

Synthesis of High Molecular Weight Copolymer of Styrene and Butadiene Bearing High 1,4-*cis* Butadiene Unit from Copolymerization with CpTiCl₃/Methylaluminoxane Catalyst

Norihiko Nakamura,¹ Yuji Yamaguchi,¹ Kiyoshi Endo²

¹ Tire Material Development Department, Toyo Tire & Rubber Co., Ltd., Nishichujocho, Ibarakisi, Osaka, Japan

² Department of Applied Chemistry, Graduate School of Engineering, Osaka City University, Sugimoto Sumiyoshi-Ku, Osaka 558-8585, Japan

Received 4 March 2002; accepted 31 July 2002

ABSTRACT: Copolymerization of styrene (St) and butadiene (Bd) with CpTiCl₃/methylaluminoxane (MAO) catalyst in the presence or absence of chloranil (CA) was investigated. The CpTiCl₃/MAO catalyst showed a high activity for the copolymerization of St with Bd. The 1,4-*cis* contents in the Bd units for the copolymerization of St and Bd with the CpTiCl₃/MAO catalyst was observed, and the 1,4-*cis* content was optimum at a MAO/Ti mole ratio of around 225. The effect of the polymerization temperature on the copolymerization was noted, as was the effect of the 1,4-*cis* microstructure in the Bd units for the copolymerization of St

and Bd. The addition of CA to the CpTiCl₃/MAO catalyst was found to influence the molecular weight of the copolymer. The high weight-average molecular weight copolymer ($M_w = \text{ca. } 50 \times 10^4$) consisting of mainly a 1,4-*cis* microstructure of Bd units (1,4-*cis* = 80.0%) was obtained from the copolymerization with the CpTiCl₃/MAO catalyst in the presence of CA (CA/Ti mole ratio = 1) at 0°C. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 2942–2946, 2003

Key words: CpTiCl₃/methylaluminoxane; styrene; butadiene; copolymerization; chloranil; 1,4-*cis* microstructure

INTRODUCTION

A high molecular weight copolymer of styrene (St) and 1,3-butadiene (Bd) is a very useful material for the rubber industry, especially for tire materials.¹ The desirable molecular characteristic of the copolymers of St and Bd for a practical use as tire materials is believed to have the following features: the molecular weight of the copolymer is high, the Bd units in the copolymer consist of a high 1,4-*cis* microstructure, and the sequence of St and Bd units in the copolymer is random. The copolymers consisting of St and Bd units are synthesized through various polymerization mechanisms. Radical or anionic polymerization is utilized for synthesizing the copolymer consisting of St and Bd units. In a radical copolymerization of St and Bd, random copolymers can be prepared, but the microstructure of Bd units in the copolymer consists of mainly 1,4-*trans* units.¹ In an anionic copolymerization of St and Bd with alkyllithiums,^{2,3} the resulting copolymer has a block sequence of both monomer units, although the molecular weights of the copolymers and 1,4-*cis* contents of the Bd units are high enough for

practical use as rubber materials. In the anionic copolymerization of St and Bd with alkyllithiums, randomizing agents such as *t*-butoxide, ethers, and amines are added to make copolymers with random sequences. However, the undesirable 1,2-*vinyl* units in the copolymer are increased by the addition of amines and ethers to the alkyllithiums.^{4,5}

The copolymerization of St and Bd was also investigated with lanthanide-based catalysts,^{6–11} metallocene catalysts,^{12,13} and nonmetallocene transition metal catalysts.^{14–16} The products obtained from copolymerization with these catalysts mainly consisted of 1,4-*cis* units in the copolymer. However, the molecular weight of the copolymer was remarkably decreased with an increase of St units in the copolymers.

Zambelli et al. reported copolymerization of St and Bd with CpTiCl₃/methylaluminoxane (MAO) catalyst, and the monomer reactivity ratios were determined to be $r_{\text{Bd}} = 11.5$ and $r_{\text{St}} = 0.14$.¹³ They also asserted that the growing chains ending with Bd units are less reactive than the chains ending with St, which is explained by the equilibrium of three-electron ligand and one-electron ligand.¹³ However, the detailed copolymerization conditions for the synthesis of high molecular weight random copolymers consisting of mainly 1,4-*cis* units were not examined. Moreover, chloranil (CA) was reported to be an effective catalyst modifier to control the 1,4-*cis* content in the polymer-

Correspondence to: K. Endo (endo@a-chem.eng.osaka-cu.ac.jp).

