Synthesis of poly(styrene-*block*-t-butyl methacrylate) diblock macromonomers possessing central vinylbenzyl groups

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Diblock macromonomers possessing central vinylbenzyl groups were synthesized by anionic addition in a three-stage process using styrene, 1,4-divinylbenzene, and t-butyl methacrylate monomers. Upon addition of 1,4-divinylbenzene monomer to polystyryl anion in tetrahydrofuran at −78°C, aggregates of polystyryl anions were formed in spite of variations in reaction time and feed mole ratio of the living ends to 1,4-divinylbenzene. However, upon reaction in toluene, linear polystyryl anions possessing terminal vinylbenzyl groups were formed. Anionic propagation of t-butyl methacrylate monomer with linear polystyryl anions end-capped with 1,4-divinylbenzene led to the formation of poly(styrene-*block*-t-butyl methacrylate) diblock macromonomers possessing central vinylbenzyl groups.

(Keywords: diblock macromonomer; anionic addition; vinylbenzyl groups; 1,4-divinylbenzene; aggregate)

INTRODUCTION

Advances in living anionic polymerization have led to the preparation of various kinds of polymers with well-defined molecular shapes. Recently, de la Cruz and Sanchez[1] have calculated from mean-field theory the phase stability criteria and static structure factors for a simple AB graft copolymer, for star copolymers with equal numbers of A and B arms (A_nB_n star) and for *n*-arm star diblock copolymers [$(AB)_n$ star]. The schematic representation of $(AB)_n$ and A_nB_n star copolymers is shown in *Figure 1*. They predicted that it is easier to phase separate star copolymers than the corresponding graft and block copolymers. In a previous work[2], we have suggested a novel architecture for star copolymers by means of organized polymerization in a micelle or microphase separated structure formed by AB-type diblock macromonomers. In principle, block copolymers form a microdomain structure in the solid state or a micelle in the selective solvent as a consequence of microphase separation of the constituent block chains. In these environments, the polymerizable groups should be oriented regularly at the domain interfaces or inside the core micelle. That is to say, the organized polymerization of diblock macromonomers possessing polymerizable groups at the terminal end or at the block junction will lead to the formation of $(AB)_n$ or A_nB_n star block copolymers, respectively. We have already reported the preparation of $(AB)_n$ star block copolymers by means of free radical polymerization[2] or anionic polymerization[3] of the vinylbenzyl group terminated poly[styrene(S)-*block*-isoprene] diblock macromonomers. More recently, Berlinova and Panayotov[4] have prepared amphiphilic block macromonomers possessing a central unsaturated group. In the radical *cis–trans* isomerization of these diblock macromonomers, four- to eight-arm amphiphilic A_nB_n star-shaped copolymers are formed.

The aim of this paper is to establish the method of synthesis of diblock macromonomers possessing central vinylbenzyl groups by anionic addition in a three-stage process using styrene, 1,4-divinylbenzene (1,4-DVB), and t-butyl methacrylate(BMA) monomers.

EXPERIMENTAL

Polymer synthesis

Poly(S-*block*-BMA) diblock macromonomers possessing central vinylbenzyl groups were prepared by the living anionic technique. Styrene was first dried over a mixture of calcium hydride–lithium aluminum hydride and then purified with triphenylmethyl sodium *in vacuo*. BMA monomer was dried over calcium hydride and then purified with n-butyllithium (n-BuLi) *in vacuo*. 1,4-DVB (Hokkō Chemical Ind. Ltd) was dried over a mixture of calcium hydride–lithium aluminum hydride. Toluene was first dried over sodium metal and then purified with n-BuLi *in vacuo*. Tetrahydrofuran (THF) was distilled from its solution of α-methylstyrene tetramer sodium anion under vacuum. Anionic polymerization was carried out in sealed glass apparatus under a pressure of 10^{-6} mmHg. The anionic polymerization of poly(S-*block*-BMA) diblock macromonomers possessing vinylbenzyl

