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Highly efficient block copolymerization of methyl and *t*-butyl methacrylates by an incomplete and slow initiation system

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Summary: Block copolymerization of methyl methacrylate (MMA) with *t*-butyl methacrylate (*t*-BMA) was carried out in toluene at -78°C with triphenylphosphine (Ph_3P)-triethylaluminum (Et_3Al) initiating system. Polymerization of MMA with Ph_3P-Et_3Al under the same conditions gave highly syndiotactic PMMA living anion with low initiator efficiency. Even though a large part of the initiator remained unreacted, polymerization of *t*-BMA with the living anion of PMMA gave block copolymer without formation of poly(*t*-BMA), since *t*-BMA alone could not be polymerized under the same conditions due to the inability of initiation with Ph_3P-Et_3Al.

INTRODUCTION

Living polymerizations have been widely used for the synthesis of block copolymers. In this method all the initiators should be consumed completely before the second monomer is charged; otherwise, there should be a possibility that the homopolymer of the second monomer is produced. A mixture of triphenylphosphine (Ph_3P) and triethylaluminum (Et_3Al) has been known to initiate the polymerization of methyl methacrylate (MMA)[1,2]. Recently, we reinvestigated the polymerization of MMA with Ph_3P-Et_3Al or triethylphosphine (Et_3P)-Et_3Al in toluene at low temperatures and found that the polymers formed were highly syndiotactic[3,4]. Although PMMA anion formed with these initiators has a living character, the initiator efficiency is less than unity. The incomplete consumption of the initiator should be a drawback in the preparation of block copolymer using the living PMMA anions. The attempted block copolymerization of ethyl methacrylate (EMA) and MMA resulted in the formation of a mixture of the block copolymer and poly(EMA)[4]. The initiators are also useful for syndiotactic-specific polymerization of methacrylates other than MMA[3,4]. Among the examined methacrylates, *t*-butyl methacrylate (*t*-BMA) behaved differently from primary and secondary alkyl methacrylates; *t*-BMA gave heterotactic polymer with Et_3P-Et_3Al and no polymer with Ph_3P-Et_3Al. On the other hand, *t*-BMA can be copolymerized with MMA by Ph_3P-Et_3Al[4]. This means that inability of *t*-BMA to homopolymerize with Ph_3P-Et_3Al should be ascribed only to non-occurrence of initiation reaction. If this is true,

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polymerization of *t*-BMA with the living PMMA anion formed with Ph_3P-Et_3Al should give the block copolymer but no homopolymer of *t*-BMA even in the presence of the unreacted initiator. This communication reports an example of highly efficient formation of block copolymer of MMA and *t*-BMA by the polymerization with Ph_3P-Et_3Al, which is a slow initiation system with low initiator efficiency.

EXPERIMENTAL

Materials MMA and *t*-BMA were purified in a usual manner, dried over calcium dihydride and vacuum-distilled just before use. Et_3Al was obtained commercially and used as a heptane solution. Commercially obtained Ph_3P was purified by recrystallization from hexane and used as a toluene solution. Toluene and heptane were purified in usual manner, dried over sodium metal and distilled. The purified solvents were mixed with a small amount of butyllithium to remove a trace amount of water and vacuum distilled just before use.

Polymerization Polymerization reaction was carried out in a glass ampule filled with dried nitrogen. The polymerizations were terminated with a small amount of methanol. The reaction mixture was concentrated under high vacuum and the residue was dissolved in benzene. Insoluble materials were removed by centrifugation and the benzene solution was freeze-dried. The recovered polymer was dried under vacuum at 50°C.

Tacticity determination PMMA-*block*-poly(*t*-BMA) was hydrolyzed to obtain PMMA-*block*-poly(methacrylic acid) in a mixture of benzene and methanol (3/2 vol/vol) containing 1% of concentrated hydrochloric acid (12N) under reflux for 2 days. Under the same conditions PMMA block was not hydrolyzed and the composition of the PMMA-*block*-poly(methacrylic acid) was the same as that of PMMA-*block*-poly(*t*-BMA). Tacticity of the poly(methacrylic acid) block and PMMA block in the block copolymer could be determined from the corresponding carbonyl carbon NMR signals[5]. ^{13}C NMR spectra were measured in dimethyl sulfoxide-d_6 at 110°C on a JEOL JNM GX-270 spectrometer. The chemical shift of the solvent was referred as 39.50ppm from tetramethylsilane. Tacticity of PMMA was determined from ^1H NMR spectra measured in $CDCl_3$ at 55°C.

GPC measurement Molecular weight and its distribution were measured on a JASCO TRI ROTOR-V chromatograph equipped with Shodex GPC columns K-806L (30cm x 2) using chloroform as an eluent. The chromatogram was calibrated against standard polystyrenes.

