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Polymer 41 (2000) 4467–4472

polymer

Polymerization of *t*-butyl acrylate using organoaluminum complexes and correlation between main-chain tacticity and glass transition temperature of the obtained polymers

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Received 30 January 1999; received in revised form 1 September 1999; accepted 7 September 1999

Abstract

The polymerization of *tert*-butyl acrylate (*t*BA) was performed with triethylaluminum-(−)-sparteine, triethylaluminum–tertiary phosphine, triethylaluminum–*n*-BuLi and bis(2,6-di-*tert*-butyl-4-methylphenoxide)methylaluminum–*t*-BuLi complexes in toluene. The poly(*t*BA)s obtained with these initiators were rich in syndiotactic diad as observed by ^{1}H NMR analysis. On the basis of the triad and tetrad stereochemical information of the poly(*t*BA)s obtained using triethylaluminum-(−)-sparteine and triethylaluminum–*n*-BuLi, the polymerization reactions were found to obey Bernoullian statistics. Glass transition temperatures of the poly(*t*BA)s were measured by differential scanning calorimetry (DSC). A syndiotactic poly(*t*BA) (racemo (r) diad content: 65%) and an isotactic one (r = 19%) exhibited higher glass transition temperature (50 and 43°C, respectively) than an atactic one (r = 50%, $T_g = 21$°C). © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(*t*-butyl acrylate); Tacticity; Glass transition temperature

1. Introduction

Stereospecific synthesis of acrylic polymers is an important topic because the polymers find wide industrial applications and their properties are often dependent on their tacticity. In general, stereocontrol in the acrylate polymerization is more difficult than that in the polymerization of methacrylates since acrylates lack α-methyl group which plays an important part in the stereochemistry of methacrylate polymerization [1]. Hence, the examples of stereospecific acrylate polymerizations are limited. A highly isotactic poly(*tert*-butyl acrylate) (poly(*t*BA)) was synthesized using a chiral zirconocene [2] (isotactic diad (m): 83%) and also by polymerization with *n*-BuLi in the presence of LiOH (m = 85%) [3]. However, it is difficult to synthesize a highly syndiotactic polyacrylate. The highest syndiotactic diad (r) value so far reported is r = 63% of poly(*t*BA) prepared by radical polymerization at low temperature [4]. A triad syndiotacticity (rr) of about 40% was recently reported for the anionic polymerization of *t*BA with diphenylmethyllithium, -potassium or -cesium [5].

In the present study, we carried out the anionic polymerization of *t*BA using triethylaluminum ($AlEt_3$)-(−)-sparteine (Sp), $AlEt_3$–tertiary phosphine, $AlEt_3$–*n*-BuLi and bis(2,6-di-*tert*-butyl-4-methylphenoxide)methylaluminum [$MeAl(ODBMP)_2$]–*t*-BuLi initiator systems. Though the initiators are known to be effective for stereospecific polymerization of methacrylates [6–12], the polymerization of *t*BA with these initiators has not been examined in detail. The stereostructures of the obtained polymers were studied by NMR, and the effects of tacticity on glass transition temperature (T_g) of the polymers were investigated.

2. Experimental

2.1. Materials

Toluene was purified in the usual manner, mixed with a small amount of *n*-BuLi and distilled under vacuum immediately before use. *t*BA (Wako) was purified in a usual manner, dried over calcium hydride, and vacuum-distilled immediately before use. *n*-BuLi (Aldrich, a hexane solution,

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PII: S0032-3861(99)00669-2

Table 1
Polymerization of *t*BA by $AlEt_3$-tertiary amine or phosphine in toluene at −78°C for 24 h ($[tBA]_0 = 1.0$ M)