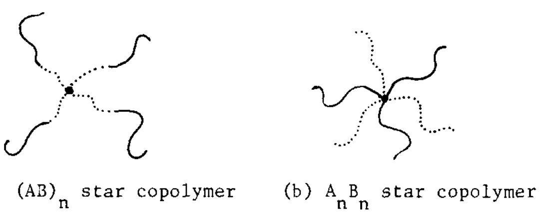

Figure 1 Schematic representation of (a) $(AB)_n$ and (b) A_nB_n star block copolymers

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groups was carried out by the three-stage addition of styrene, 1,4-DVB (both monomers were diluted with toluene), and BMA (THF solution) at −78°C, using n-BuLi as the initiator. Both anionic polymerizations of styrene and BMA were carried out at concentrations below 6 wt%. The end of the polystyryl anions was capped with a small amount of 1,4-DVB in toluene for 10 min. At the end of the polymerization of the styrene monomer, an aliquot was removed to recover the polymer for characterization. Polymerization of BMA was carried out at −78°C for 30 min. After the polymerization, the solvents in the polymerization system (toluene and THF) were distilled off under high vacuum. The polymerization product was purified twice by reprecipitation from THF solution with methanol/water (7/3 v/v).

Molecular characterization

The number-average molecular weight ($\bar{M}_n$) of the polystyrene (PS) prepolymers was determined by gel permeation chromatography (g.p.c., Tosoh high-speed liquid chromatograph HLC 802-A), with THF as eluent at 38°C, a TSK gel GMH column and a flow rate of 1.0 ml min^{-1}. The content of poly(t-butyl methacrylate) (PBMA) blocks was determined by ^{1}H n.m.r. (90 MHz, Jeol FX-90Q n.m.r. spectrometer in $CDCl_3$). The $\bar{M}_n$ of poly(S-*block*-BMA) diblock macromonomers was determined by vapour pressure osmometry on a Corona NA 117 vapour pressure osmometer in benzene. The polydispersity ($\bar{M}_w/\bar{M}_n$) was determined from g.p.c. distribution functions improved by the reshaping method[5] with a NEC personal computer PC-8801. The content of terminal vinylbenzyl groups of end-capped PSs was determined by the area ratio of the refractive index (RI) and u.v. (292 nm) intensities in a g.p.c. chart (using a calibration curve constructed from a mixture of PS prepolymer and *p*-methylstyrene (*Figure 2*). In order to separate diblock macromonomer free from PS prepolymer, the turbidimetric measurements of PS precursor and polymerization product were carried out at a wavelength of 500 nm. Each polymer sample (10 mg) was dissolved in THF (70 ml), then methanol/water (7/3 v/v) mixture was added stepwise with vigorous stirring in the cell (Pyrex cylinder, 150 ml) for turbidimetric measurements at 20°C (Hitachi Perkin-Elmer 139 u.v.-vis. spectrometer).

RESULTS AND DISCUSSION

In the anionic polymerization the reactivity of the double bond (1-position) in 1,4-DVB is 10-fold greater than the pendant double bond (4-position)[6]. So, essentially the linear PS chains possessing terminal vinylbenzyl groups must be formed in the initial reaction stage of the polystyryl anion with 1,4-DVB.

At first, the preliminary experiments for the reactions of polystyryl anion with 1,4-DVB were carried out varying the kinds of solvents used. The chemical reactions are presented in *Scheme 1*. *Table 1* lists the reaction conditions and results for the reactions P11–P13 of polystyryl anion with 1,4-DVB in THF at −78°C for 5 min, varying the feed molecular ratio of 1,4-DVB to living anion ends ([1,4-DVB]/[LE]). The concentration of living anion ends was in the range of 3×10^{-3}–5×10^{-3} mol l^{-1} for these reaction systems. *Figure 3* shows g.p.c. profiles of the reaction products P11–P13 taken with RI

