Polymer Bulletin 27, 615–622 (1992)

Polymer Bulletin

Preparation of stereoregular block copolymer comprising isotactic PMMA and polyisobutylene blocks and its characterization

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Summary

A triblock copolymer of isotactic(it)-poly(methyl methacrylate) (PMMA) and polyisobutylene (PIB), it-PMMA-block-PIB-block-it-PMMA, was prepared by anionic polymerization of triphenylmethyl methacrylate initiated with α, ω-dilithiated PIB diisobutyrate in tetrahydrofuran at -78°C, and subsequent hydrolysis and methylation with diazomethane. Molecular weight distribution of the triblock copolymer was narrow, and the stereoregularity of the PMMA block was highly isotactic. Proton spin-lattice relaxation times of the block copolymer in acetone-d_6, which is non-solvent for PIB but dissolves the block copolymer, indicate the aggregation of the copolymer through PIB block. Stereocomplex formation between the it-block copolymer and syndiotactic(st)-PMMA-block-PIB-block-st-PMMA was also studied.

Introduction

In the previous publication[1] we have shown that triblock copolymer comprising polyisobutylene (PIB) and PMMA blocks, PMMA-block-PIB-block-PMMA, can be readily prepared by the polymerization of MMA in tetrahydrofuran (THF) initiated with bifunctional polymeric initiator, α, ω-dilithiated PIB diisobutylate (DLPIB). Recently Kennedy and Price also reported the preparation of PMMA-block-PIB-block-PMMA; α, ω-ditolyl PIB was lithiated with s-BuLi in the presence of N,N,N',N'-tetramethylethylenediamine, reacted with 1,1-diphenylethylene and used as a polymeric initiator in the polymerization of MMA in THF[2]. Stereoregularity of PMMA blocks of these triblock copolymers was predominantly syndiotactic.

Stereoregularity is one of the most important molecular characteristics of polymers and often affects polymer properties. Control of stereoregularity of block copolymer may provide additional means to alter the properties of block copolymer together with control of copolymer composition and block length.

Stereoregular polymerization of methacrylates has been well surveyed in regard of polymerization conditions and structure of ester group[3,4]. Triphenylmethyl methacrylate (TrMA) is a unique monomer which gives isotactic polymers irrespective of polarity of polymerization media[5,6]. Hogen-Esch and his coworker prepared block copolymer of TrMA and diphenylmethyl methacrylate in THF and converted it to stereoblock PMMA.[7] Taking an advantage that the block copolymerization by the PIB dianion DLPIB gives triblock copolymer in one step process, we examined polymerization of TrMA with DLPIB in THF in the present work. The block copolymer could be readily converted to the block copolymer comprising isotactic (it-) PMMA and PIB blocks. Some of the properties of the isotactic block

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*To whom offprint requests should be sent copolymer and stereocomplex formation with the syndiotactic (st-)triblock copolymer[1] were also studied.

Experimental

Materials

TrMA was synthesized in diethyl ether from methacrylic acid and triphenylmethyl chloride in the presence of triethylamine[8]. The crude product was purified by recrystallization from diethyl ether. Polyisobutylene diisobutylate (PIBDIB) (Mn=4270, end functionality=0.92) was synthesized from polyisobutylene with hydroxyl groups on both ends and purified as reported previously[1]. THF was purified as reported previously[1].

Preparation of it-PMMA-block-PIB-block-it-PMMA

TrMA was placed in a glass ampoule, and the ampoule was then evacuated on a vacuum line and flushed with dry nitrogen. After this procedure was repeated three times, a three-way stopcock was attached to the ampoule and THF was added with a syringe to dissolve TrMA. The benzene solution containing 313mg of PIBDIB was prepared as reported previously (conc. 22.5wt%)[1] and mixed with 20ml of THF in a glass ampoule with a side arm(Figure 1). The PIBDIB was lithiated with an equimolar amount of lithium diisopropylamide (LDA) at 0°C for 2hr (eq 1). The capillary tube attached to the side arm was cut and opened under dry nitrogen stream, and the THF solution of TrMA (3.93mmol/2ml) was introduced to the side arm with a syringe. Then the capillary was sealed off again.