Run	Initiator	$[Al]_0/[L]_0/[M]_0$[a]	Yield (%)[b]	M_n ($\times 10^{-4}$)[c]	M_w/M_n[c]	Tacticity (m/r)[d]	T_g (°C)
1	$AlEt_3$–Sp	1/2/40	53	6.40	3.14	42/58	36
2	$AlEt_3$–PPh_3	1/1/40	55	6.92	1.82	38/62	40
3	$AlEt_3$–PPh_3	2/1/40	16	2.50	2.89	37/63	44
4	$AlEt_3$-(S)-BINAP	1/1/40	>99	10.2	2.22	35/65	50
5	$AlEt_3$-(S)-BINAP	1/2/80	30	10.2	1.58	36/64	46
6	$AlEt_3$-(S)-BINAP	5/1/40	69	11.4	1.50	36/64	47

[a] L: nitrogen or phosphine.
[b] Methanol–water (4/1, v/v)-insoluble part.
[c] Determined by SEC with polystyrene standard.
[d] Determined by ^1H NMR (400 MHz, $CDCl_3$, 60°C).

conc. 1.54 M) was used as received. *t*-BuLi (Aldrich, a pentane solution, conc. 1.70 M), obtained commercially, was used as a heptane solution. *n*-BuLi and *t*-BuLi were titrated using butan-2-ol. $AlEt_3$ and $MeAl(ODBMP)_2$ (TCI, a toluene solution) were used as received. Triphenylphosphine (Ph_3P) was purified by recrystallization from hexane. Sp (Aldrich) was dried over calcium hydride and distilled under reduced pressure. (S)-(−)-2, 2′-bis(diphenylphosphino)-1,1′-binaphthyl ((S)-BINAP) (TCI) was used as received.

2.2. Polymerization

The polymerization was carried out in a dry glass ampule under a dry nitrogen atmosphere. Ligand or BuLi was mixed with an aluminum compound in toluene cooled to the reaction temperature, and the mixture was aged for 10 min. The polymerization reaction was initiated by adding the monomer to this mixture with a hypodermic syringe. The reaction was terminated by adding a small amount of methanol. The obtained polymer was precipitated into a methanol–water mixture (4/1, v/v), washed first with dilute aq. HCl and then with water, and dried under vacuum. The polymer was further purified by reprecipitation from a THF solution to a methanol–water mixture.

2.3. Measurements

^1H and ^{13}C NMR spectra were measured in chloroform-*d* at 60°C with a Varian Gemini 2000 spectrometer at 400 and 100 MHz, respectively. The center peak of chloroform-*d* was used as an internal standard (77.0 ppm) in the ^{13}C measurement. The size exclusion chromatographic (SEC) analysis was accomplished on a Shodex System-21 SEC system equipped with an ultraviolet detector (254 nm) and a refractive index detector using a Shodex KF-803 and a KF-806L column connected in series (eluent, THF). The molecular weight was calibrated with standard polystyrenes. DSC measurement was performed on a Seiko SSC-5200 calorimeter at a heating rate of 20°C/min under a nitrogen atmosphere. After the first heating up to 100°C to eliminate thermal history, the sample was cooled to the starting temperature (−30°C), and the second heating was run immediately. The midpoint of the heat capacity transition of the second heating was taken as T_g [13].

3. Results and discussion

3.1. Polymerizations with $AlEt_3$–Sp and $AlEt_3$–tertiary phosphine complexes

Polymerizations of *t*BA with $AlEt_3$–Sp and $AlEt_3$–tertiary phosphine were carried out in toluene at −78°C (Table 1). $AlEt_3$–Sp shows polymerization activity for polar vinyl monomers such as acrylonitrile and methyl methacrylate (MMA) [7]. The polymerization of methyl acrylate with $AlEt_3$–Sp has been revealed to give only the liquid polymer of low molecular weight probably through some side reaction involving the abstraction of the somewhat acidic α-hydrogen of the monomer [7]. However, in the polymerization of *t*BA with $AlEt_3$–Sp in this work, a polymer with high molecular weight was obtained. This may be due to the fact that side reactions including α-hydrogen abstraction and end-cyclization are hindered by the bulky *t*-butyl group of monomeric units in the vicinity of the living end and the monomer.

