerizations, the stereospecificity strongly depends on the kinds of solvents as well.

Dialkyl itaconates (DRIs) are 1,1-disubstituted bulky monomers that have two ester groups at the side chains. They do not undergo anionic polymerization because of the high acidity of the methylene protons at the position between the vinyl and carbonyl groups.[8] However, DRIs readily give high polymers through free-radical polymerization, despite their bulky substituents. Furthermore, the propagating polymer radical of DRIs are easily observed by electron spin resonance (ESR) under the actual polymerization conditions. Therefore, we kinetically studied the radical polymerizations of DRIs and related monomers with ESR.[9–12] In the course of such kinetic studies, we found that the stereospecificity in the radical polymerization of some DRIs highly depends on the temperature as compared with those of usual vinyl monomers such as methacrylates and styrene. In this article, we report the effect of the polymerization temperature on the stereospecificity in the radical polymerization of di-*n*-butyl itaconate (DBI).

EXPERIMENTAL

Commercially obtained DBI was purified by fractional distillation under reduced pressure. Di-*t*-butyl peroxide (DBPO) was purified by distillation. Dimethyl 2,2′-azobisisobutyrate (MAIB) and 1,1′-azobis(cyclohexanecarbonitrile) (ACN) were recrystallized from methanol. Tri-*n*-butylborane (*n*-Bu₃B) was obtained as a tetrahydrofuran (THF) solution (1.0 M) and was used without purification for the polymerization reaction.

The polymerization was carried out in a degassed and sealed tube. The polymerization mixture was poured into a large amount of a methanol/H$_2$O mixture (9/1 v/v). Isolated polymers were purified three times by being dissolved in benzene and then poured into a large amount of a methanol/H$_2$O mixture. For the polymerization with *n*-Bu₃B at low temperatures, the polymerization was carried out in a glass tube without degassing and was terminated by the addition of a toluene

Table I. Bulk Polymerization of DBI with Radical Initiators at Various Temperatures[a]

| Initiator	Temperature (°C)	Time (h)	Yield (%)	$\bar{M}_n \times 10^{-3}$ [b]	$\bar{M}_n/\bar{M}_w$ [b]
DBPO	120	40	57	4.5	1.19
ACN	100	40	56	6.7	1.36
ACN	80	20	70	14.8	1.86
MAIB	60	25	81	36.3	1.90
MAIB	50	10	35	87.0	1.86
MAIB	40	30	31	141.5	1.86
MAIB	30	30	23	291.0	1.89
n-Bu$_3$B$_{+\text{air}}$	0	48	32	20.9	4.92
n-Bu$_3$B$_{+\text{air}}$	−20	48	24	25.3	5.15
n-Bu$_3$B$_{+\text{air}}$	−78	168	7	40.5	4.99

[a] $[I] = 5.0 \times 10^{-2}$ mol L^{-1}.
[b] Determined by SEC.

solution of t-butylcatechol as an inhibitor. The resulting polymers were isolated in the same way as those prepared at higher temperatures. The results are summarized in Table I.

Tacticities of the polymers were determined from ^{13}C NMR signals due to carbonyl carbons measured in CDCl$_3$ at 55 °C on a JEOL EX-400 spectrometer operated at 100 MHz. The molecular weight and molecular weight distribution of the polymers were determined by size exclusion chromatography (SEC; TOSO-HLC 802A instrument) with THF as an eluent. The SEC chromatogram was calibrated with standard polystyrene samples.

RESULTS AND DISCUSSION

Figure 1 shows expanded ^{13}C NMR spectra of quaternary, methylene, and carbonyl carbons of poly(DBI)s prepared at various temperatures. The notations (a–e) of individual carbons are shown in the following structure [cf. Fig. 1(d)]:
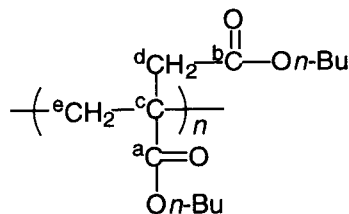
All the signals became simpler as the polymerization temperature was lowered from 120 to −78 °C. This means that the propagating radical species shows higher stereoselectivity at lower temperatures. The quaternary (c) and side-chain methylene (d) carbon resonances showed complicated splittings that were probably due to triad stereosequences or longer stereosequences. Furthermore, the signals overlapped one another, particularly in the spectra of the polymers