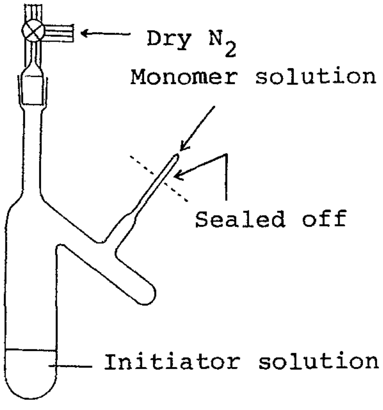
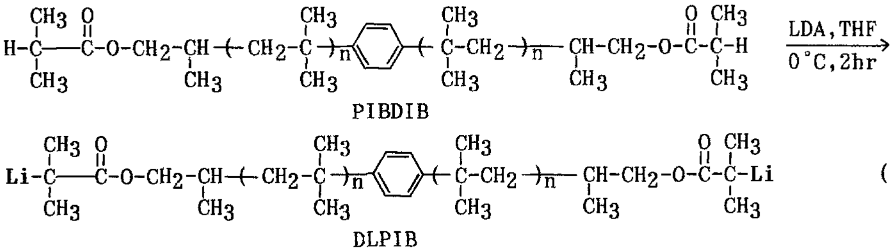


Figure 1 Reaction vessel for the block copolymerization



$$\underset{\text{PIBDIB}}{\mathrm{H{-}C(CH_3)_2{-}C(=O){-}O{-}CH_2{-}CH(CH_3){-}\!\left(CH_2{-}C(CH_3)_2\right)_n\!{-}C_6H_4{-}\!\left(C(CH_3)_2{-}CH_2\right)_n\!{-}CH(CH_3){-}CH_2{-}O{-}C(=O){-}C(CH_3)_2{-}H}} \xrightarrow[0^\circ C,\,2hr]{LDA,\,THF}$$

$$\underset{\text{DLPIB}}{\mathrm{Li{-}C(CH_3)_2{-}C(=O){-}O{-}CH_2{-}CH(CH_3){-}\!\left(CH_2{-}C(CH_3)_2\right)_n\!{-}C_6H_4{-}\!\left(C(CH_3)_2{-}CH_2\right)_n\!{-}CH(CH_3){-}CH_2{-}O{-}C(=O){-}C(CH_3)_2{-}Li}} \qquad (1)$$

The resulting dianion solution and the THF solution of TrMA were cooled to -78°C, and the latter solution was added to the former solution from the side arm at once with vigorous stirring. After 2 hr, the reaction mixture was quenched by adding a small amount of methanol and poured into a large amount of methanol. The precipitated polymer was recovered by centrifugation as soon as possible, and dried under vacuum at 40°C. The conversion of TrMA was determined from the weight increment of the product. A small amount of unreacted PIBDIB in the mixture was removed by washing with hexane, repeatedly. PIB without isobutyrate unit (8%) contained in the starting PIBDIB was also removed during this procedure.

The resulting triblock copolymer, poly(TrMA)-block-PIB-block-poly(TrMA), was hydrolyzed by refluxing in methanol containing a small amount of HCl. The resulting poly(methacrylic acid)-block-PIB-block-poly(methacrylic acid) was washed with diethyl ether to remove triphenylmethanol, and methylated with diazomethane in benzene. The derived triblock copolymer was recovered by freeze-drying from benzene solution.

Polymerization of MMA with DLPIB was also examined in toluene at -78°C to obtain it-block copolymer directly, according to the procedure for the polymerization in THF reported previously[1].

Measurement

^{1}H NMR spectra of the block copolymer were recorded on a JNM GSX-270 NMR spectrometer (JEOL) at 270MHz or on a JNM GX-500 NMR spectrometer at 500MHz. Proton spin-lattice relaxation time (^{1}H-T_1) was measured at 30°C and 55°C on a JNM FX-100 NMR spectrometer at 100MHz by inversion recovery method.

Gel permeation chromatography (GPC) was performed on a JASCO 880-PU chromatograph equipped with Shodex GPC columns KF-80M (30 cm x 0.80 cm) and KF-802.5 (30 cm x 0.80 cm) with maximum porosities of 2×10^7 and 2×10^4, respectively, using THF as an eluent at 40.0°C. The chromatograms were calibrated against standard polystyrene samples.

Differential scanning calorimetric analysis was performed with a Rigaku DSC 8230 calorimeter at a heating rate of 10°C/min.