The results of the polymerization using $AlEt_3$–PPh_3 were quite contrary to the reported results of *t*-butyl methacrylate (*t*BMA) polymerization with the same initiator [8]. While *t*BMA did not give a polymer using $AlEt_3$–PPh_3, *t*BA produced polymers (runs 2 and 3 in Table 1) with the same initiator. $AlEt_3$-(S)-BINAP also afforded polymers of *t*BA.

The stereostructure of the poly(*t*BA)s obtained with the $AlEt_3$–Sp and $AlEt_3$–tertiary phosphine initiation was analyzed by means of ^1H NMR spectroscopy. On the basis of the peak splitting of methylene protons, diad tacticity (m/r) can be calculated [3]. The polymers obtained in the present study were rich in r diad, and the r content was large for the polymers prepared with the Al–phosphine complexes. The r content of the poly(*t*BA)s synthesized using $AlEt_3$–PPh_3 was lower than that of PMMA under

Table 2
Polymerization of *t*BA with $AlEt_3$–*n*-BuLi in toluene for 24 h ($[M]_0 = 1.0$ M; $[n\text{-BuLi}]_0 = 0.025$ M)

Run	Initiators	Temperature (°C)	Yield (%)[a]	M_n ($\times 10^{-4}$)[b]	M_w/M_n[b]	Tacticity (m/r)[c]	T_g (°C)
1	*n*-BuLi	−78	99	7.10	2.44	63/37	32
2	$AlEt_3$/*n*-BuLi (1/1)	−78	0	–	–	–	–
3	$AlEt_3$/*n*-BuLi (3/1)	−78	99	10.9	1.69	41/59	44
4	$AlEt_3$/*n*-BuLi (5/1)	−78	92	9.10	1.69	42/58	37
5	$AlEt_3$/*n*-BuLi (3/1)	−40	>99	7.44	1.92	35/65	47
6	$AlEt_3$/*n*-BuLi (3/1)	0	>99	2.80	1.96	40/60	45
7[d]	$AlEt_3$	−78	0	–	–	–	–

[a] Methanol–water (4/1, v/v)-insoluble part.
[b] Determined by SEC with polystyrene standard.
[c] Determined by ^1H NMR.
[d] $[AlEt_3]_0 = 0.025$ M.

similar conditions [8]. The stereochemistry of polymerization was little affected by the ratio of aluminum to phosphine and the kind of phosphine.

3.2. Polymerizations with Al compound–BuLi complexes

Tables 2 and 3 show the results of the polymerization of *t*BA by $AlEt_3$–*n*-BuLi and $MeAl(ODBMP)_2$–*t*-BuLi, respectively. $AlEt_3$–*n*-BuLi (1/1) complex did not polymerize *t*BA at −78°C. This result is similar to that for the polymerization of fluoroalkyl acrylates with the same initiator at −78°C [14]. $AlEt_3$ itself did not initiate the polymerization of *t*BA, either. However, the monomer was polymerized almost quantitatively when Al/Li ratio was 3 or larger. This may suggest that the excess Al species interact with the monomer to activate it though the precise mechanism of the $AlEt_3$–*n*-BuLi-initiated polymerization is not clear. The activation may be necessary to cause polymerization. The results obtained here are quite in contrast to the report that MMA affords a polymer using $Al(n\text{-}C_8H_{17})$–*t*-BuLi even at $Al/Li = 1/1$ [10]. The molecular weight distribution of the polymers prepared with $AlEt_3$–*n*-BuLi was narrower compared with that of polymer obtained by *n*-BuLi alone. The polymer obtained with $AlEt_3$–*n*-BuLi was rich in r diad fraction whereas the one prepared with *n*-BuLi alone under similar conditions was rich in m diad. The introduction of $AlEt_3$ thus changed the stereochemistry of the polymerization as observed in the case of MMA polymerization [10]. The tacticity of the polymers obtained using $AlEt_3$–*n*-BuLi (3/1) depended on polymerization temperature and the dependence was not simple. This may be due to some change in the structure of growing species with temperature. A similar effect has been found in the polymerization of ethyl methacrylate with bis(2,6-di-*t*-butylphenoxy)methylaluminum–*t*-BuLi (5/1) [12].