TABLE I
Effect of Mixing Order in Copolymerization of St and Bd with CpTiCl₃/MAO Catalyst in Toluene at 60°C for 2 h

Mixing Order ^a	St in Monomer (mol%)	Copolymer							
		Yield (%)	M_n ($\times 10^{-4}$)	M_w ($\times 10^{-4}$)	M_w/M_n	St (mol %)	Microstructure of Bd Unit (%)		
							1,4- <i>cis</i>	1,4- <i>trans</i>	1,2- <i>vinyl</i>
A	40	47.3	6.3	20.9	3.32	11.9	62.2	7.7	30.2
B	40	42.4	11.5	14.3	1.24	42.0	64.0	8.1	28.0
A	60	37.6	11.0	12.5	1.14	43.7	69.2	9.6	21.2
B	60	55.3	6.8	7.6	1.12	73.9	65.3	10.1	24.6

[St + Bd] = 5.2 mol/L, [Ti] = 2.1×10^{-3} mol/L, MAO/Ti mole ratio = 500.

^a A, reagents were introduced in the following order; CpTiCl₃, MAO, St, and Bd; B, reagents were introduced in the following order; St, Bd, MAO, and CpTiCl₃.

ization of Bd with an $[(\eta^3\text{-ally})\text{Ni}(\text{OCOCF}_3)_2]$ catalyst.¹⁷ Based on these reported results, we firmly believed that the target copolymer of St and Bd may be synthesized from a copolymerization with a CpTiCl₃/MAO catalyst in the presence of CA.

In this article we study the copolymerization of St and Bd with CpTiCl₃/MAO catalyst in the presence or absence of CA to obtain copolymers in which the high molecular weight copolymer consists of mainly 1,4-*cis* units.

EXPERIMENTAL

Materials

Commercially available St and Bd were purified by distillation over calcium hydride before use. CA (Tokyo Kasei Co.) and CpTiCl₃ (Aldrich) were used without further purification. MAO diluted toluene, which was kindly supplied by Tosoh-Akzo Co., was used as received. Solvents and other reagents were used after purification by conventional methods.

Copolymerization procedure

Copolymerization was carried out in a sealed glass tube connected to a vacuum system. The required amounts of reagents except for Bd were introduced into the tube by syringes through a rubber septum. The Bd was induced into the tube under vacuum distillation after its purification over calcium hydride. Two methods were used for mixing the reagents in the

tube; CpTiCl₃ is activated by MAO in either the presence or absence of monomers. The copolymerization was carried out in a thermostat at a constant temperature for a given time. After the copolymerization, the tube was opened and the contents in the tube were poured into a large amount of methanol containing a small amount of hydrochloric acid and *p*-*tert*-butylcatechol as an antioxidant to precipitate the copolymer that was formed. The polymer was then washed with an excess of methanol and dried under high vacuum for overnight at room temperature. The polymer yields were calculated by gravimetry.

Characterization of copolymers

The number-average (M_n) and weight-average (M_w) molecular weights of the polymer were determined by GPC using a Shimadzu LC10A series system in THF at 40°C as calibrated with polystyrene standards. The microstructure of the Bd units in the copolymer was determined from IR spectroscopy according to the reported method.^{18,19} The IR spectra of the polymers were recorded on a Perkin-Elmer Paragon1000 spectrometer at 23°C.

RESULTS AND DISCUSSION

Effect of catalyst activation method

In binary catalysts, there are different mixing orders of reagents to form an active site for polymerization, and it is known that the activity for polymerization some-

TABLE II
Effect of Reaction Temperature on Copolymerization of St and Bd with CpTiCl₃/MAO Catalyst in Toluene

Temp. (°C)	Time (h)	Copolymer							
		Yield (%)	M_n ($\times 10^{-4}$)	M_w ($\times 10^{-4}$)	M_w/M_n	St (mol %)	Microstructure of Bd Unit (%)		
							1,4- <i>cis</i>	1,4- <i>trans</i>	1,2- <i>vinyl</i>
60	2	47.3	6.3	20.9	3.32	11.9	62.2	7.7	30.2
0	20	77.1	23.1	38.3	1.66	42.4	70.3	4.8	24.9
-78	20	29.3	20.4	23.4	1.15	8.8	75.9	0.2	23.8

[St] = 2.1 mol/L, [Bd] = 3.0 mol/L, [Ti] = 2.1×10^{-3} mol/L, MAO/Ti ratio = 500.