RESULTS AND DISCUSSION

Polymerization of MMA with Ph_3P-Et_3Al (1/2 mol/mol) in toluene at -78°C gives a highly syndiotactic PMMA quantitatively (Table 1). The polymerization proceeds by the attack of Ph_3P to MMA activated through the coordination of Et_3Al with the carbonyl group of the monomer[4]. The amounts of polymer molecule formed were 3.4 ~ 5.7 % of those of Ph_3P used, indicating

the low initiator efficiency in this polymerization. Thus a large part of the

Table 1 Block Copolymerization of MMA and *t*-BMA with Ph_3P-Et_3Al(1/2) in toluene at -78°C[a]

M_1	M_2	$\frac{M_1}{Ph_3P}$	Time (h)	Yield (%)	Mn[b]	$\frac{Mw}{Mn}$[b]	N[c] x10^3 (mmol)	Tacticity(%)[d] PMMA block			Poly(*t*-BMA) block		
								mm	*mr*	*rr*	*mm*	*mr*	*rr*
MMA	—	40	48	100	118500	1.73	8.4	0	10	90	—	—	—
MMA	*t*-BuMA	40	96	100	295800	2.66	8.1	0	12	88	2	39	59
MMA	—	20	48	100	35260	2.05	28.4	0	10	90	—	—	—
MMA	*t*-BuMA	20	96	100	91050	2.43	26.4	0	12	88	2	45	53

[a] Toluene 20ml, M_1 10mmol, M_2 9.9mmol.
[b] Determined by GPC.
[c] Number of polymer molecules.
[d] Determined by ^{13}C NMR of hydrolyzed polymers.

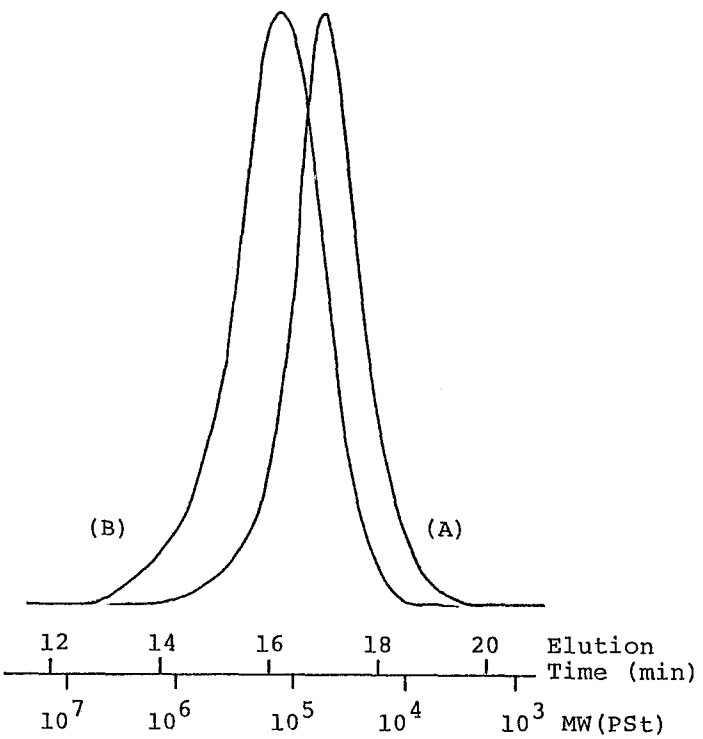

Figure 1 GPC curves of PMMA (A) and PMMA-*block*-poly(*t*-BMA) (B) prepared with Ph_3P-Et_3Al (1/2) in toluene at -78°C ([MMA] 10 mmol, *t*-BMA 9.9 mmol, $[MMA]_0/[Ph_3P]_0$=20)

initiator should remain unreacted. Block copolymerization of MMA and *t*-BMA was examined by adding *t*-BMA to the polymerization mixture of MMA

with Ph_3P-Et_3Al after all the MMA was consumed. The reaction product did not form precipitate but turbid inhomogeneous solution in hexane/toluene (10/1 vol/vol), which is a precipitant for PMMA and a good solvent for poly(*t*-BMA). The result suggests the formation of block copolymer of PMMA and poly(*t*-BMA). Molecular weight distribution of the obtained copolymers were not narrow but unimodal and the GPC curve shifted clearly to the higher molecular weight side in the chromatogram as compared with that of the PMMA formed in the control experiment (Figure 1). The numbers of the block copolymer molecule formed were almost the same as those of the PMMA (Table 1). These results clearly indicate that initiation reaction of *t*-BMA by Ph_3P-Et_3Al did not occur and the homopolymer of *t*-BMA was not included in the product.

t-BMA alone is not polymerized with Ph_3P-Et_3Al, though it is copolymerized with MMA. The steric bulkiness of *t*-butyl group of *t*-BMA may prevent the coordination of Et_3Al, resulting in insufficient activation of the monomer to be attacked by Ph_3P. In the block copolymerization, even though appreciable amounts of Ph_3P and Et_3Al remain unreacted, they can not initiate the second monomer, *t*-BMA, which is thus consumed only by the polymerization initiated with PMMA anions to form the block copolymer.