Similar to $AlEt_3$, $MeAl(ODBMP)_2$ itself did not initiate the polymerization of *t*BA at 0°C. However, the $MeAl(ODBMP)_2$–*t*-BuLi initiator system polymerized *t*BA. The polymer yield varied depending on the Al/Li ratio and monomer concentration, and was nearly quantitative under selected conditions (runs 3, 4 and 8 in Table 3). $MeAl(ODBMP)_2$–*t*-BuLi (5/1) affords only a trace amount of polymer at −78°C in 24 h, indicating that the $MeAl(ODBMP)_2$–*t*-BuLi systems may be less active

Table 3
Polymerization of *t*BA by $MeAl(ODBMP)_2$–*t*-BuLi in toluene at 0°C for 24 h ($[Li]_0 = 0.025$ M)

Run	$[Al]_0/[Li]_0$	$[M]_0$ (M)	Yield (%)[a]	M_n ($\times 10^{-4}$)[b]	M_w/M_n[b]	Tacticity (m/r)[c]
1	0/1	1.0	>99	2.24	6.19	71/29
2[d]	2/1	1.0	51	0.58	1.84	50/50
3[e]	5/1	1.0	>99	2.27	2.53	35/65
4	10/1	1.0	>99	1.61	2.33	35/65
5[f]	1/0	1.0	0	–	–	–
6	5/1	0.2	54	0.49	1.66	34/66
7	5/1	0.5	90	1.51	3.34	34/66
8	5/1	2.0	>99	1.83	2.14	33/67
9[g]	10/1	1.0	75	1.36	2.65	39/61

[a] Methanol–water (4/1, v/v)-insoluble part.
[b] Determined by SEC with polystyrene standard.
[c] Determined by ^1H NMR of poly(methyl acrylate) derived from the original polymers (400 MHz, $CDCl_3$, 60°C).
[d] $T_g = 21$°C.
[e] $T_g = 50$°C.
[f] $[Al]_0 = 0.025$ M.
[g] *t*BA was first added to the MAD solution at 0°C, the mixture was kept for 10 min, and then *t*-BuLi was introduced.

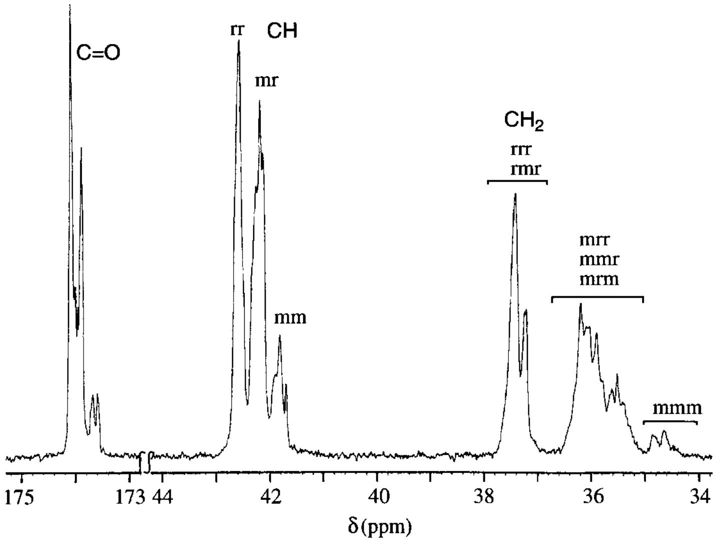

Fig. 1. ^{13}C NMR spectrum of poly(*t*BA) (run 5 in Table 2) (100 MHz, $CDCl_3$, 60°C).

