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PMMA-*block*-polyisobutylene-*block*-PMMA prepared with α,ω-dilithiated polyisobutylene and its characterization

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Summary

A triblock copolymer of PMMA and polyisobutylene(PIB), PMMA-*block*-PIB-*block*-PMMA, was prepared by anionic polymerization of methyl methacrylate initiated with α, ω-dilithiated poly(isobutylene) diisobutylate in tetrahydrofuran at -60°C. The molecular weight distribution of the block copolymer was close to that of the starting PIB. The stereoregularity of PMMA block was predominantly syndiotactic. Proton spin-lattice relaxation time and solution viscosity of the block copolymer in acetone, which is non-solvent for PIB, indicate that the block copolymer forms rigid spherical particles. Stereocomplex formation with isotactic PMMA was also studied.

Introduction

Block copolymers comprising blocks of different properties such as solubility and glass transition temperature (Tg) have received much attention from the veiwpoint of polymer material applications in polymeric surfactants, elastomers and so on. Sequential monomer addition in living polymerization is one of the plausible means for preparation of block copolymer. The method, however can not be applied to a pair of monomers which polymerize in different mechanisms such as anionic and cationic ones. An alternative for the above method is polymerization by polymeric initiators; a monofunctional polymeric initiator affords diblock copolymer and an α, ω-difunctional one triblock copolymer.

Isobutylene can polymerize only via cationic mechanism. Kennedy and his coworkers have established polymerization of isobutylene by the inifer method to afford well-defined end functionalized poly(isobutylene) (PIB), in which *p*-dicumyl chloride is used as an initiator and BCl_3 as a coinitiator[1]. They also reported preparation of dihydroxy terminated PIB (DHPIB)[2].

This communication reports preparation of triblock copolymer comprising poly(methyl methacrylate) (PMMA) blocks and PIB block by anionic polymerization of methyl methacrylate (MMA) with α, ω-dilithiated PIB diisobutylate derived from DHPIB. Some solution properties of the block copolymer and stereocomplex formation with isotactic PMMA are also described.

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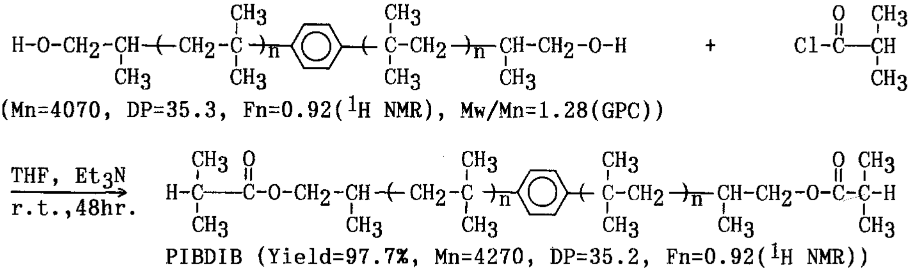
Experimental

Materials

Tetrahydrofuran (THF) was purified by distillation and was distilled again over lithium aluminium hydride ($LiAlH_4$). The THF thus purified was mixed with a small amount of 1,1-diphenylhexyllithium to remove a trace of water and was vacuum-distilled just before use. MMA was purified in the usual manner and then distilled over calcium dihydride (CaH_2) under high vacuum just before use. Lithium diisopropylamide (LDA) was purchased as a cyclohexane solution and was used as recieved.

Preparation of Polyisobutylene diisobutyrate(PIBDIB)

PIBDIB was prepared from DHPIB (Mn=4070, DP=35.3, end functionality(Fn)=0.92 (^1H NMR), Mw/Mn=1.28(GPC)) and isobutyroyl chloride in the presence of triethylamine in THF at room temperature for 48hr according to the procedure by Suzuki et al.[3] (eq.1). PIBDIB thus obtained was purified by precipitation from hexane to acetone. DHPIB was obtained from Akron Cationic Polymer Development Corporation.