Stereochemical structure of the block copolymer could be studied from ^{13}C NMR spectra of PMMA-*block*-poly(methacrylic acid) derived from the

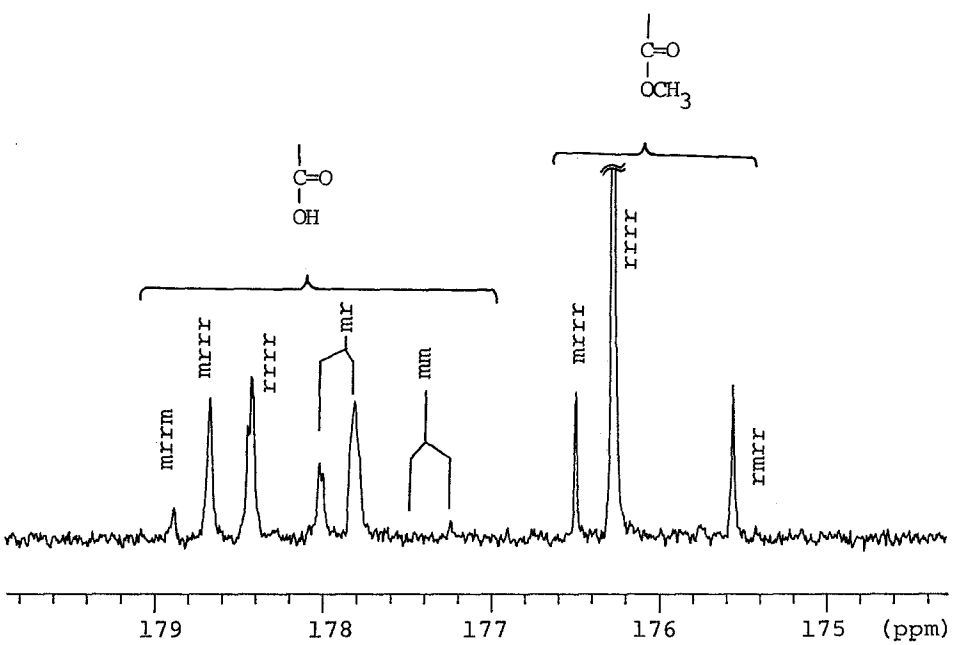

Figure 2. 67.9MHz ^{13}C NMR spectrum of carbonyl carbons in PMMA-*block*-poly(methacrylic acid) derived from PMMA-*block*-poly(*t*-BMA) prepared with Ph_3P-Et_3Al(1/2) in toluene at -78°C (DMSO-d_8, 110°C)

block copolymer through acid hydrolysis. Figure 2 illustrates the carbonyl carbon region of the ^{13}C NMR spectrum, which is almost the superposition of those of PMMA and poly(methacrylic acid). The ester carbonyl (PMMA) and the acid carbonyl (poly(methacrylic acid)) carbon signals are observed separately and each shows further splittings due to different stereochemical configurations[6]. Triad tacticities for both the blocks could be determined from the spectra as listed in Table 1. The PMMA block is highly syndiotactic (*mm* :*mr* :*rr* = 0:12:88) as expected from the result of homopolymerization and shows only *rrrr*, *mrrr*, and *rmrr* pentad signals. Although poly(methacrylic acid) block derived from poly(*t*-BMA) block is less syndiotactic, the syndiotacticity is higher than that of poly(*t*-BMA) prepared with Et_3P-Et_3Al(*mm* :*mr* :*rr* = 6:57:37)[4]. Direct comparison of stereospecificity of Ph_3P-Et_3Al with that of Et_3P-Et_3Al is impossible for the polymerization of *t*-BMA because the latter does not initiate the polymerization. However, the above result suggests that the stereospecificities of Ph_3P-Et_3Al and Et_3P-Et_3Al are different from each other and the former exhibits higher syndiotactic-specificity than the latter. Another important conclusion to be drawn from these observations is that the unreacted phosphine component in these initiator systems should coordinate with the propagating species and be involved in the stereoregulation in the polymerization of *t*-BMA.

For the preparation of block copolymer by living polymerization using the sequential monomer addition method, complete consumption of initiator in the first step of polymerization is the necessary requirement. The present work, however, demonstrated that the polymerization system of low initiator efficiency can be used for the preparation of pure block copolymer when the initiator exhibits remarkably different reactivities toward both monomers in the initiation process, as far as the polymer anion is living.

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