compared with the $AlEt_3$–*n*-BuLi systems for *t*BA polymerization presumably due to its bulkiness. It is also notable that initiator efficiency appeared higher with the $MeAl(ODBMP)_2$–*t*-BuLi systems than with the $AlEt_3$–*n*-BuLi systems. This could mean that the $AlEt_3$–*n*-BuLi initiator system causes carbonyl attack to some extent leading to the lower initiator efficiency while the $MeAl(ODBMP)_2$–*t*-BuLi initiator system more selectively attacks the vinyl group of *t*BA because of higher steric hindrance based on the bulkiness of $MeAl(ODBMP)_2$.

The introduction of $MeAl(ODBMP)_2$ affected the stereochemistry of polymerization similar to $AlEt_3$ and resulted in the polymers rich in r diad fraction. With an increase in the ratio of Al/Li from 0/1 to 5/1, syndiotacticity (r diad) increased from 29 to 65%, but a further raise of Al/Li from 5/1 to 10/1 resulted in little change of the stereoregularity. The order of addition of reagents also affected the stereochemistry of propagation as observed in runs 4 and 9 in Table 3. The method (run 4) in which *t*-BuLi was first mixed with $MeAl(ODBMP)_2$ and was stood for 10 min at reaction temperature to form a complex resulted in a higher syndiotacticity than the other way (run 9, footnote g to Table 3). The monomer concentration scarcely affected the stereochemistry of propagation in contrast to the polymerization with *n*-BuLi in toluene [3].

3.3. Stereochemical statistics

^{13}C NMR analysis of poly(*t*BA) gives triad and tetrad tacticity information (Fig. 1). The triad fractions were determined using the peaks of methine group. The triad tacticity calculated from the ^{13}C NMR data was coincided with the diad tacticity obtained by the ^{1}H NMR analysis. The peak splitting of the methylene carbon is based on tetrad stereochemistry but has been only partially assigned [15]. Using the triad and the partial tetrad information, we tested the Bernoullian model for the polymers obtained with $AlEt_3$–Sp (run 1 in Table 1), $AlEt_3$–PPh_3 (run 2 in Table 1), $AlEt_3$–

Table 4
Statistical analysis of stereostructure of poly(*t*BA)s

	Configuration	Sample I (run 1 in Table 1)			Sample II (run 5 in Table 2)		
		Experimental[a]	Bernoullian ($P_m = 0.42^b$)		Experimental[a]	Bernoullian ($P_m = 0.35^b$)	
$-\underset{\mid}{CH}-$	mm	0.17	0.18		0.13	0.12	
	mr	0.49	0.49		0.45	0.46	
	rr	0.34	0.34		0.42	0.42	
	mmm	0.07	0.07		0.05	0.04	
$-CH_2-$	mmr	0.60	0.21	0.59	0.54	0.16	0.54
	mrm		0.10			0.08	
	mrr		0.28			0.30	
	rmr	0.33	0.14	0.34	0.41	0.15	0.42
	rrr		0.20			0.27	

[a] Determined by ^{13}C NMR (100 MHz, $CDCl_3$, 60°C).
[b] Determined by ^{1}H NMR (400 MHz, $CDCl_3$, 60°C).

