

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### Synthesis and Characterization of Triblock Copolymer of Poly(tetramethylene Oxide) and Poly(methyl Methacrylate)

Toshimitsu Suzuki<sup>a</sup>; Yoshimasa Murakami<sup>a</sup>; Osamu Yamada<sup>a</sup>; Yoshinobu Takegami<sup>a</sup>

<sup>a</sup> Department of Hydrocarbon Chemistry Faculty of Engineering, Kyoto University, Kyoto, Japan

**To cite this Article** Suzuki, Toshimitsu , Murakami, Yoshimasa , Yamada, Osamu and Takegami, Yoshinobu(1982) 'Synthesis and Characterization of Triblock Copolymer of Poly(tetramethylene Oxide) and Poly(methyl Methacrylate)', Journal of Macromolecular Science, Part A, 18: 5, 817 – 829

**To link to this Article:** DOI: 10.1080/00222338208074436

**URL:** <http://dx.doi.org/10.1080/00222338208074436>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## Synthesis and Characterization of Triblock Copolymer of Poly(tetramethylene Oxide) and Poly(methyl Methacrylate)

TOSHIMITSU SUZUKI, YOSHIMASA MURAKAMI, OSAMU YAMADA,  
and YOSHINOBU TAKEGAMI

Department of Hydrocarbon Chemistry  
Faculty of Engineering  
Kyoto University  
Kyoto 606, Japan

### ABSTRACT

Anionic polymerization of methyl methacrylate (MMA) was initiated with the disodium salt of dihydroxy-poly(tetramethylene oxide) (PTMO) in tetrahydrofuran in the presence and the absence of a crown ether. The resulting block copolymer of poly(methyl methacrylate) (PMMA) and PTMO was characterized by  $^1\text{H}$  NMR spectroscopy, gel permeation chromatography, and solvent extractions. In the absence of the crown ether, a linear triblock copolymer of PMMA-PTMO-PMMA was predominantly obtained, showing a unimodal and relatively narrow molecular weight distribution. In the presence of the crown ether, a linear triblock copolymer and a PTMO grafted block copolymer due to the transesterification reaction between PTMO and a methoxy group in MMA were produced with an increase in polymer yield. The stereosequence distributions of the PMMA part in the copolymers were essentially atactic and the addition of the crown ether increased the fraction of the rr triad.

A-B-A type triblock copolymers have recently received much attention because they contain physically and chemically incompatible segments in one macromolecular chain. A large number of block copolymers have been synthesized by various techniques [1]. Due to the low melting and glass transition temperatures of poly(tetramethylene oxide) (PTMO), it is suitable for the center block. Several attempts have been made to synthesize block copolymers of PTMO and a few monomers [2-10]. Tobolsky and his co-workers prepared a peroxide-terminated PTMO and tried to initiate the radical polymerization of methyl methacrylate (MMA) [5]. However, appreciable amounts of MMA homopolymer and unreacted PTMO existed in the product in addition to the block copolymer of PTMO and poly(methyl methacrylate) (PMMA). They could not isolate the pure block copolymer and could not characterize the resulting copolymer.

In previous papers we have studied syntheses of the A-B-A type triblock copolymers of poly(ethylene oxide) (PEO) and PMMA [11, 12] and of PEO and polymethacrylonitrile [13] by using the disodium salt of PEO as an initiator. As an extension of this technique, we have investigated the capability of initiating the polymerization of MMA with the disodium salt of PTMO, which is considered to be inferior to PEO in cation-binding ability.

The present paper describes the synthesis and characterization of a triblock copolymer of PTMO and PMMA. The effect of the addition of a crown ether on the polymerization is discussed.

## EXPERIMENTAL SECTION

### Materials

Tetrahydrofuran (THF) and benzene were distilled twice over  $\text{LiAlH}_4$  under a nitrogen atmosphere and were stored over Molecular Sieve 4A. Commercial MMA was purified by the usual method and was distilled over calcium hydride at reduced pressure and stored over Molecular Sieve 4A. Sodium naphthalene and lithium naphthalene were prepared in THF by the usual methods. Dicyclohexyl-18-crown-6 (Nakarai Chemical) and 15-crown-5 (Nakarai Chemical) were freeze-dried from benzene solutions and stored as benzene solutions. Dihydroxy-PTMO was a commercial PTG-100 (Nihon Polyurethane,  $M_n = 1070$  and  $M_w/M_n = 2.22$ ) and was freeze-dried from a benzene solution before use.