(Mn=4070, DP=35.3, Fn=0.92(^1H NMR), Mw/Mn=1.28(GPC))

PIBDIB (Yield=97.7%, Mn=4270, DP=35.2, Fn=0.92(^1H NMR))

(1)

Preparation of PMMA-block-PIB-block-PMMA

The solution of PIBDIB in benzene was dried over CaH_2, filtered under dry nitrogen and freeze-dried[4]. The PIBDIB thus obtained was redissolved in benzene (conc. 16.4wt%) under dry nitrogen and stored at 5°C under dark. The benzene solution (2.38g) containing 390mg of PIBDIB was mixed with 20ml of THF and the PIBDIB was lithiated with an equimolar amount of LDA at 0°C for 2hr. The resulting dianion solution was cooled to -60°C, and 14.9mmol of MMA in THF(2ml) was added at once with vigorous stirring (eq.2). After 30 min, the reaction mixture was quenched by adding a small amount of 1N solution of HCl in methanol and poured into a large amount of methanol. The precipitated polymer mixture was recovered by centrifugation, and dried under vacuum at 60°C. The conversion of MMA was determined from the increased amount of the product from PIBDIB used. The unreacted PIBDIB in the mixture was removed by repeated reprecipitation from toluene to hexane. PIB without isobutyrate unit(8%) contained in the starting PIB was also removed during this procedure. The triblock copolymer was recovered as hexane-insoluble part.

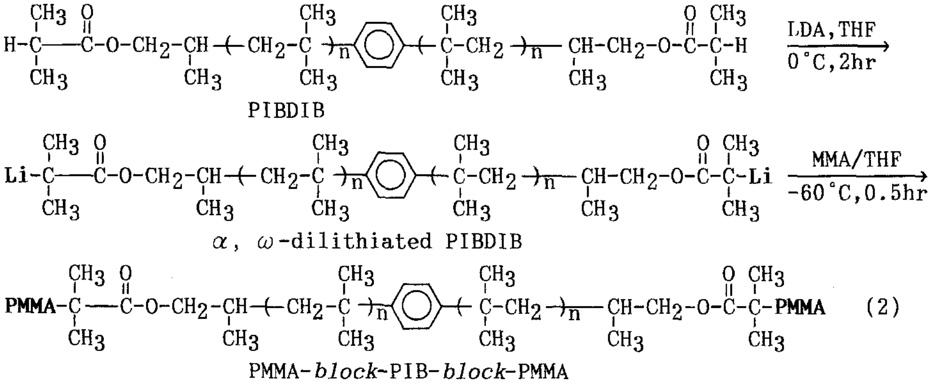
Measurement

^1H 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, ^{13}C NMR spectra of the copolymer were measured in $CDCl_3$ at 55°C on the JNM GSX-270 NMR spectrometer at 67.8MHz. Proton spin-lattice relaxation time 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 TRI ROTAR-V 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 x 10^7 and 2 x 10^4, respectively, using THF as an eluent. 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.



PIBDIB

α, ω-dilithiated PIBDIB

PMMA-*block*-PIB-*block*-PMMA

(2)

Results and Discussion

Preparation and characterization of PIBDIB

PIBDIB was prepared from DHPIB and isobutyroyl chloride in the presence of triethylamine as mentioned in the Experimental section. The ^1H NMR spectra of the starting diol DHPIB and the resulting PIBDIB are shown in Figure 1. DHPIB shows the signals due to the methylene protons of $-\underline{CH_2}-O-$ at 3.400ppm and phenylene protons at 7.250ppm (Figure 1a). The DHPIB was derived from the PIB prepared from *p*-dicumyl chloride and thus contains one phenylene unit in the middle part of the chain as shown in eq.1. The number of hydroxy group per DHPIB molecule could be determined from the intensity ratio of these two signals[4] as 0.92. In the spectrum of the PIBDIB the methylene signals of $-\underline{CH_2}-O-$ shifted to 3.850ppm and new signals ascribable to methine proton of the isobutyroyl group appeared at 2.525ppm (Figure 1b). The number of the isobutyroyl group per PIBDIB molecule was calculated to be 0.92 from the intensities of the signals due to the methine protons and the phenylene protons. The results indicate the complete conversion of the hydroxy group $-CH_2-OH$ into the ester group $-CH_2-O-CO-CH(CH_3)_2$.