Table 5
T_g for poly(tBA)s obtained by anionic and radical polymerization (the polymers were available from our recent work (Ref. [3]); reaction conditions: reaction time, 24 h; run 1, $[LiOH]_0/[n\text{-BuLi}]_0 = 1$, $[n\text{-BuLi}]_0 = 0.025$ M, $[M]_0 = 1.0$ M, 0°C; run 2, $[LiOH]_0/[n\text{-BuLi}]_0 = 1$, $[n\text{-BuLi}]_0 = 0.025$ M, $[M]_0 = 1.0$ M, −78°C; run 3, $[n\text{-BuLi}]_0 = 0.10$ M, $[M]_0 = 1.0$ M, −78°C; run 4, $[n\text{-BuLi}]_0 = 0.050$ M, $[M]_0 = 4.0$ M, −78°C; run 5, $[n\text{-BuLi}]_0 = 0.075$ M, $[M]_0 = 0.15$ M, −78°C; run 6, $[n\text{-BuLi}]_0 = 0.05$ M, $[M]_0 = 1.0$ M, −15°C; run 7, $[AIBN] = 0.02$ M, $[M]_0 = 1.0$ M, 60°C)

Run	Initiator	M_n ($\times 10^{-4}$)[a]	M_w/M_n[a]	r (%)[b]	T_g (°C)
1	LiOH/n-BuLi	12.4	4.89	15	42
2	LiOH/n-BuLi	17.9	4.82	19	43
3	n-BuLi	5.85	2.68	33	34
4	n-BuLi	5.24	3.85	44	29
5	n-BuLi	0.28	4.68	29	9
6	n-BuLi	1.82	4.97	29	34
7	AIBN	2.75	2.44	60	46

[a] Determined by SEC with polystyrene standard.
[b] Determined by ^{1}H NMR.

n-BuLi (run 5 in Table 2) and MeAl(ODBMP)$_2$–t-BuLi (run 3 in Table 3). The conditional probability $P_{r/m}$ that a monomer adds to a growing end having a racemo configuration in meso fashion and the reverse probability, $P_{m/r}$, are given by the following relations [16]:

$$P_{r/m} = mr/(2rr + mr) \qquad (1)$$

$$P_{m/r} = mr/(2mm + mr) \qquad (2)$$

When $P_{r/m} + P_{m/r} = 1$, then chain propagation obeys Bernoullian statistics. The results for the polymers synthesized with AlEt$_3$–Sp and AlEt$_3$–n-BuLi (5/1) are listed in Table 4. The sums of the $P_{r/m}$ and $P_{m/r}$ for the two samples are 1.01 and 0.98, respectively, indicating that the polymerizations can be described by Bernoullian model. Similar results were obtained for the other two samples: AlEt$_3$–PPh$_3$ (run 2 in Table 1) mm/mr/rr = 14/49/37, $P_{r/m} + P_{m/r} = 1.01$; MeAl(ODBMP)$_2$–t-BuLi (run 3 in Table 3) mm/mr/rr = 12/46/41, $P_{r/m} + P_{m/r} = 1.00$. Thus, the polymerizations obey Bernoullian statistics.

In addition, the partial tetrad information allowed us to further examine the model. As shown in Table 4, the obtained tetrad fractions were in fair agreement with those calculated by Bernoullian statistics.

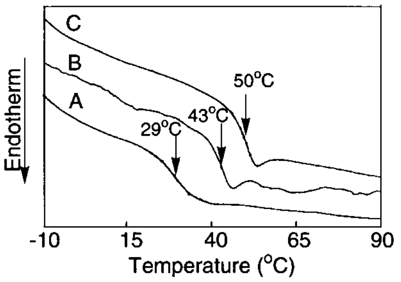

Fig. 2. Typical DSC curves of poly(tBA)s (A: run 4 in Table 5, B: run 2 in Table 5, C: run 4 in Table 1).

In ^{13}C NMR spectra of acrylic polymers, side-chain carbonyl group is often most sensitive to the stereochemical isomerism of the main-chain [15,17,18]. However, the carbonyl peak assignment has not been reported so far for poly(tBA) [15]. The three major groups of peaks of carbonyl group at 174.20–173.98, 173.98–173.78 and 173.78–173.50 (two peaks) ppm seem not simply based on rr-, mr-, and mm-centered pentads unlike those of PMMA because the triad fraction content obtained from this assignment is inconsistent with the diad tacticity based on the ^{1}H NMR information. Also, a recent report adopted a different peak assignment in which the three groups of the peaks were rr-, mr-, and mm-triads in the order from up field to down field [5]. In addition, for poly(cyclohexyl acrylate) carbonyl peaks, rather complicated peak assignments have been proposed [18]. Hence, we did not use the carbonyl peaks for the stereochemical discussion.