### Polymerization Procedure

The polymerization was carried out in a three-necked flask under an argon atmosphere. A certain amount of PTMO was introduced into

the flask and freeze-dried from the benzene solution for 5 h under vacuum. THF was distilled directly into the flask under vacuum. After the system was flushed with argon and cooled to 0°C, the THF solution of sodium naphthalene or lithium naphthalene was added (double the molar quantity of PTMO). A calculated amount of benzene solution of a crown ether (double the molar quantity of PTMO) was added to this solution at 30°C. A certain amount of MMA was introduced at 30°C after an hour. Polymerization was stopped after 17 h by adding 2 mL of 2-propanol containing a small amount of hydrochloric acid. The reaction mixture was concentrated to one-third of its volume and poured into a large amount of petroleum ether. The polymer was filtered off, washed with petroleum ether, and dried in vacuo at an ambient temperature. In some cases the polymers were fractionated using chloroform solutions of polymer (1.0 g in 15 mL) with methanol (100 mL).

### Characterization of the Copolymers

Gel permeation chromatograms (GPC) were recorded on a Waters ALC/GPC 244, equipped with four  $\mu$ -styragel columns ( $10^5 + 10^4 + 10^3 + 500$  Å) with THF as the eluent (1.5 mL/min, 25°C). The weight-average molecular weights ( $M_w$ ) and the number-average molecular weights ( $M_n$ ) of the polymers were estimated from their GPC traces.  $^1\text{H}$  NMR spectra were recorded at 100 MHz on a JEOL-FX100 using  $\text{CDCl}_3$  solutions of the polymers at ambient temperature. Triad stereosequence distributions of the PMMA part in the copolymers were determined from the  $\alpha$ -methyl proton resonances.

## RESULTS AND DISCUSSION

### Initiation with Disodium Salt of PTMO

The results are summarized in Table 1. The  $M_n$ -expected was simply calculated from the mole ratio of monomer to initiator ( $M/I$ ). The  $M_n$ -GPC was estimated from the GPC trace of the copolymer. Since standard polystyrenes were used for calibration in the GPC analyses, the true molecular weights of the copolymers may be somewhat different than those reported herein, due to differences in the hydrodynamic volumes of polystyrenes and the copolymers. The average numbers of MMA monomer units per PTMO segment (MMA/PTMO-NMR) in the copolymers were obtained from their  $^1\text{H}$  NMR spectra by comparing the relative intensities of the  $\alpha$ -methyl proton and PTMO methylene proton resonances.  $M_n$ -NMR was simply

TABLE 1. Polymerization of MMA with the Disodium Salt of PTMO<sup>a</sup>

No.	M/I <sup>b</sup>	Additive <sup>c</sup>	Yield <sup>d</sup> (wt%)	M <sub>n</sub> × 10 <sup>-3</sup>			MMA/PTMO <sup>h</sup>		
				Expected <sup>e</sup>	GPC <sup>f</sup>	NMR <sup>g</sup>	M <sub>w</sub> /M <sub>n</sub> <sup>f</sup>	NMR <sup>g</sup>	Calculated <sup>i</sup>
1	180	-	65.5	19.1	10.8	12.3	2.30	112.0	114.2
2	96	-	60.2	10.7	5.3	6.4	2.52	53.6	53.6
3	96	Crown	91.5	10.7	12.5	9.7	5.85	86.6	86.9
4	128	Crown	72.7	13.9	13.7	10.0	3.37	88.9	90.0
5	180	Crown	81.4	19.1	17.0	15.4	4.81	143.3	149.2

<sup>a</sup>PTMO 0.107 g and solvent (THF) 20 mL at 30°C for 17 h.