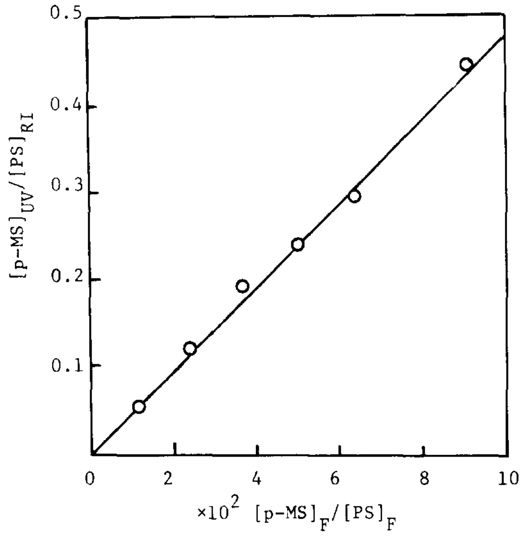
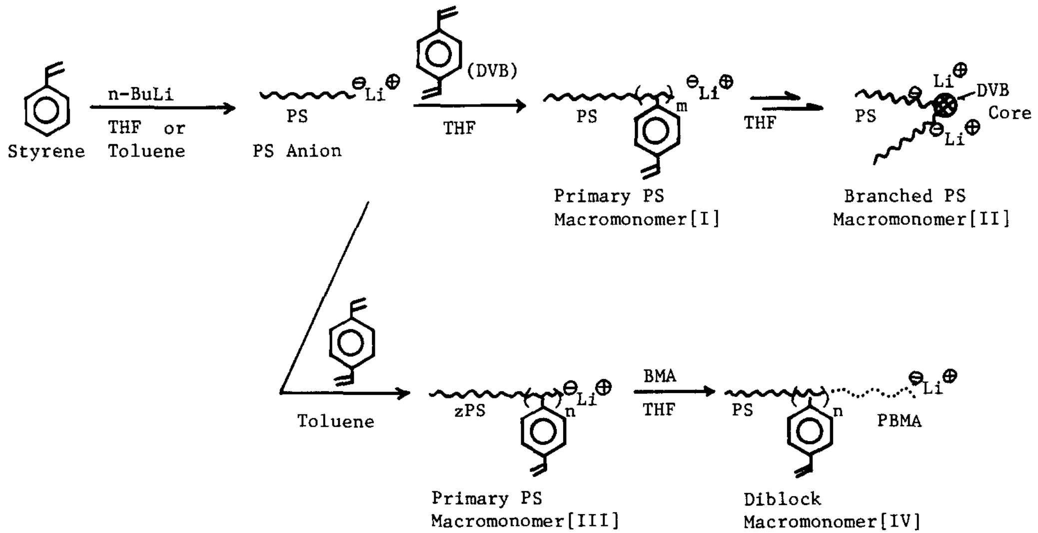


Figure 2 Calibration curve constructed from a mixture of polystyrene (PS) and *p*-methylstyrene (*p*-MS) using g.p.c. double detectors (RI and u.v. at 292 nm): $[p\text{-MS}]_{u.v.}$, area of g.p.c. distribution of *p*-MS in u.v. monitor (292 nm); $[PS]_{RI}$, area of g.p.c. distribution of PS in RI monitor; $[p\text{-MS}]_F$, feed (mol) of *p*-MS in a mixture; $[PS]_F$, feed (mol) of PS in a mixture



Scheme 1

Table 1 Reaction conditions and results for the reactions P11–P13 of polystyryl anion with 1,4-DVB[a]

Expt code	Polystyryl anion			[1,4-DVB]/[LE] (molecule/ molecule)	Vinylbenzyl groups of primary PS macromonomer (number l^{-1} polymer)
	$10^{-4} \times \bar{M}_n$[b]	$\bar{M}_w/\bar{M}_n$	$10^3 \times$ [LE] (mol l^{-1})[c]		
P11	2.2	1.11	3.2	4.6	4.0
P12	1.1	1.08	5.4	7.0	6.4
P13	1.2	1.10	5.4	8.2	8.0

[a] Polystyryl anion was prepared by living polymerization of styrene in THF at −78°C initiated by n-BuLi. THF solution of 1,4-DVB was added to polystyryl anion and reacted for 5 min at −78°C

[b] Determined by g.p.c.