3.4. Correlation between glass transition temperature and tacticity

As described so far, the poly(tBA) samples with various tacticities were obtained in this work. In addition, we have recently reported the polymerization of tBA using n-BuLi which gave the polymers rich in m diad (Table 5). With these polymers with a wide range of stereochemistry in hand, we were able to systematically examine the effects of tacticity on glass transition temperature (T_g) of poly(tBA) for the first time.

The polymers with different tacticity exhibited different DSC curves as exemplified for three polymers in Fig. 2. The polymers exhibited clear thermal transition in the DSC analysis and the T_g's were unambiguously determined as shown in the figure. Fig. 3 indicated the plot of T_g vs. tacticity (r diad) for the polymers with the Mn range of $5.0\text{–}12 \times 10^4$. For the plot, two data points reported by the other groups were added to our own results: the imported T_g's are those for the polymer obtained using a chiral zirconocene catalyst by Soga [2] ($M_n = 4.8 \times 10^4$, r = 17%, T_g = 41°C, square symbol) and for the polymer prepared with an Sm catalyst by Yasuda [19] ($M_n = 1.6 \times 10^4$, r = 50%, T_g = 21°C, triangular symbol). As seen from the plot, the effects of tacticity on T_g was not monotonous. T_g appears to be lowest in the atactic region (r ~ 50%) and to increase with an increase either in m or r content T_g, resulting in a U-shaped relation of T_g vs. tacticity. The relationship between T_g and tacticity of poly(tBA) with a minimum in the atactic region found in the present work is obviously different from that of PMMA which T_g increases simply with an increase in syndiotactic fraction [8]. A similar relationship between melting point and tacticity has been known for poly(vinyl alcohol) [20] and polystyrene [21]. A U-shaped relationship between tacticity and phase transition temperature may be characteristic to α-monosubstituted vinyl polymers.

In order to confirm that the observed effects arise merely from tacticity, the extent of possible molecular-weight

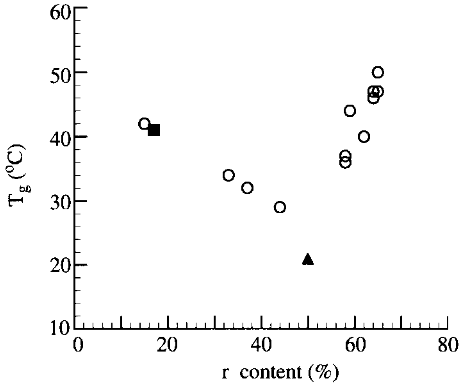

Fig. 3. Correlation between T_g and tacticity (■ Soga's polymer (Ref. [2]); ▲ Yasuda's polymer (Ref. [19])).

effect was investigated in the syndiotactic, atactic and isotactic regions. In the syndiotactic region, the samples of run 4 in Table 2 and run 3 in Table 3 having the identical r content (65%) and different molecular weights ($M_n = 7.44 \times 10^4$ and 2.27×10^4, respectively) exhibited the same glass transition temperature (50°C). In the atactic region, the sample of run 2 in Table 3 ($M_n = 5.8 \times 10^3$, r = 50%, $T_g = 21$°C) and Yasuda's polymer ($M_n = 1.6 \times 10^4$, r = 50%, $T_g = 21$°C) having the identical tacticity exhibited the identical T_g. In the isotactic region, although the polymer of run 6 in Table 5 (r = 29%, $M_n = 1.82 \times 10^4$) exhibited a 25°C higher T_g than that of run 5 in Table 5 (r = 29%, $M_n = 2.8 \times 10^3$), this can be ascribed to the much lower M_n sample of run 5 in Table 5. We also compared the samples of runs 1 and 2 in Table 5 and found that the molecular weight has only a small effect on T_g in the range of $M_n > 5.0 \times 10^4$. Hence, we can reasonably conclude that the effect of molecular weight on the observed T_g-vs.-tacticity relation should be negligible in the M_n range of $5.0–12 \times 10^4$ for the data listed in Fig. 3.