prepared at higher temperatures. It is, therefore, difficult to determine the tacticity from these peak intensities. The main-chain methylene carbons (e) also
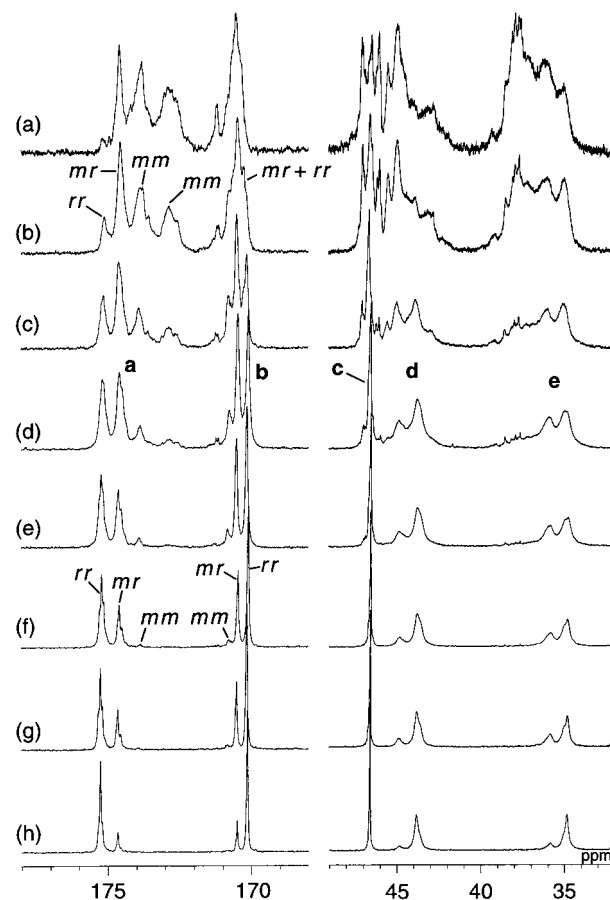

Figure 1. 100-MHz ^{13}C NMR spectra of quaternary, methylene, and carbonyl carbons of poly(DBI)s prepared at (a) 120 °C, (b) 100 °C, (c) 80 °C, (d) 60 °C, (e) 40 °C, (f) 0 °C, (g) −20 °C, and (h) −78 °C.

Table II. Triad Tacticity Distribution in Radically Prepared Poly(DBI)s Formed at Various Temperatures, as Determined from Carbonyl Carbon Resonances

Temperature (°C)	Carbonyl Carbon (a)				Triad Tacticity (%) Carbonyl Carbon (b)				
	1 mm (173.4–174.3)[a]	2 mr (174.3–174.9)	3 rr (174.9–175.9)	4 mm (172.1–173.4)	5 $mr + rr$ (169.8–171.6)	6 mm (170.8)	7 mr (170.4)	8 rr (170.0)	4IS/H^2 [b]
120	63.6	34.8	1.6	41.8	58.2	nd[c]	nd	nd	0.34
100	47.6	44.3	8.1	26.7	73.3	nd	nd	nd	0.79
80	28.8	47.5	23.7	15.4	84.6	17.6	51.2	31.2	1.21
60	13.3	47.8	38.9	7.8	92.2	13.9	45.0	41.1	0.91
50	7.8	43.8	48.4	nd	nd	6.9	42.6	50.5	0.79
40	5.6	42.0	52.4	nd	nd	6.6	39.9	53.5	0.67
30	3.0	39.3	57.7	nd	nd	4.1	40.1	58.8	0.45
0	1.6	35.4	63.0	nd	nd	3.7	34.4	61.9	0.32
−20	1.2	31.7	67.1	nd	nd	2.9	31.1	66.0	0.32
−78	0.5	19.0	80.5	nd	nd	1.6	19.4	79.0	0.45

[a] Parts per million.
[b] Calculated from the triad tacticity determined from carbonyl carbon (a) signals.
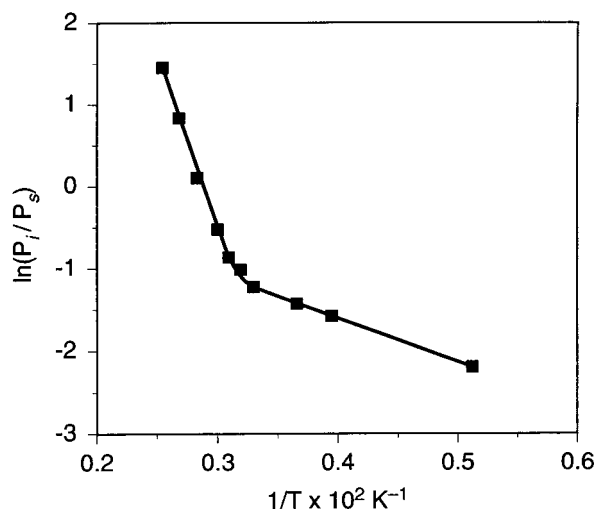[c] Not determined.

Figure 2.   Temperature dependence of tacticity in the polymerization of DBI in bulk.

showed confused splittings that were probably due to tetrad stereosequences or longer stereosequences, so it is hard to determine the tacticity.