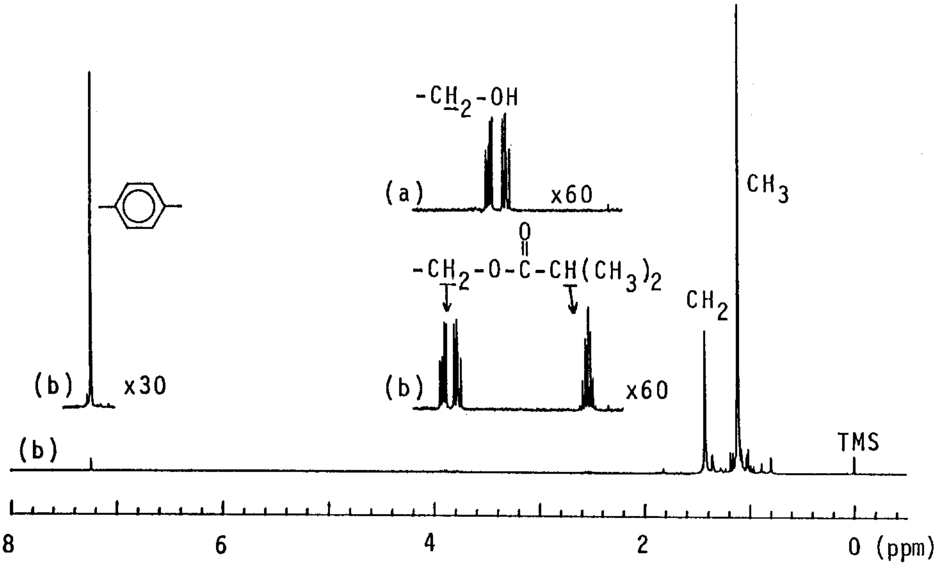


Figure 1 270 MHz ^{1}H NMR spectra of DHPIB (a) and PIBDIB (b) measured in chloroform-d at 55°C

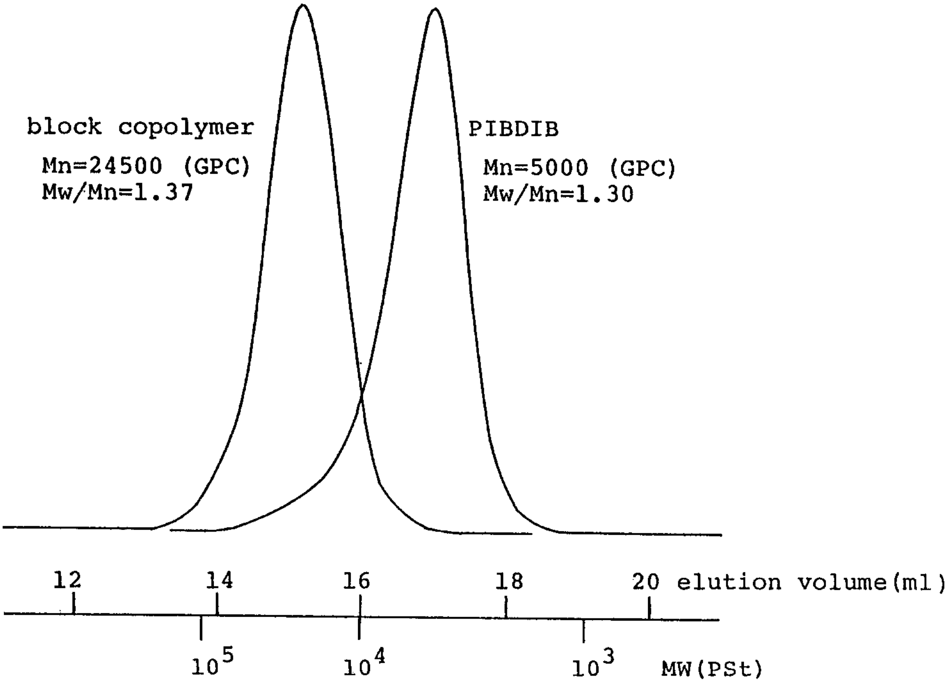


Figure 2 GPC curves of PMMA-*block*-PIB-*block*-PMMA and the starting PIBDIB

Preparation and characterization of PMMA-block-PIB-block-PMMA

The triblock copolymer, PMMA-*block*-PIB-*block*-PMMA, was prepared by the polymerization of MMA initiated with α, ω-dilithiated PIBDIB in THF. The results are summerized in Table 1. The polymerization was conducted at -60°C instead of -78°C because of the low solubility of PIB at lower temperature. The GPC curve of the block copolymer is shown in Figure 2 together with that of the starting PIBDIB. The number average molecular weight(Mn) of the block copolymer determined from the GPC curve is close to the value expected from the $[\text{monomer}]_0/[\text{Li}]_0$ ratio and monomer conversion. The molecular weight distribution of the block copolymer was fairly narrow although it was only slightly broader than that of the starting PIBDIB.

Table 1 Polymerization of MMA with α, ω-dilithiated PIBDIB in THF at -60°C for 30min[a]

$[\text{MMA}]_0/[\text{Li}]_0$	Conversion of MMA(%)	Mn GPC	Mn NMR	Mn Calc.	Mw/Mn[b]	Tacticity(%)[c] mm	mr	rr
88	93.7	24500	23500	20800	1.37	2	23	75

[a] THF 20ml, PIBDIB 390mg(containing 0.17mmol of isobutyrate units), LDA 0.17mmol.