[c] [LE], concentration of polystyryl anion

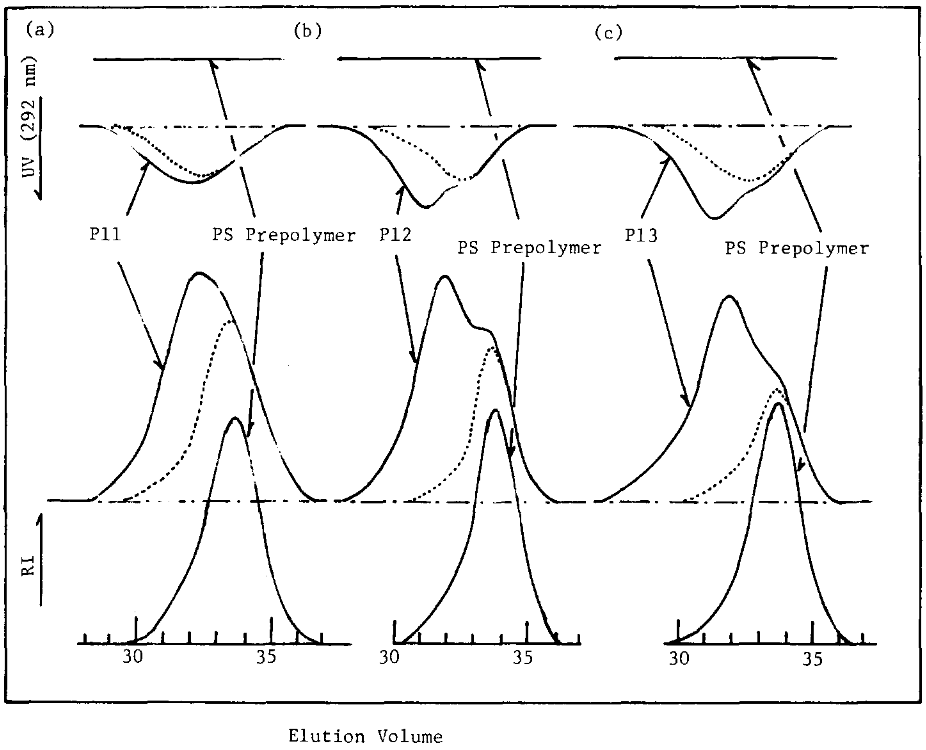


Figure 3 G.p.c. profiles of the reaction products P11–P13 taken with RI and u.v. detectors: (a) P11 series; (b) P12 series; (c) P13 series

and u.v. detectors. The wavelength of the u.v. detector was set at 292 nm to the characteristic absorption of vinylbenzyl groups. The g.p.c. curve of P11 shows a broad distribution compared with the corresponding PS precursor. The g.p.c. curves of P12 and P13 are bimodal as found from the RI and u.v. monitors. It is found from the u.v. monitor that the intensities of the u.v. absorptions for P11–P13 are larger than those of the corresponding PS precursors. These results indicate that two species of PS macromonomers (products [I] and [II] shown in *Scheme 1*) were formed in the addition reaction. Each g.p.c. elution pattern indicated by the dotted lines (primary PS macromonomer [I]) is identical to that of the PS prepolymer. The second peaks (branched PS macromonomer [II]) at higher elution volume are ascribed to the polymer with just twice (P11) or three times (P12 and P13) the molecular weight of the PS precursors, respectively. The terminal vinylbenzyl groups of primary PS macromonomers increase with increase in the feed ratio of [1,4-DVB]/[LE], and the values are almost identical to the feed ratio of [1,4-DVB]/[LE]. However, a large quantity of PS aggregates [II] is formed in the addition reactions of polystyryl anion with 1,4-DVB in THF. When 1,4-DVB monomer is consumed by the addition reaction, the aggregates are formed competitively by the intermolecular crosslinking reaction of primary PS macromonomers having terminal functional groups (as presented in *Scheme 1*). We also observed that the amount of these aggregates increased gradually during the reaction (30 min).