Results and Discussion

Preparation of triblock copolymer having it-PMMA block was examined in two ways. The results are shown in Table 1. The first one is polymerization of MMA in toluene. The polymerization gave a block copolymer having it-PMMA blocks, but molecular weight of the block copolymer was much larger than the expected value and its distribution was extremely broad. Initiator efficiency, which was obtained from the expected and observed values of molecular weight was 21%. This may be due to the multiplicity of active species, arising from various states of aggregation of active species in the polymerization in toluene.

It is well known that polymerization of TrMA gives highly isotactic polymer not only in toluene but also in THF[5,6]. Poly(TrMA) can be easily converted to it-PMMA by hydrolysis and subsequent methylation with diazomethane[9]. Hence, polymerization of TrMA with DLPIB, followed by hydrolysis and methylation, should give it-PMMA-block-PIB-block-it-PMMA. The GPC curve of the block copolymer is shown in Figure 2 together with that of the starting PIBDIB. The molecular weight distribution of block copolymer obtained by this method was narrow (Mw/Mn=1.17) and PMMA block was highly isotactic (mm=94%).

Table 1 Preparation of it-PMMA-block-PIB-block-it-PMMA[a]

Monomer	Solvent	Time (hr)	Conversion of Monomer(%)	Mn		Mw[b]/Mn	Tacticity(%)[c]		
				GPC	Calc.		mm	mr	rr
MMA	Toluene	24	97	78000	20000	10.9	86	12	2
TrMA	THF	2	100	15900	10100	1.17	94	5	1

[a] Solvent 20ml, PIBDIB 313mg(containing 0.135mmol of isobutyrate units), LDA 0.135mmol, temperature -78°C.

[b] Determined by GPC.

[c] Determined by ^{1}H NMR.

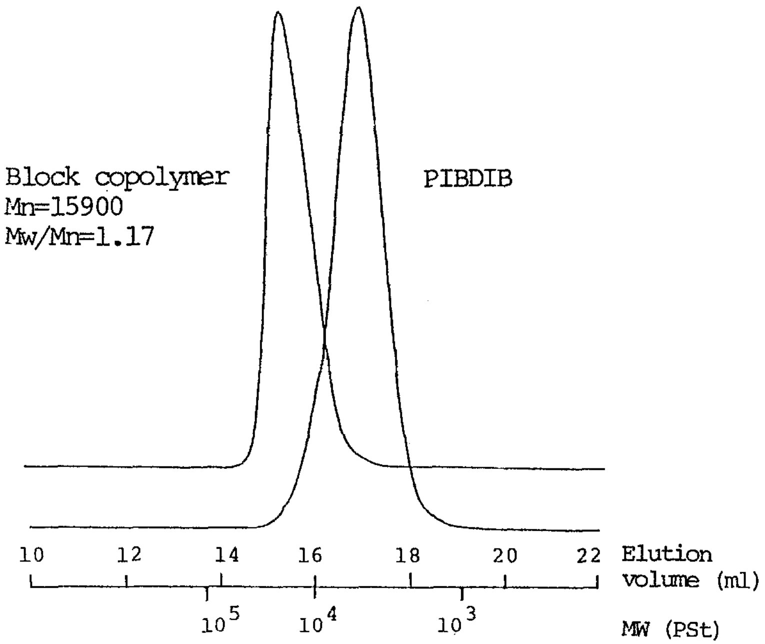


Figure 2 GPC curves of it-PMMA-block-PIB-block-it-PMMA and the starting PIBDIB.