<sup>b</sup>Feed mole ratio of monomer (MMA) to initiator (PTMO-Na<sub>2</sub>).

<sup>c</sup>Dicyclohexyl-18-crown-6 (crown) was added (double the molar quantity of PTMO).

<sup>d</sup>Against (PTMO + MMA) charged.

<sup>e</sup>Calculated from the value of M/I.

<sup>f</sup>Estimated from GPC traces.

<sup>g</sup>Obtained by <sup>1</sup>H NMR spectra.

<sup>h</sup>The molar ratio of MMA monomer units to one PTMO molecule in a copolymer.

<sup>i</sup>Calculated from the yield of the copolymer and the amount of PTMO used on the assumption that all of the initiator was reacted and was incorporated into the copolymer.

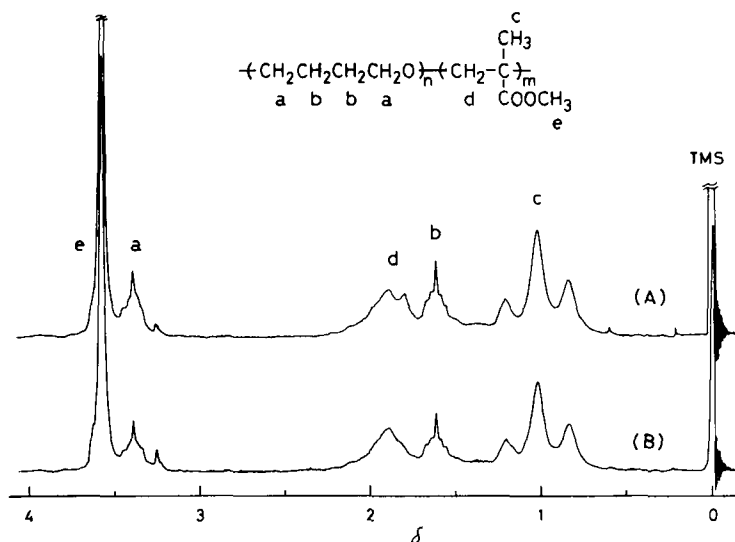


FIG. 1. 100 MHz  $^1\text{H}$  NMR spectra of PTMO-*b*-PMMA (No. 2 in Table 1) prepared in the absence of the crown ether: chloroform-methanol insoluble (A) and soluble (B) fractions.

calculated from the value of MMA/PTMO-NMR on the assumption that only one PTMO molecule was incorporated into one copolymer molecule. The average number of MMA monomer units per PTMO segment in the copolymers (MMA/PTMO-calculated) was also calculated from the yield of the copolymer and the amount of PTMO used, on the assumption that all of the initiator was reacted and was incorporated into the copolymer.

The polymerization of MMA initiated by the dilithium salt of PTMO in the presence of 15-crown-5 or dicyclohexyl-18-crown-6 did not proceed at all as well as did initiation with the dilithium salt of PEO as was previously reported [12].

In general, alkali metal salts of primary alcohols, except lithium *t*-butoxide, cannot initiate the anionic polymerization of MMA unless a complexing agent like hexamethylphosphoramide is added [14-16]. Since PEO has a complexation capability toward alkali metal cations [17-19], the disodium salt of PEO initiated the anionic polymerization of MMA in the absence of the crown ether [12]. It has not been reported that PTMO has a cation-binding ability like PEO. As can be seen from Table 1, the polymerization of MMA initiated by the disodium salt of PTMO proceeded even in the absence of the crown ether (Nos. 1 and 2) as well as in the presence of the crown ether (Nos. 3-5). This can be interpreted as follows: (1) PTMO effectively

captures the sodium cations to enhance the nucleophilicity of alkoxy anions of PTMO; (2) an alkoxy anion of PTMO is "soft" in comparison with lower molecular-weight alkoxy anions such as sodium methoxide, which is advantageous for addition to the carbon-carbon double bond in MMA. The latter possibility seems to be more reasonable.