Figure 4 shows g.p.c. profiles of the reaction products P21–P23 of polystyryl anion ($\bar{M}_n = 2.2 \times 10^4$) with 1,4-DVB in toluene at −78°C for 5 min. The concentration of polystyryl anions was almost constant (3.0×10^{-3} mol l^{-1}) for all the reaction series. The feed ratios of [1,4-DVB]/[LE] were 3.0, 5.0 and 10.0 (molecule/molecule) for P21, P22 and P23, respectively. The g.p.c. curves of P21–P23 (primary PS macromonomer [III]) are unimodal in the RI and u.v. monitors. The g.p.c. elution patterns agree well with that of the PS precursor. Moreover, the molecular weight distribution of these PS macromonomers is very narrow ($\bar{M}_w/\bar{M}_n = 1.04$). It is found from these results that 1,4-DVB monomers are not consumed by addition reactions within this reaction time (5 min). These reaction products have the primary molecular structure of the linear PS macromonomers possessing terminal pendant double bonds. In a solvent of non-polar media, such as toluene, the active species are occupied by ion pairing. Hence, ion-pair propagation is very slow in comparison with free-ion propagation in polar solvents, such as THF. The content of terminal vinylbenzyl groups may be controlled in non-polar solvents by changing the feed ratio of [1,4-DVB]/[LE] and the reaction time. Thus the effect of solvent is especially dramatic on polymerization rates for the formation of linear PS macromonomers.

The relative electronegativities of some selected substituents are: –CN > –COOR > –C_6H_5. Hence the polystyryl anion will polymerize polar monomers like methacrylic acid esters, whereas living poly(methacrylic acid ester) is impossible to add to the pendant double bonds. The BMA monomer is adopted in the third stage of the addition in this study. In order to obtain 'monodispersed' diblock macromonomers, it is necessary to have the following conditions: (1) no termination or transfer during chain growth; (2) the initiation step is at least as rapid as the propagation step; and (3) all the monomer molecules have equal probability of reacting (perfect mixing). In practice, even when conditions (1) and (2) are possible, the requirement of perfect mixing is difficult to meet. On the basis of the above information, poly(S-*block*-BMA) diblock macromonomers were prepared by anionic addition in a three-stage process. *Table 2* lists the polymerization conditions and results of poly(S-*block*-BMA) diblock macromonomers. In the polymerization BN1, the toluene solution of BMA was added to the toluene solution of polystyryl anion end-capped with 1,4-DVB. A typical g.p.c. profile of BN1 is shown in *Figure 5a*. The g.p.c. profile shows that the PS precursor has a single and narrow molecular weight distribution. However, the g.p.c. curve of BN1 is bimodal from both RI and u.v. monitors. The first peak at lower elution volume is ascribed to that of the PS precursor. The g.p.c. elution pattern of the second peak is shifted to the side of high molecular weight as compared with its precursor and has the intensity of u.v. absorption. The second peak corresponds to the poly(S-*block*-BMA) macromonomer. In this polymerization system, the initiation step is very slow due to ion pairing of the active species. Hence we adopted the method where a THF solution of BMA was added to toluene solution of polystyryl anion end-capped with 1,4-DVB (expt BP1). The g.p.c. profile of BP1 is shown in *Figure 5b*. It is also found from these results that the g.p.c. curve of BP1 is bimodal. The yield of poly(S-*block*-BMA) diblock macromonomer [IV] increases compared to that obtained in a hydrocarbon solvent system. In the polymerization of BP1 two active species, ion pairs and free ions, compete in the initiation step of end-capped polystyryl anion reacting with BMA monomers. This system seems to be effective for the formation of diblock macromonomers compared with the hydrocarbon solvent system.