TABLE III
Effect of Polymerization Solvent on Copolymerization of St and Bd with CpTiCl₃/MAO Catalyst at 60°C for 2 h

Solvent	Copolymer							
	Yield (%)	M_n ($\times 10^{-4}$)	M_w ($\times 10^{-4}$)	M_w/M_n	St (mol %)	Microstructure of Bd Unit (%)		
						1,4- <i>cis</i>	1,4- <i>trans</i>	1,2- <i>vinyl</i>
Toluene	47.3	6.3	20.9	3.32	11.9	62.2	7.7	30.2
CH ₂ Cl ₂	91.5	0.13	0.25	1.96	67.4	58.0	29.1	12.9

[St] = 2.1 mol/L, [Bd] = 3.0 mol/L, [Ti] = 2.1×10^{-3} mol/L, MAO/Ti mole ratio = 500.

times depends on the mixing order of the reagents.^{20,21} In the copolymerization of St and Bd with the CpTiCl₃/MAO catalyst, which can produce syndiotactic polystyrene,²² we examined two methods for the mixing order of the reagents. One is that the reagents are charged into the tube by subsequently introducing CpTiCl₃, MAO, St, and Bd (method A). Another is that the reagents are charged by subsequently introducing St, Bd, MAO, and CpTiCl₃ (method B). The results for the copolymerization at 60°C are shown in Table I. When method A was applied to the copolymerization, the St content in the copolymer was higher than method B. The molecular weight of the copolymers and the 1,4-*cis* content of Bd units in the copolymer were not significantly influenced by the charging method of the reagents.

Effect of reaction temperature

The effect of the reaction temperature on the copolymerization of St and Bd with the CpTiCl₃/MAO catalyst was examined. The copolymerization was performed at 60, 0, and -78°C, and the results are shown in Table II. The activity for the copolymerization decreased with a decreasing reaction temperature, and the 1,4-*cis* contents of Bd units in the copolymer increased with a decreasing reaction temperature. The molecular weight of the copolymer obtained at 0°C is higher than that obtained at 60°C. Moreover, the molecular weight distribution (M_w/M_n) became narrow as a function of the reaction temperature. It is interesting that, when the polymerization was carried out at -78°C, the M_w/M_n value of the copolymer was

1.15. This suggests that chain termination and chain transfer reactions might be neglected at the low reaction temperature in the copolymerization of St and Bd with the CpTiCl₃/MAO catalyst.

Effect of polymerization solvent

The effect of polymerization solvents on the copolymerization of St and Bd with the CpTiCl₃/MAO catalyst was examined, and the results are shown in Table III. The copolymer yield in CH₂Cl₂ was higher than that in toluene, although the molecular weight of the copolymer in CH₂Cl₂ was significantly decreased as compared with that in toluene. Probably because CH₂Cl₂ is reported to produce free ions at active centers rather than the contact ion pairs,^{23,24} the copolymerization rate is enhanced in CH₂Cl₂; but the active site for the copolymerization in CH₂Cl₂ seems to tend to induce chain transfer reactions.

Effect of MAO/CpTiCl₃ mole ratio

The effect of MAO/CpTiCl₃ mole ratio on the copolymerization of St and Bd with the CpTiCl₃/MAO catalyst was also examined, and the results are shown in Table IV. The activity for the copolymerization decreased with a decrease of the MAO/CpTiCl₃ mole ratio (Fig. 1), but the 1,4-*cis* content of Bd units in the copolymer did not increase as a function of the MAO/CpTiCl₃ mole ratio (Fig. 2). Thus, the optimum conditions may be present for producing a copolymer bearing high molecular weight and a high 1,4-*cis* microstructure of Bd units as obtained from the

TABLE IV
Effect of MAO/Ti Mole Ratio on Copolymerization of St and Bd with CpTiCl₃/MAO Catalyst in Toluene at 0°C for 20 h