In Fig. 1 are shown the  $^1\text{H}$  NMR spectra of the chloroform-methanol-soluble and -insoluble fractions of copolymer No. 2, which was prepared in the absence of the crown ether. In both spectra the resonances of methylene protons adjacent to oxygen atom (a, 3.46) and of internal methylene protons (b, 1.66) in PTMO are observed in addition to those of PMMA. The spectra of copolymers prepared in the presence of the crown ether were essentially identical to the spectra shown in Fig. 1. Since PTMO is soluble and PMMA is insoluble in methanol, the appearance of the absorptions ascribed to PTMO and PMMA in the spectrum of the methanol-insoluble fraction indicates that a block copolymer of PTMO and PMMA was formed. [The PTMO used in this study (PTG-100) was soluble in methanol; higher molecular weight PTMO was insoluble.]

### Incorporation of PTMO into the Copolymer

Figure 2 shows the molecular weight distributions (MWDs) of the PTMO homopolymer and of the copolymers prepared at various M/I ratios. Since the GPC curves of the copolymers did not indicate the presence of any components having a molecular weight of 1000, it seems reasonable to conclude that no unreacted PTMO was present in these materials. As seen in Table 1, all the values of MMA/PTMO-calculated are in good agreement with those of MMA/PTMO-NMR. It can be concluded from these results that all the PTMO used as the initiator was reacted and was completely incorporated into the copolymer.

### The Copolymer Prepared in the Absence of the Crown Ether

The values of  $M_n$ -GPC and  $M_n$ -NMR of the copolymers prepared in the absence of the crown ether (Nos. 1 and 2) are in fair agreement. As shown in Fig. 2, the MWDs of the two copolymers are relatively narrow and unimodal, and shift according to the M/I ratios. In this case, therefore, the polymerizations probably proceeded uniformly, without any side reactions, to give linear triblock copolymers of PTMO and PMMA.

The fractionation of the copolymer No. 2 was carried out with a chloroform-methanol system. The results are summarized in Table 2 and the MWDs of the original copolymer and of the methanol-soluble and -insoluble fractions are shown in Fig. 3. 75% of the

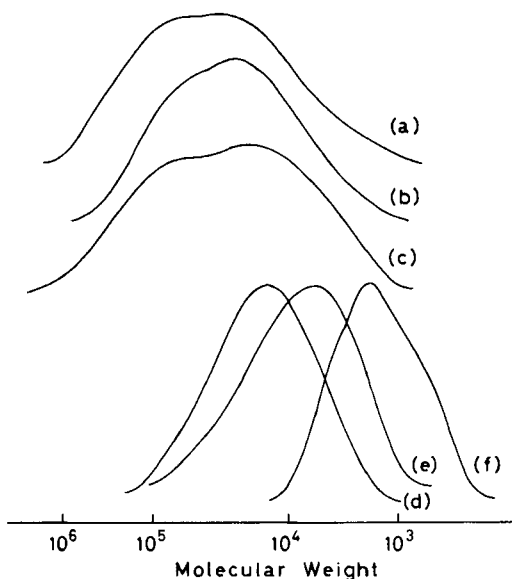


FIG. 2. Gel permeation chromatograms of PTMO homopolymer and of PTMO-*b*-PMMA prepared at various M/I ratios in the presence or absence of the crown ether: (a) No. 5 (M/I = 180, crown ether), (b) No. 4 (M/I = 128, crown ether), (c) No. 3 (M/I = 96, crown ether), (d) No. 1 (M/I = 180, no additive), (e) No. 2 (M/I = 96, no additive), (f) PTMO homopolymer.

copolymer was soluble in methanol and 25% was insoluble. The values of  $M_n$ -GPC and  $M_n$ -NMR of the methanol-soluble fraction were in good agreement. In the  $^1\text{H}$  NMR spectrum of the methanol-soluble fraction of this copolymer, the relative intensity of  $\alpha$ -methyl to methoxy proton resonances of the PMMA part was unity. In addition, the MWD of this fraction is narrow and unimodal as shown in Fig. 3. Consequently, the methanol-soluble fraction of this copolymer is considered to be essentially a linear triblock copolymer of PTMO and PMMA.