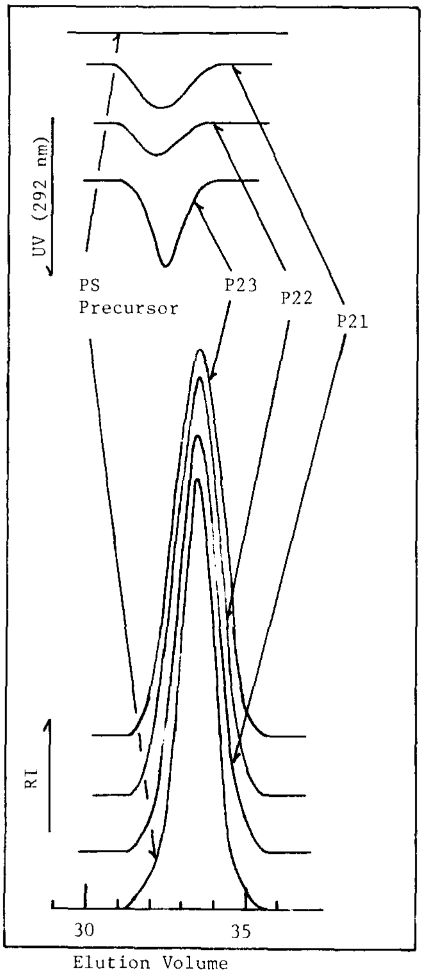


Figure 4 G.p.c. profiles of the reaction products P21–P23

In order to separate the unpropagated PS from the polymerization product, the precipitation fractionations were carried out in a THF–precipitant (methanol/water 7/3 v/v mixture) system. The turbidity of the PS precursor and the polymerization products was measured initially by a spectrophotometer at 500 nm. Typical turbidity curves of the BP1 series are shown in *Figure 6*. It is found from these curves that the PS precursor is precipitated at a value of 0.45 for the precipitant fraction (indicated by an arrow). A typical g.p.c. profile of fraction BP1-F is shown in *Figure 5b*. The g.p.c. profile shows that this fraction has a single molecular weight distribution. *Table 3* lists the characteristics of the fractionated poly(S-*block*-BMA) diblock macro-

Table 2 Polymerization of poly(S-*block*-BMA) diblock macromonomers[a]

Expt code	n-BuLi $\times 10^4$ (mol)	S (mol)	1,4-DVB $\times 10^3$ (mol)	BMA (mol)	[1,4-DVB]/[LE] (molecule/molecule)
BN1[b]	6.8	0.131	2.66	0.035	4.1
BP1[c]	9.8	0.131	3.64	0.143	3.8

[a] Styrene was polymerized in toluene (250 ml) at −78°C. Subsequently, a toluene solution (50 ml) of 1,4-DVB was added to polystyryl anion at −78°C for 10 min

[b] Toluene solution (200 ml) of BMA was added to polystyryl anion end-capped with 1,4-DVB at −78°C for 30 min

[c] THF solution of BMA was added to polystyryl anion end-capped with 1,4-DVB

Table 3 Characteristics of poly(S-*block*-BMA) diblock macromonomers possessing central vinylbenzyl groups

Expt code	PS precursor $10^{-4} \times \bar{M}_n{}^a$	Diblock macromonomer $10^{-4} \times \bar{M}_n{}^b$	$\bar{M}_w/\bar{M}_n{}^a$	PS block^c (wt%)	Vinylbenzyl^d groups (number l^{-1} polymer)
BN1-F	2.05	3.12	1.15	64	2.3
BP1-F	1.43	4.06	1.16	35	2.0

^{a}Determined by g.p.c.
^{b}Determined by osmometry
^{c}Determined by ^{1}H n.m.r.
^{d}Determined by g.p.c. using double detectors