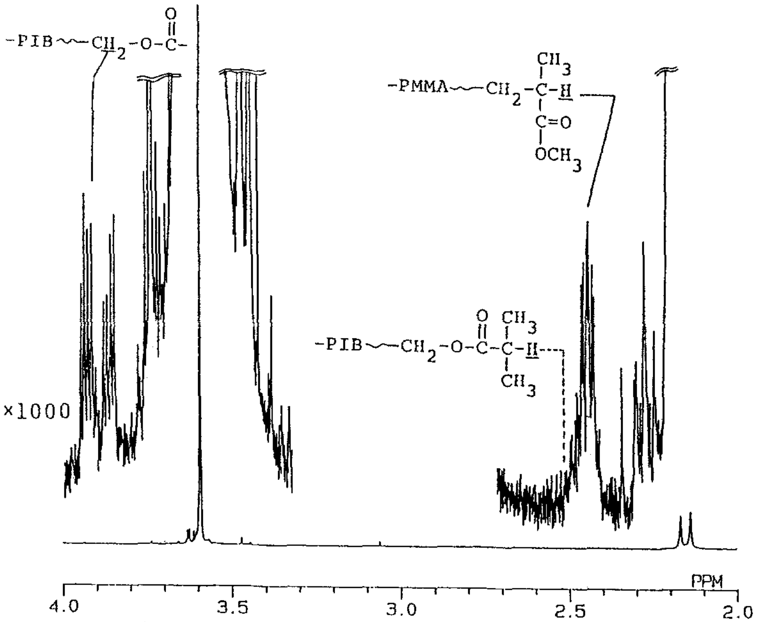


Figure 3 500MHz ^{1}H NMR spectrum of it-PMMA-block-PIB-block-it-PMMA measured in chloroform-d at 55°C.

Contamination of the product by the diblock copolymer, which would form when the dianion is partially destroyed before the polymerization of TrMA proceeds, was ruled out from end group analysis by ^1H NMR spectroscopy. As shown in Figure 3, even a thousand times expanded spectrum of the block copolymer does not show the methine signal due to the isobutyrate unit which would appear at 2.525ppm[1], but the spectrum does show the signal due to the PMMA chain end at 2.450ppm. The result suggests that the block copolymer obtained in THF is truly the triblock copolymer and does not contain diblock one. The Mn of the block copolymer could be estimated from the ^1H NMR spectrum in the following way[1,2]. From the intensity ratio of methylene (PIB) and methoxy (PMMA) proton signals, the ratio of MMA and isobutylene units in the copolymer was found to be 1.58. Assuming the average degree of polymerization (DP) of the PIB block is the same as that of the starting PIBDIB (70.4), the average DP of PMMA blocks was estimated to be 55.6. Mn calculated from these data was 15390 and agreed well with the observed value (*cf.* Table 1).

The 270MHz ^1H NMR spectra of the block copolymers were measured in chloroform-d and in acetone-d_6 at 35°C (Figure 4). Chloroform is a good solvent for both PIB and PMMA. Acetone is a good solvent for PMMA and a non-solvent for PIB but dissolves the block copolymer due to the long sequences of MMA units. From the methylene and α-methyl proton signals of the PMMA blocks it is very clear that the blocks are highly isotactic.

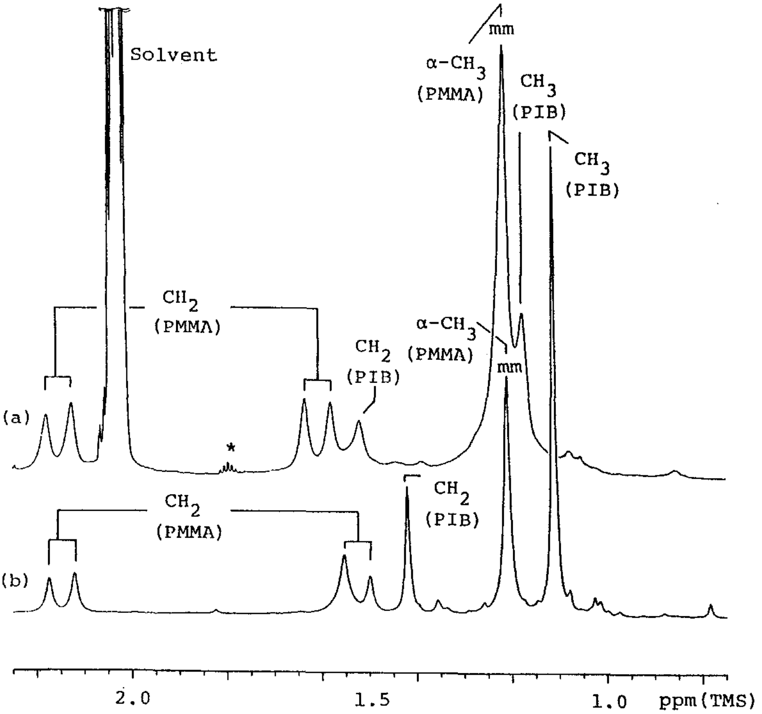


Figure 4 270MHz ^1H NMR spectra of it-PMMA-block-PIB-block-it-PMMA measured in acetone-d_6 (a) and in chloroform-d (b) at 35°C.
* signals due to ^{13}C satellite band of the solvent.