The effect of heating rate in the DSC experiment on the T_g was also considered because the T_g data for Soga's polymer was taken at 10°C/min while the data for the other polymers at 20°C/min. The polymer (run 5 in Table 2) exhibited a T_g of 45°C at 10°C/min and that of 47°C at 20°C/min. Thus, the difference was 2°C which was much lower than the T_g differences discussed in this paper.

4. Conclusion

The polymerization of *t*BA using organoaluminum complexes led to the polymers rich in diad syndiotacticity. On the basis of the triad and tetrad stereochemical information of poly(*t*BA) observed by ^{13}C NMR analysis, the polymerization reactions were found to obey Bernoullian statistics. The glass transition temperature of poly(*t*BA) was found to be influenced by its tacticities. Both isotactic and syndiotactic polymers exhibit higher T_g than atactic ones.

Acknowledgements

This work was supported in part by the New Energy and Industrial Technology Development Organization (NEDO) for the project on Technology for Novel High-Functional Materials in Industrial Science and Technology Frontier Program, AIST.

References

[1] Hatada K, Kitayama T, Ute K. Prog Polym Sci 1988;13:189.
[2] Deng H, Soga K. Macromolecules 1996;29:1847.
[3] Liu W, Nakano T, Okamoto Y. Polym J 1999;31:479.
[4] Matsuzaki K, Uryu T, Kanai T, Hosonuma K, Matsubara T, Tachikawa H, Yamada M, Okuzono S. Makromol Chem 1977;178:11.
[5] Ishizone T, Yoshimura K, Hirao A, Nakahama S. Macromolecules 1998;31:8706.
[6] Ikeda M, Hirano T, Tsuruta T. Makromol Chem 1971;150:127.
[7] Ikeda M, Hirano T, Nakayama S, Tsuruta T. Makromol Chem 1974;175:2775.
[8] Kitayama T, Masuda E, Yamaguchi M, Nishiura T, Hatada K. Polym J 1992;24:817.
[9] Schlaad H, Schmitt B, Muller AHE, Jungling S, Weiss H. Macromolecules 1998;31:573.
[10] Kitayama T, Shinozaki T, Masuda E, Yamamoto M, Hatada K. Polym Bull 1988;20:505.
[11] Nakagawa O, Fujimoto N, Nishiura T, Kitayama T, Hatada K. Polym Bull 1992;29:579.
[12] Kitayama T, Zhang Y, Hatada K. Polym J 1994;26:868.
[13] Sanchis A, Masegosa RM, Rubio RG, Prolongo MG. Eur Polym J 1994;30:781.
[14] Narita T, Hagiwara T, Hamana H, Goto M. Makromol Chem 1986;187:731.
[15] Suchoparek M, Spevacek J. Macromolecules 1993;26:102.
[16] Bovey FA, Mirau PA. NMR of polymers, San Diego: Academic Press, 1996.
[17] Bara A, Dutta K. Polym J 1998;30:304.
[18] Bulai A, Jimeno M, Roman J. Macromolecules 1995;28:7363.
[19] Ihara E, Morimoto M, Yasuda H. Macromolecules 1995;28:7886.
[20] Yamada K, Nakano T, Okamoto Y. Macromolecules 1998;31:7598.
[21] Ishihara N, Seimiya T, Kuramoto M, Uoi M. Macromolecules 1986;19:2465.