MAO/Ti Mole Ratio	Copolymer							
	Yield (%)	M_n ($\times 10^{-4}$)	M_w ($\times 10^{-4}$)	M_w/M_n	St (mol %)	Microstructure of Bd Unit (%)		
						1,4- <i>cis</i>	1,4- <i>trans</i>	1,2- <i>vinyl</i>
500	77.1	23.1	38.3	1.66	42.4	70.3	4.8	24.9
225	50.6	22.2	40.7	1.83	8.2	83.7	0.1	16.2
100	38.5	31.4	57.5	1.83	0.0	83.0	0.0	17.0
50	15.2	16.1	31.4	1.95	0.0	78.6	2.0	19.4

[St] = 2.1 mol/L, [Bd] = 3.0 mol/L, [Ti] = 2.1×10^{-3} mol/L.

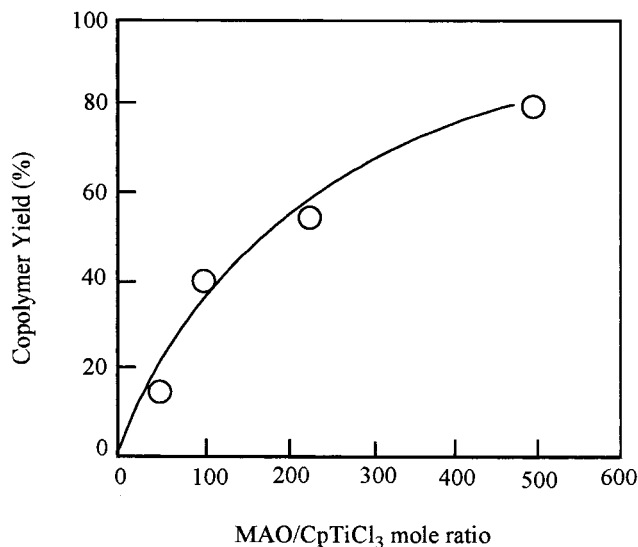


Figure 1 The effect of the MAO/CpTiCl₃ mole ratio on the copolymerization of St and Bd with the CpTiCl₃/MAO catalyst. For the copolymerization conditions, see the footnote to Table IV.

copolymerization of St and Bd with the CpTiCl₃/MAO catalyst.

Additive effect of CA to CpTiCl₃/MAO catalyst

Although the CpTiCl₃/MAO catalyst revealed a high activity for the copolymerization of St and Bd to give 1,4-*cis* rich copolymers, both the higher content of 1,4-*cis* Bd units in the copolymer and the higher M_n of the copolymer are required for practical use as a rubber material. For this purpose, an addition effect of CA to the CpTiCl₃/MAO catalyst in the copolymerization of St and Bd was examined. Because CA was reported to be an effective catalyst modifier to produce 1,4-*cis* microstructures in the polymerization of Bd with an $[(\eta\text{-ally})\text{Ni}(\text{OCOFC}_3)_2]$ catalyst,¹⁷ we used CA as a modifier of the CpTiCl₃/MAO catalyst, and the copolymerization of St and Bd with the CpTiCl₃/MAO/CA catalyst was carried out. The results are shown in Table V. Both the copolymer yield and the molecular weight of the copolymer increased with the addition of CA to the CpTiCl₃/MAO catalyst. The copolymer with an M_w of 58.5×10^4 , and an M_w/M_n

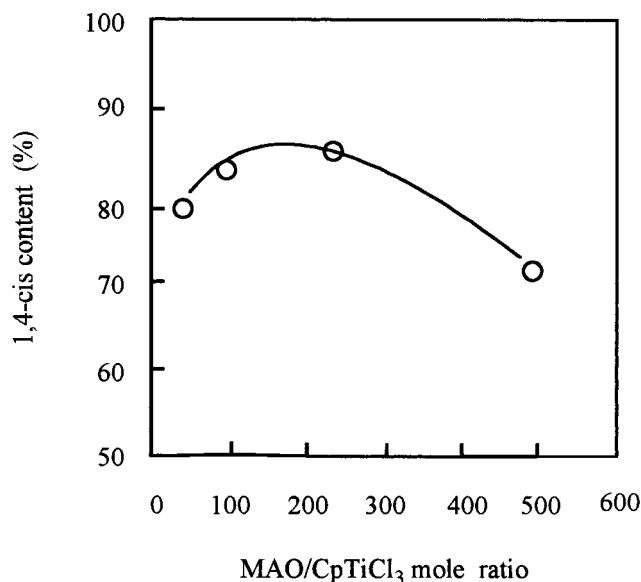


Figure 2 The effect of the MAO/CpTiCl₃ mole ratio on the microstructure in the copolymerization of St and Bd with the CpTiCl₃/MAO catalyst. For the copolymerization conditions, see the footnote to Table VI.