However, the resonances due to two kinds of carbonyl carbons [(a) C—**CO**—O—R and (b) —CH$_2$—**CO**—O—R] were already assigned at a triad level for poly(dibenzyl itaconate) [poly(1-benzyloxycarbonyl-1-benzyloxycarbonylmethylethylene)] and poly(benzyl hydrogen itaconate) [poly(1-carbonyloxy-1-benzyloxycarbonyl-methylethylene)].[13] If the carbonyl carbon signals of poly(DBI) split in the same way as those of poly(benzyl hydrogen itaconate) described in the literature,[13] we could assign the signals as shown in Figure 1(b) and calculate the tacticities of poly(DBI)s as summarized in Table II (columns 1–5). If the assignment is correct, tacticity distributions determined from both carbonyl carbon signals should correspond to each other. However, the *mm* triad contents determined from the carbonyl carbon (a) signals (column 1) was rather larger than those from the carbonyl carbons (b) (column 4). This result indicates that the assignment may be wrong. For the polymers prepared at lower temperatures, resonances due to both carbonyl carbons split into three peaks [cf. Fig. 1(e–h)]. If the carbonyl carbon (b) signals show the splittings due to triad tacticity as those of poly(dibenzyl itaconate),[13] these peaks could be assigned as shown in Figure 1(f). The tacticity determined from the signals due to the carbonyl carbon (b) according to the aforementioned assignment (columns 6–8) shows better correspondence with those due to the carbonyl carbon (a) (columns 1–3) compared with the assignment based on that of poly(benzyl hydrogen itaconate)[13] (columns 4 and 5). Moreover, the determined tacticities fit significantly with the Bernoullian statistics, also supporting this assignment.

It is reasonably expected that the resonances due to the carbonyl carbon (a) should be influenced by the main-chain stereoregularity more than those due to the carbonyl carbon (b) because the carbonyl carbons (a)

directly attach to the quaternary carbons, whereas methylene groups exist as a spacer between the carbonyl carbons (b) and the quaternary carbons. These results suggest that the resonances due to both carbonyl carbons principally split into three peaks at a triad level, and the broad peaks around 172.1–173.4 ppm and the small peaks at 171.2 ppm are assigned to unexpected structures formed during the polymerization reaction at higher temperatures. One possible explanation for the unexpected signals is that these signals are due to monomeric units near the chain ends because these peak intensities increase and the molecular weights of polymers decrease as the temperature increases (cf. Figure 1 and Table I). However, these peaks were not observed in the spectra of polymers prepared at 0 and −20 °C, whose molecular weights are between those of polymers prepared at 60 and 80 °C. Furthermore, the polymers prepared at 60 °C, which had different molecular weights, showed almost the same pattern in the region of carbonyl carbons regardless of their molecular weights. Another possibility is reactions between substituents of the resulting polymer at high temperatures, leading to the formation of an anhydride structure. No change, however, was observed in the ^{13}C NMR spectrum of poly(DBI) prepared at 0 °C, which was annealed at 100 °C for 10 h under vacuum. Thus, we cannot assign these peaks exactly at this time.

If the unexpected structure is randomly formed regardless of stereoregularity in the main chain and the tacticity expresses the stereospecificity in polymerization based on the fact that the tacticity significantly obeys the Bernoullian statistics, one finds, interestingly, that polymers with a wide range of stereoregularity, from isotactic to syndiotactic, are obtained only by changes in the polymerization temperature (see Table II). It is known that *rr* triad contents in radically prepared poly(methyl methacrylate)s (PMMAs) gradually increase by the polymerization temperature being lowered, whereas *mm* triad contents are kept at low levels: 135 °C, *rr* = 53.5%, *mm* = 7.5% → −55 °C, *rr* = 78.5%, *mm* = 4.0%.[14] However, poly(DBI) showed much more drastic changes in both *rr* and *mm* triad contents with the polymerization temperature being lowered: 120 °C, *rr* = 1.6%, *mm* = 63.6% → −78 °C, *rr* = 80.5%, *mm* = 0.5%. These results suggest that the probability of *m*-addition in the polymerization of more bulky DBI depends on the temperature more significantly than that of the less bulky methyl methacrylate in addition to the fact that isotactic specificity in the polymerization of bulky TrMA increases with rising temperature.[3] The values of 4IS/H^2 (Table II) were relatively close to unity for the polymers prepared at 60 and 80 °C, but the values gradually deviated from unity as the temperature was lowered or raised. This implies that it is better to treat the tacticity with higher order statistics, such as first-order Markovian statistics, as in the case of common polymers such as PMMA.[14]

Figure 2 shows the temperature dependence of tacticity in the radical polymerization of DBI in bulk.[15] Two