In the methanol-insoluble fraction of copolymer No. 2, the value of  $M_n$ -NMR (7,300) appeared considerably smaller than that of  $M_n$ -GPC (14,800) and the relative intensity of methoxy proton resonance was slightly smaller than that of the  $\alpha$ -methyl proton resonance ( $\text{CH}_3:\text{CH}_3\text{O} = 3.00:2.90$ ). These results strongly suggest that a transesterification reaction occurred between the disodium salt of PTMO and either ester groups present in the PMMA part of the copolymer or the ester groups present on MMA monomer. Such reactions would



TABLE 2. Fractionation of the Copolymers Nos. 2 and 3<sup>a</sup>

No.	Fraction	Wt%	$M_n \times 10^{-3}$		$M_w/M_n$ <sup>b</sup>	MMA/PTMO-NMR <sup>d</sup>
			GPC <sup>b</sup>	NMR <sup>c</sup>		
2	Original	-	5.3	6.4	2.52	53.6
	Insoluble	25	14.8	7.3	1.87	61.9
	Soluble	75	4.2	6.1	1.67	50.6
3	Original	-	12.5	9.7	5.85	86.6
	Insoluble	72	27.3	9.5	3.73	84.2
	Soluble	28	4.5	9.8	1.76	87.7

<sup>a</sup>Nos. 2 and 3 were prepared in the absence and the presence of the crown ether, respectively ( $M/I = 96$ ). The copolymers were fractionated with the chloroform-methanol system.

<sup>b</sup>Estimated from GPC traces.

<sup>c</sup>Obtained by <sup>1</sup>H NMR spectra.

<sup>d</sup>MMA monomer units/PTMO obtained by <sup>1</sup>H NMR spectra.

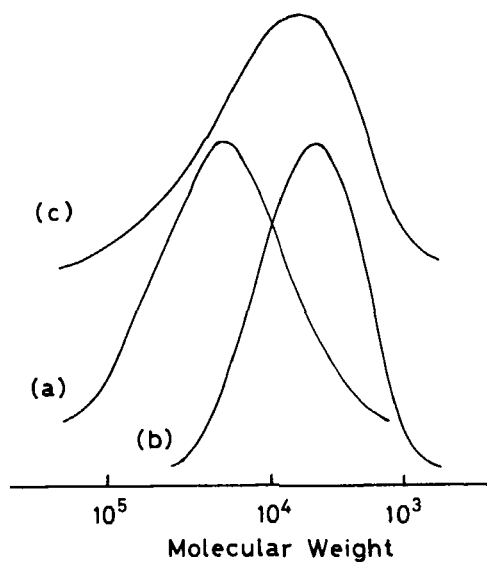


FIG. 3. Gel permeation chromatograms of PTMO-*b*-PMMA (No. 2) prepared in the absence of the crown ether: chloroform-methanol insoluble (a) and soluble (b) fractions and unfractionated copolymer (c);  $M/I = 96$ .

result in the formation of PTMO grafted block copolymers, just as was reported previously for polymerizations of MMA initiated by the disodium salt of PEO [12]. Since the MWD of this fraction is relatively narrow and unimodal, the extent of the transesterification reaction must be small. Considering the small portion of this fraction (25%), the contribution of the transesterification reaction to the whole copolymer should not be significant.

In conclusion, polymerization in the absence of the crown ether proceeds uniformly to give mainly a linear triblock copolymer of PMMA-PTMO-PMMA and to give a small amount of PTMO grafted block copolymer which is insoluble in methanol.

### The Copolymer Prepared in the Presence of the Crown Ether

The values of  $M_n$ -NMR of the copolymers prepared in the presence of the crown ether are smaller than those of  $M_n$ -GPC (Nos. 3-5).

The MWDs of these copolymers are fairly broad and bimodal, and are quite similar regardless of the M/I ratios, as shown in Fig. 2. These results suggest the occurrence of the transesterification reaction.