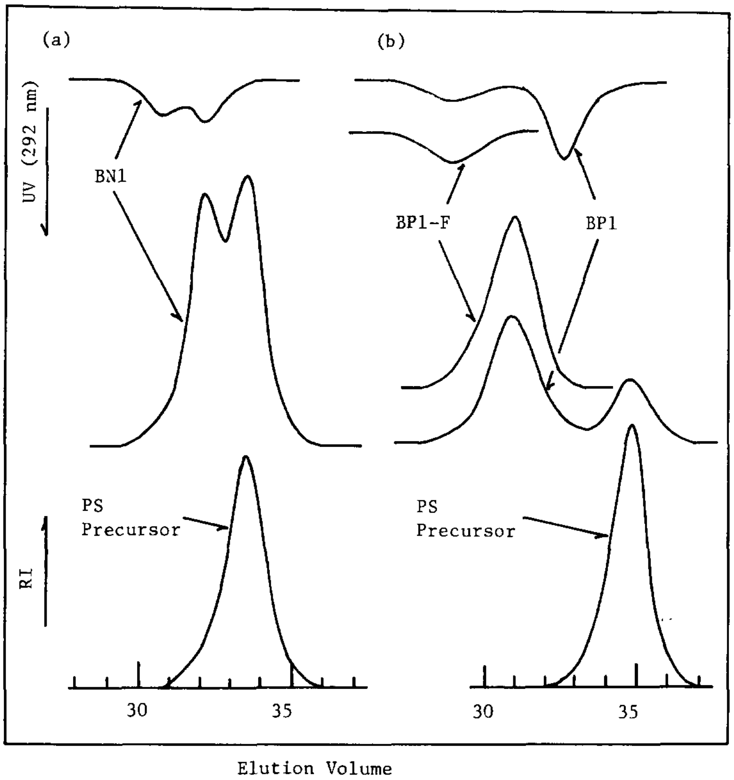


Figure 5 G.p.c. profiles of the diblock polymerization BN1 and BP1: (a) BN1 series; (b) BP1 series

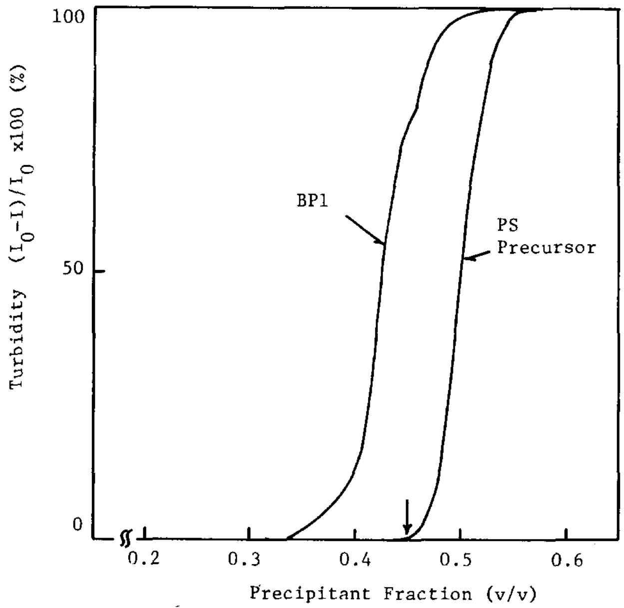


Figure 6 Turbidity curves of BP1 and PS precursor: precipitant, methanol/water (7/3 v/v)

monomers. Both diblock macromonomers (BN1-F and BP1-F) have about two vinylbenzyl groups at the block junction. We are investigating the organized polymerization of a micelle or microphase separated structure formed by diblock macromonomers possessing central vinylbenzyl groups. The information obtained from these investigations will be reported shortly.

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REFERENCES

1 de la Cruz, M. O. and Sanchez, I. C. *Macromolecules* 1986, **19**, 2501
2 Ishizu, K., Shimomura, K. and Fukutomi, T. *J. Polym. Sci., Polym. Chem. Edn* 1991, **29**, 923
3 Ishizu, K., Shimomura, K., Saito, R. and Fukutomi, T. *J. Polym. Sci., Polym. Chem. Edn* 1991, **29**, 607
4 Berlinova, I. V. and Panayotov, I. M. *Makromol. Chem.* 1989, **190**, 1515
5 Pierce, P. E. and Armonas, J. E. *J. Polym. Sci. C* 1968, **21**, 23
6 Worsfold, D. J. *Macromolecules* 1970, **3**, 514