Table III. Activation Parameters for the Polymerization of DBI and Methacrylates

Monomer	$\Delta H_i^{\neq} - \Delta H_s^{\neq}$ (cal/mol)	$\Delta S_i^{\neq} - \Delta S_s^{\neq}$ (cal/mol · K)
DBI (50–120 °C)	2118	6.10
DBI (−78–30°C)	266	0.26
Methacrylates[a]		
Methyl	775	0.0
sec-Butyl	725	0.06
tert-Butyl	870	0.92
1-Phenylethyl	810	0.41
Cyclohexyl	310	−1.12
Menthyl	280	0.31
Triphenylmethyl[b]	3843	13.32

[a] Data from ref. 16.
[b] Calculated from the data for the polymerizations at $[M]_0$ = 0.18 mol/L in ref. 3.

linear dependencies with different slopes were observed from −78 to 30 °C and 50 to 120 °C, although only one linear dependence was observed for the polymerization of common monomer such as methacrylates and vinyl esters. The difference in activation enthalpy ($\Delta H^{\neq}$) and the difference in activation entropy ($\Delta S^{\neq}$) between isotactic and syndiotactic propagation can be determined by the plots according to the following equation:

$$\ln\left(\frac{P_i}{P_S}\right) = \frac{\Delta S_i^{\neq} - \Delta S_s^{\neq}}{R} - \frac{\Delta H_i^{\neq} - \Delta H_s^{\neq}}{RT}$$

where P_i and P_s denote the mole fractions of isotactic and syndiotactic diads, respectively, R is a gas constant (1.987 cal/mol · K), and T is the polymerization temperature (K). In Table III are summarized the obtained values of $\Delta H_i^{\neq} - \Delta H_s^{\neq}$ and $\Delta S_i^{\neq} - \Delta S_s^{\neq}$ for the bulk polymerization of DBI along with the data for the polymerizations of some methacrylates.[16] From −78 to 30 °C, both values were close to those for methacrylates, particularly menthyl methacrylate. However, from 50 to 120 °C, both values were much larger than those for methacrylates and were rather close to those for TrMA. As mentioned in the introduction, TrMA exhibits unique stereoregulation because of the bulkiness and gives isotactic polymers regardless of the polymerization conditions. Thus, these results suggest that at least two kinds of propagating species with different stereospecificities exist in this polymerization system.

In conclusion, we found a pronounced dependence of stereospecificity in the radical polymerization of DBI on the polymerization temperature. Poly(DBI)s with a wide range of stereoregularity could be obtained only by changes in the polymerization temperature, although the polymers prepared at higher temperatures involved unexpected structures. A more detailed investigation using monomers with other ester groups is in progress to suppress the formation of unexpected structures, keeping the large temperature dependence of the stereochemical control.

REFERENCES AND NOTES

1. Porter, N. A.; Allen, T. R.; Breyer, R. A. J Am Chem Soc 1992, 114, 7676.
2. Yuki, H.; Hatada, K.; Niinomi, Y.; Kikuchi, Y. Polym J 1970, 1, 36.
3. Nakano, T.; Matsuda, A.; Okamoto, Y. Polym J 1996, 28, 556.
4. Nakano, T.; Mori, M.; Okamoto, Y. Macromolecules 1993, 26, 867.
5. Yamada, K.; Nakano, T.; Okamoto, Y. Macromolecules 1998, 31, 7598.
6. Habaue, S.; Uno, T.; Okamoto, Y. Polym J 1999, 31, 900.
7. Gotoh, Y.; Yamashita, M.; Nakamura, M.; Toshima, N. Chem Lett 1991, 53.
8. Tate, B. E. In Vinyl and Diene Monomers; Leonard, E. C., Ed.; Wiley: New York, 1970; Part 1, Chapter 4, pp 205–261.
9. Sato, T.; Inui, S.; Tanaka, H.; Ota, T. J Polym Sci Part A: Polym Chem 1987, 25, 637.
10. Sato, T.; Hirose, Y.; Seno, M.; Tanaka, H.; Uchiumi, N.; Matsumoto, M. Eur Polym J 1994, 30, 347.
11. Sato, T.; Hirose, Y.; Seno, M.; Tanaka, H. J Polym Sci Part A: Polym Chem 1995, 33, 797.
12. Nakamura, H.; Seno, M.; Sato, T. J Polym Sci Part A: Polym Chem 1997, 35, 153.
13. Horta, A.; Hernández-Fuentes, I.; Gargallo, L.; Radic, D. Makromol Chem Rapid Commun 1987, 8, 523.
14. Reinmöller, M.; Fox, T. G. Polym Prepr (Am Chem Soc Div Polym Chem) 1966, 7, 999.
15. Fordham, J. W. L. J Polym Sci 1959, 39, 321.
16. Otsu, T. In Radical Polymerization (in Japanese); Saegusa, T.; Otsu, T.; Higashimura, T., Eds.; Kagakudojin: Kyoto, 1971; Part 1, Chapter 3, pp 79–122.