The fractionation of copolymer No. 3 was also carried out with the chloroform-methanol system. The results are summarized in Table 2, and the MWDs of the original copolymer, methanol-soluble, and methanol-insoluble fractions are presented in Fig. 4. In contrast to

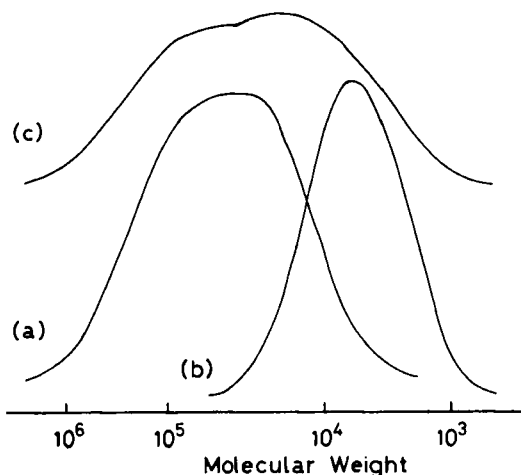


FIG. 4. Gel permeation chromatograms of PTMO-*b*-PMMA (No. 3) prepared in the presence of the crown ether: chloroform-methanol insoluble (a) and soluble (b) fractions and (c) unfractionated copolymer; M/I = 96.

the results obtained with copolymer No. 2, 28% of the copolymer was soluble in methanol and 72% was insoluble.

The values of  $M_n$ -GPC and  $M_n$ -NMR of the methanol-soluble fraction are not so different from each other compared to those of the insoluble fraction. The relative intensity of  $\alpha$ -methyl to methoxy proton resonances was exactly unity in the  $^1\text{H}$  NMR spectrum of the methanol-soluble fraction of copolymer No. 3. As the MWD of this fraction is narrow and unimodal, a linear triblock copolymer is contained in the methanol-soluble fraction, as in the case of copolymer No. 2.

In the methanol-insoluble fraction of copolymer No. 3, the value of  $M_n$ -NMR (9,500) is considerably smaller than that of  $M_n$ -GPC (27,300) and the relative intensity of methoxy proton resonance was smaller than that of  $\alpha$ -methyl proton resonance ( $\text{CH}_3:\text{CH}_3\text{O} = 3.00:2.84$ ). The MWD of this fraction is broad. Therefore, this fraction seems to be a PTMO grafted block copolymer that has been modified considerably by the transesterification reaction. Thus polymerization in the presence of the crown ether gives predominantly the PTMO grafted block copolymer of PTMO and PMMA as well as a small amount of linear triblock copolymer.

The addition of the crown ether resulted in an increase in the copolymer yield and showed a marked tendency to give fairly high molecular weight copolymers regardless of the M/I ratios. The high molecular weight copolymers thus obtained contained the PTMO grafted block copolymer due to the transesterification reaction. Taking into account the result regarding the stereosequence distributions of the PMMA part in the copolymers described below, the crown ether accelerates not only the transesterification reaction but the propagation reaction as well.

### Stereosequence Distributions of PMMA Part in the Copolymers

The observed and calculated triad stereosequence distributions of the PMMA part in the copolymers are summarized in Table 3. The stereosequence distributions of the PMMA part are essentially atactic. In general, an anionic polymerization of MMA in a polar solvent is considered to proceed in a solvent-separated ionic manner to give a syndiotactic PMMA ( $rr \approx 0.60$ ) [20]. It is also well-known that fluorenyl sodium exists as an equilibrium mixture of contact and solvent-separated ion pairs in THF at room temperature [21].

In the copolymers prepared in the absence of the crown ether, the fractions of  $rr$  triads (0.30-0.37) are considerably smaller than 0.60. This is attributed to association of sodium counterions with carbonyl groups present at living chain ends. The triad stereosequence distributions of samples No. 1 and No. 2 deviate slightly from those calculated from Bernoullian statistics. In the absence of

TABLE 3. Stereosequence Distributions of the PMMA Part in the Copolymers

No.	Additive	Observed <sup>b</sup>						Calculated <sup>c</sup>			
		m	r	mm	mr + rm	rr	mm	mr + rm	rr		
1	-	0.385	0.615	0.143	0.484	0.373	0.148	0.474	0.378		
2	-	0.442	0.558	0.186	0.513	0.301	0.195	0.494	0.311		
3	Crown	0.322	0.678	0.105	0.435	0.460	0.104	0.436	0.460		
4	Crown	0.327	0.673	0.108	0.438	0.454	0.107	0.440	0.453		
5	Crown	0.335	0.665	0.114	0.441	0.445	0.112	0.446	0.442		

<sup>a</sup>Dicyclohexyl-18-crown-6 (crown) was used.