value of 1.8 was obtained in the copolymerization with the CpTiCl₃/MAO catalyst in the presence of CA (CA/CpTiCl₃ = 1.0 mole ratio) at 0°C. With the addition of CA to the CpTiCl₃/MAO catalyst, the 1,4-*cis* content of Bd in the copolymer was somewhat increased, but the St contents in the copolymer were somewhat decreased. This is in contrast to the reported results that CA did not influence the copolymer structure in the copolymerization of St and Bd with the Cp₂Ni/MAO catalyst.¹⁶

In the polymerization of Bd with Co(octanoate)₂/MAO catalyst, the effect of organic chlorides such as *tert*-butyl chloride on the polymer yield, stereoregularity, and molecular weight of the polymer were observed.²⁵ An increase of the molecular weight of the polymer and polymer yield were explained by the stability of the active sites for the polymerization. Similar effects might be applied to the copolymerization in this study.

The effect of the MAO/CpTiCl₃ mole ratio on the copolymerization with the CpTiCl₃/MAO in the pres-

TABLE V
Effect of CA on Copolymerization of St and Bd with CpTiCl₃/MAO Catalyst in Toluene at 0°C for 20 h

CA (mmol/L)	Yield (%)	M_n ($\times 10^{-4}$)	M_w ($\times 10^{-4}$)	M_w/M_n	St (mol %)	Microstructure of Bd Unit (%)		
						1,4- <i>cis</i>	1,4- <i>trans</i>	1,2- <i>vinyl</i>
None	77.1	23.1	38.3	1.66	42.4	70.3	4.8	24.9
1.1	72.8	29.2	49.8	1.70	26.5	68.5	5.1	26.4
2.1	77.5	32.8	58.5	1.79	19.3	71.2	5.0	23.8

[St] = 2.1 mol/L, [Bd] = 3.0 mol/L, [Ti] = 2.1×10^{-3} mol/L, MAO/Ti mole ratio = 500.

TABLE VI
Effect of MAO/Ti Mole Ratio on Copolymerization of St and Bd with CpTiCl₃/MAO/CA Catalyst in Toluene at 0°C for 20 h

MAO/Ti Mole Ratio	Copolymer							
	Yield (%)	M_n ($\times 10^{-4}$)	M_w ($\times 10^{-4}$)	M_w/M_n	St (mol %)	Microstructure of Bd Unit (%)		
						1,4- <i>cis</i>	1,4- <i>trans</i>	1,2- <i>vinyl</i>
500	77.5	32.8	58.5	1.79	19.3	71.2	5.5	23.8
225	62.4	25.2	43.3	1.72	14.4	80.0	0.1	20.1
100	48.1	13.7	44.2	3.24	0.0	81.7	0.3	18.0
50	27.4	9.3	25.8	2.77	0.0	83.5	0.0	16.5

[St] = 2.1 mol/L, [Bd] = 3.0 mol/L, [Ti] = 2.1×10^{-3} mol/L, [CA] = 2.1×10^{-3} mol/L.

ence of CA was also examined, and the results are listed in Table VI. The copolymer yields and the molecular weight of the copolymers decreased as a function of the MAO/CpTiCl₃ mole ratio. Concerning the microstructure of the Bd units in the copolymer, the 1,4-*cis* contents of the Bd units increased with a decrease of the MAO/CpTiCl₃ mole ratio, but the St contents in the copolymer increased with an increase of the mole ratio. At a lower ratio, it is difficult to incorporate St units in the copolymer, suggesting that the active sites for the polymerization to both monomers were produced at a lower mole ratio, but the active site for the polymerization seems to be different at a higher MAO/CpTiCl₃ mole ratio.

The molecular weight of the copolymer increased with the CpTiCl₃/MAO catalyst in the presence of CA, but the copolymer composition was not different from the reported results obtained with the CpTiCl₃/MAO catalyst at the same feed.¹³ This indicates that the monomer sequence seems to be a block sequence rather than a random sequence, although we did not analyze the monomer sequence in the resulting copolymer.