[b] Determined by GPC.

[c] Determined by ^{13}C NMR.

The Mn could also be estimated from the copolymer composition. The copolymer composition was isobutylene : MMA = 1 : 2.74, which leads to the Mn of 23500. The value is close to the Mn values mentioned above. These results indicate the living character of this block copolymerization. NMR signal of carbonyl carbon of the block copolymer shows that the PMMA block of the block copolymer is predominantly syndiotactic.

There is a possibility that the product contains diblock copolymer in the case that a part of the anion is destroyed before the polymerization of MMA proceeds. The possible diblock copolymer should bear the methine proton of isobutyrate unit, which shows the multiplet signal at 2.525ppm (Figure 2b). Figure 3 shows an amplified ^{1}H NMR spectrum of the block copolymer, which does not show the methine signal due to isobutyrate unit, but that of PMMA chain end (2.485ppm). The result suggests that the block copolymer obtained in this work is truly the triblock copolymer and does not contain diblock one.

The 270MHz ^{1}H NMR spectra of the block copolymers were measured in chloroform-d and in acetone-d_6 at 35°C (Figure 4). Signals of methyl and methylene protons of PIB block are much broader in acetone-d_6 than in chloroform-d, indicating lower segmental mobility in the former solution. Acetone is a non-solvent for PIB and a good solvent for PMMA, while chloroform is a good solvent for both polymers. Thus, in acetone solution, PIB block is forced to be dissolved by the good solubility of PMMA blocks flanking the PIB block, and may aggregate due to the stronger interaction between PIB segments than that between PIB block and acetone.

Proton spin-lattice relaxation time (^1H-T_1) of the block copolymer was measured in acetone-d_6 and in chloroform-d at 30°C and 55°C using 1% solutions. The results are summarized in Table 2.

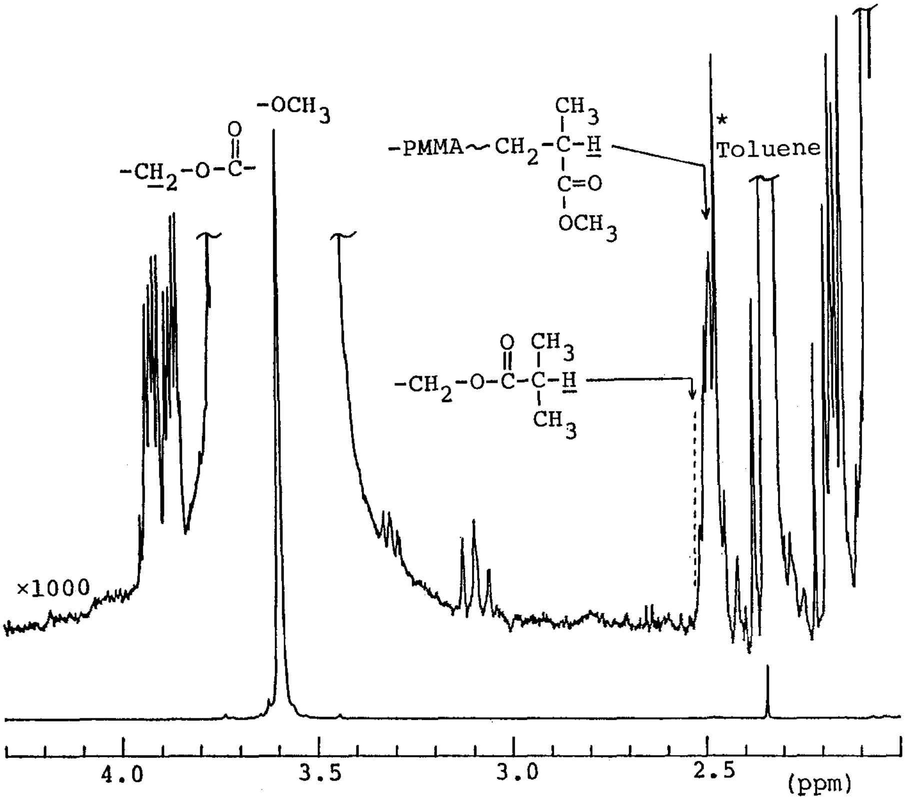


Figure 3 500MHz ^1H NMR spectrum of block copolymer measured in chloroform-d at 55°C
* ^{13}C satellite signal of CH_3 protons of toluene

All the ^1H-T_1 values increased as the temperature increased, indicating that the T_1 value increases as the segmental mobility increases. ^1H-T_1 of methyl protons of PIB block in acetone-d_6 was a half of that in chloroform-d, supporting the lower segmental mobility in acetone-d_6. ^1H-T_1's of methoxy, methylene, and α-methyl protons of PMMA blocks showed much smaller solvent dependence, even though the peak widths observed in acetone-d_6 were slightly larger than those in chloroform-d.