<sup>b</sup>Observed values from <sup>1</sup>H NMR spectra.

<sup>c</sup>Calculated values based on Bernoullian statistics.

the crown ether, therefore, not only a solvent-separated ion pair but a contact ion pair should be considered to exist in the polymerization system.

In the presence of the crown ether, the fractions of rr triads increase significantly and the triad stereosequence distributions are in good agreement with those calculated from Bernoullian statistics. It is obvious, therefore, that a sodium cation is captured by the crown ether to form a propagating chain end that is predominantly an agent (crown ether) separated ion pair.

#### REFERENCES

- [1] A. Noshay and J. E. McGrath, Block Copolymers, Academic, New York, 1977.
- [2] G. Berger, M. Levy, and D. Vofsi, J. Polym. Sci., Polym. Lett. Ed., **4**, 183 (1966).
- [3] J. Furukawa, S. Takamori, and S. Yamashita, Angew. Makromol. Chem., **1**, 92 (1967).
- [4] J. L. Lambert and E. J. Goethals, Makromol. Chem., **133**, 289 (1970).
- [5] N. Z. Erdy, C. F. Ferraro, and A. V. Tobolsky, J. Polym. Sci., A-1, **8**, 763 (1970).
- [6] Y. Yamashita, M. Hirota, K. Nobutoki, Y. Nakamura, A. Hirao, S. Kozawa, K. Chiba, H. Matsui, and G. Hattori, J. Polym. Sci., Polym. Lett. Ed., **8**, 481 (1970).
- [7] J. M. Hammond, J. F. Hooper, and W. G. P. Robertson, J. Polym. Sci., A-1, **9**, 265 (1971).
- [8] Y. Yamashita, M. Hirota, H. Matsui, A. Hirao, and K. Nobutoki, Polym. J., **2**, 43 (1971).
- [9] D. H. Richards, S. B. Kingston, and T. Souel, Polymer, **19**, 68 (1978).
- [10] D. H. Richards, S. B. Kingston, and T. Souel, Ibid., **19**, 806 (1978).
- [11] T. Suzuki, Y. Murakami, Y. Tsuji, and Y. Takegami, J. Polym. Sci., Polym. Lett. Ed., **14**, 675 (1976).
- [12] T. Suzuki, Y. Murakami, and Y. Takegami, Polym. J., **12**, 183 (1980).
- [13] T. Suzuki, Y. Murakami, and Y. Takegami, Ibid., **14**, 431 (1982).
- [14] N. S. Wooding and W. C. E. Higginson, J. Chem. Soc., p. 774 (1952).
- [15] J. Trekoval, J. Polym. Sci., A-1, **9**, 2575 (1971).
- [16] M. Tomoi, K. Sekiya, and H. Kakiuchi, Polym. J., **6**, 438 (1974).
- [17] I. M. Panayotov, C. B. Tsvetanov, and D. K. Dimov, Makromol. Chem., **177**, 279 (1976).
- [18] T. Sotobayashi, T. Suzuki, and K. Yamada, Chem. Lett., p. 77 (1976).

- [ 19] S. Yanagida, K. Takahashi, and M. Okahara, Bull. Chem. Soc. Jpn., 50, 1386 (1977).
- [ 20] H. Yuki, K. Hatada, K. Ohta, and Y. Okamoto, J. Macromol. Sci.-Chem. A9, 983 (1975).
- [ 21] T. E. Hogen-Esch and J. Smid., J. Am. Chem. Soc., 88, 307 (1966).

Accepted by editor November 23, 1981

Received for publication December 7, 1981