Signals of methyl and methylene protons of the PIB block are much broader in acetone-d_6 than in chloroform-d, indicating lower segmental mobility of the PIB sequence in the acetone solution. The results may be caused by the aggregation of the block copolymer due to the stronger interaction between PIB segments than that between PIB block and acetone[1].

To investigate further the aggregation of the block copolymer, proton spin-lattice relaxation times (^1H-T_1's) for the block copolymer were measured in acetone-d_6 and in chloroform-d at 30°C and 55°C using 1% solutions. The results are shown in Table 2 together with those of triblock copolymer having st-PMMA block[1]. All the ^1H-T_1 values measured at 55°C are larger than those measured at 30°C, indicating that the T_1 value increases as the segmental mobility increases. ^1H-T_1's of methoxy, methylene, and α-methyl protons of PMMA blocks measured in the both solvents were closed to each other. On the other hand, all the ^1H-T_1's of methyl protons of PIB blocks in acetone-d_6 are smaller than that in chloroform-d, suggesting the lower segmental mobility of PIB block in acetone and thus the aggregation of the block copolymer through the interaction between PIB chains in this solvent. At 55°C, the difference between ^1H-T_1's of the methyl protons of PIB blocks measured in chloroform-d and acetone-d_6 are almost the same for the it- and st-block copolymers. However, at 30°C, the difference between the ^1H-T_1 values in these solvents is larger for the st-block copolymer than for the it-block copolymer, suggesting the stronger interaction between PIB blocks in the st-block copolymer than in the it-block copolymer in acetone. Thus, the lower segmental mobility of st-PMMA block than that of it-PMMA block[10,11] facilitates a higher extent of the aggregation of PIB blocks in the st-block copolymer in acetone-d_6.

Table 2 ^1H-T_1's (sec) of PMMA-block-PIB-block-PMMA measured at 100MHz in acetone-d_6 and in chloroform-d at 30 and 55°C[a]

Proton	30°C		55°C	
	Chloroform-d	Acetone-d_6	Chloroform-d	Acetone-d_6
Isotactic				
CH_3 (PIB)	0.17	0.13	0.29	0.22
CH_2 (PMMA)	0.08	0.08	0.11	0.13
α-CH_3 (PMMA)	0.09	0.10	0.14	0.16
OCH_3 (PMMA)	0.36	0.32	0.39	0.42
Syndiotactic				
CH_3 (PIB)	0.20	0.08	0.26	0.22
CH_2 (PMMA)	0.08	0.05	0.07	0.09
α-CH_3 (PMMA)	0.07	0.06	0.08	0.09
OCH_3 (PMMA)	0.33	0.30	0.33	0.36

[a] Conc. 1.0 wt/v%

When the it-triblock copolymer was mixed with st-PMMA-block-PIB-st-PMMA[1] in toluene, gel formation took place due to the stereocomplex formation between PMMA blocks in the it- and st-block copolymers. The DSC thermogram of the stereocomplex recovered therefrom is shown in Figure 5 together with that of it-PMMA-block-PIB-block-it-PMMA. The melting point and heat of fusion (ΔH) of the stereocomplex were 163°C and 6.4cal/g-PMMA. the values for the stereocomplex formed between it-PMMA (Mn=5600, mm/mr/rr = 96/3/1) and st-PMMA (Mn=8800, mm/mr/rr = 2/24/74) of similar