CONCLUSION

Copolymerization of St and Bd with a CpTiCl₃/MAO catalyst was investigated. The CpTiCl₃/MAO catalyst showed high activity for the copolymerization of St and Bd. In the copolymerization of St and Bd with this catalyst, the MAO/CpTiCl₃ mole ratio and reaction temperature influenced the 1,4-*cis* contents of the Bd units in the copolymer. In the presence of CA, a high molecular weight copolymer consisting of St and Bd units was obtained in good yields.

References

1. Tate, D. P.; Bethea, T. W. *Encyclopedia of Polymer Science and Engineering*; Wiley: New York, 1985; Vol. 2, p. 537.
2. Szwarc, M. *Carbanions, Living Polymers and Electron Transfer Processes*; Interscience: New York, 1968.
3. Morton, M. *Anionic Polymerization: Principles and Practice*; Academic: New York, 1983; p. 134.
4. Young, R. N.; Quirk, R. P.; Fetters, L. J. *Adv Polym Sci* 1984, 56, 1.
5. Wofford, C. F.; Hsieh, H. L. *J Polym Sci Part A* 1969, 7, 461.
6. Kobayashi, E.; Kaita, S.; Aoshima, S.; Furukawa, J. *J Polym Sci Part A Polym Chem* 1994, 32, 1195.
7. Kobayashi, E.; Kaita, S.; Aoshima, S.; Furukawa, J. *J Polym Sci Part A Polym Chem* 1995, 33, 2175.
8. Kobayashi, E.; Hayashi, N.; Aoshima, S.; Furukawa, J. *J Polym Sci Part A Polym Chem* 1998, 36, 241.
9. Kobayashi, E.; Hayashi, N.; Aoshima, S.; Furukawa, J. *J Polym Sci Part A Polym Chem* 1998, 36, 1707.
10. Jin, Y. T.; Wang, P. X.; Pei, F. K.; Cheng, G. L.; Cui, L. Q.; Song, C. L. *Polymer* 1996, 37, 349.
11. Oehme, A.; Gebauer, U.; Gehrke, K. *Macromol Rapid Commun* 1995, 16, 563.
12. Zambelli, A.; Ammendola, P.; Proto, A. *Macromolecules* 1989, 22, 2126.
13. Zambelli, A.; Proto, A.; Longo, P.; Oliva, L. *Macromol Chem* 1994, 195, 2623.
14. Endo, K.; Matsuda, Y. *J Polym Sci Part A Polym Chem* 1999, 37, 3838.
15. Endo, K.; Matsuda, Y. *Macromol Chem Phys* 2000, 201, 1426.
16. Endo, K.; Matsuda, Y. *Polym Int* 2001, 50, 59.
17. Hadjiandreou, P.; Julemont, M.; Teyssie, P. *Macromolecules* 1984, 19, 2455.
18. Duch, M. W.; Grant, D. M. *Macromolecules* 1976, 3, 165.
19. Tanaka, Y.; Takeuchi, Y.; Kobayashi, M. *J Polym Sci Part A-2* 1971, 9, 43.
20. Oliva, L.; Longo, P.; Grassi, A.; Ammendola, P.; Pellechia, C. *Makromol Chem Rapid Commun* 1990, 11, 519.
21. (a) Ricci, G.; Italia, S.; Comitani, C.; Porri, L. *Polym Commun* 1991, 32, 514; (b) Endo, K.; Yamanaka, Y. *Macromol Chem Phys* 2001, 202, 201.
22. Ishihara, N.; Kuramoto, M.; Uoi, M. *Macromolecules* 1988, 21, 3356.
23. Coevoet, D.; Cramail, H.; Deffieux, A. *Macromol Chem Phys* 1996, 197, 855.
24. Fink, G.; Herfert, N.; Montag, P. In *Ziegler Catalysts*; Fink, G., Mulhaupt, R., Brintzinger, H., Eds.; Springer: Berlin, 1995; p. 159.
25. Cass, P.; Pratt, K.; Mann, T.; Laslett, B.; Rizzardo, E.; Burford, R. *J Polym Sci Part A Polym Chem* 1999, 37, 3277.