Solution viscosity of the block copolymer was measured in acetone and in chloroform at 30.0°C; [η]=0.117dl/g, Huggins'constant K'=0.44 in acetone; [η]=0.220dl/g, K'=0.62 in chloroform. The reduced viscosity, η_{red} in acetone scarcely shows concentration dependence, indicating that the PIB block of the triblock copolymer forms rigid spherical particles of aggregates in acetone.

Table 2 Proton spin-lattice relaxation times(sec) at 100MHz in acetone-d_6 and in chloroform-d at 30°C and 55°C[a]

Proton	30°C		55°C	
	Chloroform-d	Acetone-d_6	Chloroform-d	Acetone-d_6
CH_3 (PIB)	0.20	0.10	0.21	0.20
CH_2 (PMMA)	0.07	0.05	0.08	0.08
α-CH_3 (PMMA)	0.07	0.06	0.09	0.09
OCH_3 (PMMA)	0.36	0.30	0.38	0.39

[a] Conc. 1.0 wt/v%

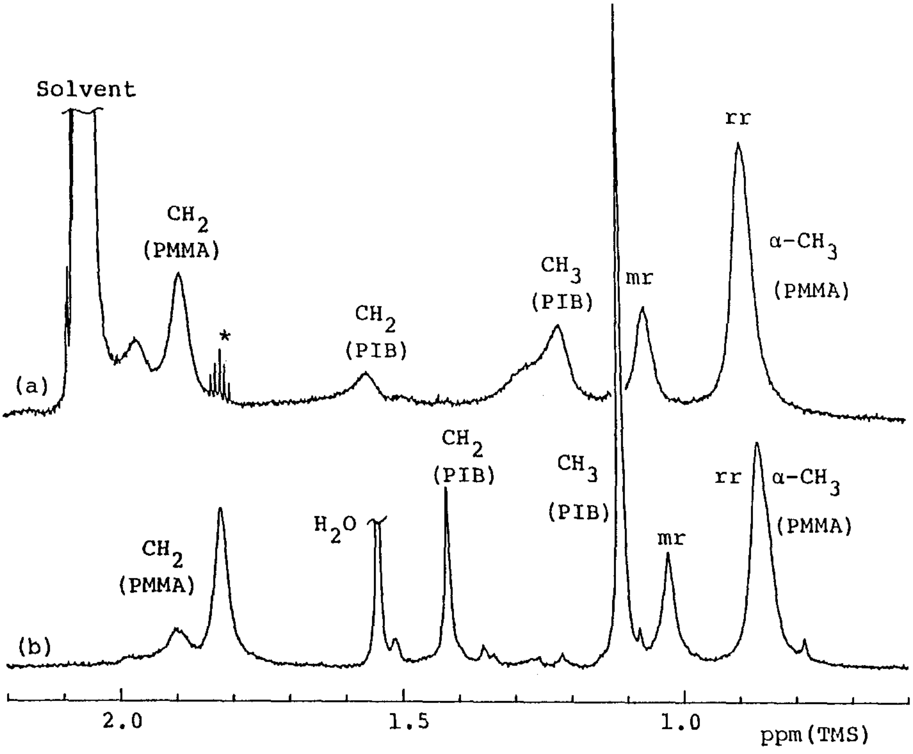


Figure 4 270MHz ^1H NMR spectra of block copolymer measured in acetone-d_6 (a) and in chloroform-d (b) at 35°C

* Signals due to ^{13}C satellite band of the solvent.

When the block copolymer was mixed with an isotactic PMMA (mm/mr/rr=97.3/1.7/1.0, Mn=33000, Mw/Mn=1.25) in toluene or in acetone, stereocomplex formation took place between PMMA blocks in the block copolymer and it-PMMA occur. The melting points of the stereocomplexes were about 170°C. The material consists of a crystalline part of the stereocomplex and a flexible amorphous part of PIB block. This type of material can be used as an elastomer in which the stereocomplex formation provides physical and reversible crosslinking.

Acknowledgements

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