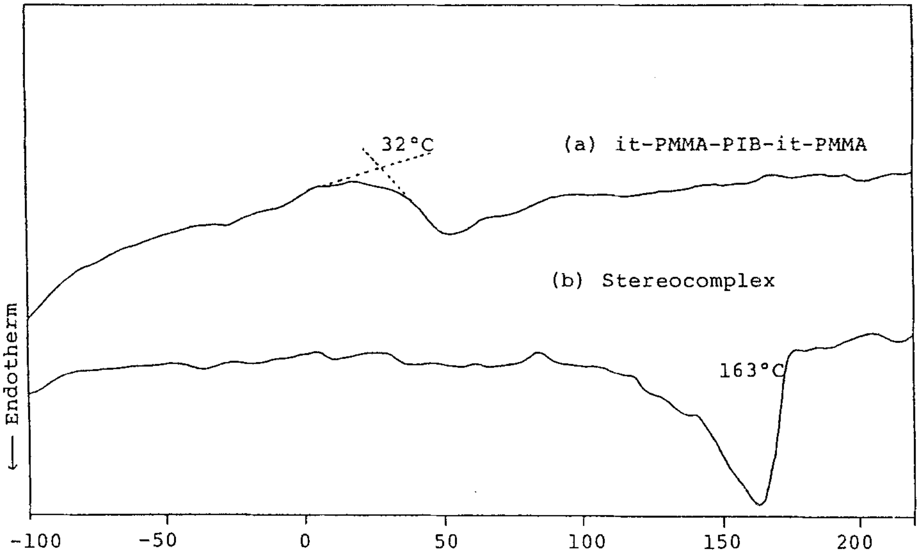


Figure 5 DSC thermograms of it-PMMA-block-PIB-block-it-PMMA (a) and a mixture of it-PMMA-block-PIB-block-it-PMMA and st-PMMA-block-PIB-block-st-PMMA recovered from toluene solution (b).

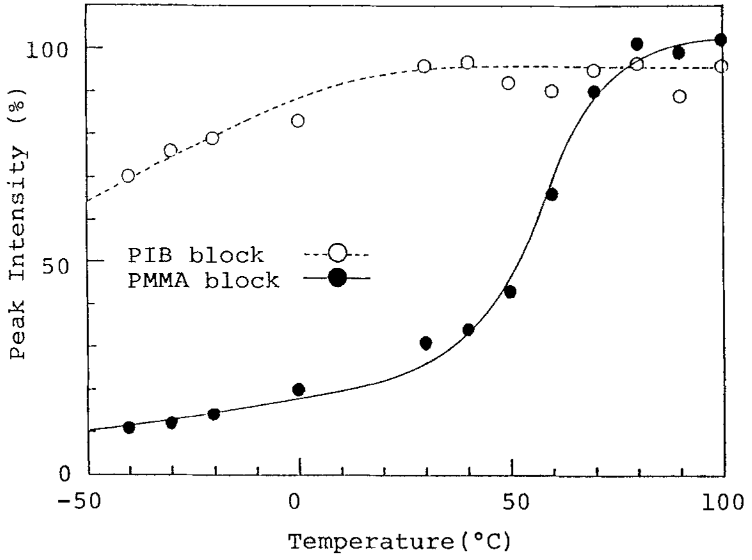


Figure 6 Temperature dependence of peak intensity in NMR spectrum of a mixture of it-PMMA-block-PIB-block-it-PMMA and st-PMMA-block-PIB-block-st-PMMA in toluene-d_8 (5%).

tacticities and molecular weight to those of the PMMA blocks in the block copolymers were 157°C and 6.8cal/g-PMMA. The results suggest that the existence of PIB block scarcely disturbs the stereocomplex formation between it- and st-PMMA blocks.

The stereocomplex formation in toluene was studied by ^{1}H NMR measurement. Figure 6 shows temperature dependence of peak intensities of methoxy protons of PMMA blocks and methyl and methylene protons of PIB blocks in the mixture of it- and st-block copolymers in toluene-d_8. The amounts of MMA units in it- and st-PMMA blocks were set to be the same. Sensitivities of the spectrometer at different temperatures were normalized using a solution of octane in toluene-d_8[12]. Maximum peak intensities expected from the concentration of the polymer solution were regarded as 100% for each signals. The steep change of peak intensity for methoxy protons of PMMA blocks around 50-70°C corresponds the stereocomplex formation. The temperature range of gel formation is close to that of PMMA stereocomplex[14]. The NMR signals due to the PIB blocks overlap with methylene and α-methyl proton signals due to the PMMA blocks, making it difficult to directly determine the peak intensity. On the assumption that the total intensity for the methylene and α-methyl proton signals are 5/3 of that of methoxy signal, the intensity of the signals due to PIB block was estimated, which was almost constant in the temperature range from 100 to 30°C. The result indicates that higher flexibility of PIB block is retained even when the PMMA blocks flanking PIB block on both ends are involved in stereocomplex formation.

Acknowledgements

A part of this work was supported by The Asahi Glass Foundation.

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Accepted December 13, 1991 S