Preparation and characterization of novel star-shaped copolymers having three different branches

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Star-shaped copolymers having three different branches, poly(styrene), poly(dimethylsiloxane), and poly(tert-butyl methacrylate), were prepared by coupling of poly(styryl) anion with end-reactive poly(dimethylsiloxane), followed by anionic propagation of tert-butyl methacrylate. End-reactive poly(dimethylsiloxane) was prepared by anionic polymerization of hexamethylcyclotrisiloxane initiated with the lithium salt of *p*-(dimethylhydroxy)silyl-α-phenylstyrene. The resultant polymers were characterized by osmometry, g.p.c., ^{1}H-n.m.r., and found to be pure and to have narrow molecular weight distributions.

(Keywords: three-component, three-arm star-shaped copolymer; poly(styrene); poly(dimethylsiloxane); poly(tert-butyl methacrylate); lithium salt of *p*-(dimethylhydroxy)silyl-α-phenylstyrene; anionic polymerization)

INTRODUCTION

For the past three decades, the synthesis, characterization, morphology, and properties of various types of multiphase polymers have been studied extensively. Such multiphase polymers include, for example, linear block copolymers [such as AB-, ABA-, and $(AB)_n$-type block copolymers[1–4], ABC-type triblock copolymers[5–17], ABA′CA-type pentablock copolymers[12–21]], star-block copolymers[22–38], and block-graft copolymers[39]. All of these are connective. Although the geometrical structures of these polymer molecules appear to be different, they connect at two adjacent different polymers. Hence the morphological properties of multiblock, star block and block-graft copolymers can be studied on the basis of the morphology of simple diblock copolymers. However, if three different polymers connect at one point, i.e. if a star-shaped copolymer having three different branches is obtained, the situation becomes entirely different. Microphase separation of the three components requires a one-dimensional arrangement of the connecting point. If such a structure is energetically unfavourable, coercive mixing of incompatible components would occur. Thus, a new structure or a new property can be expected with such a star-shaped copolymer. The purpose of this work is to establish a method of preparation for a three-component, star-shaped copolymer having three different branches by an anionic polymerization technique. Hereafter, we will call such a polymer ‘three-component, three-arm star-shaped copolymer’ or simply ‘3-arm star-shaped copolymer’.

In this work, poly(styrene), poly(dimethylsiloxane), and poly(tert-butyl methacrylate) (abbreviated PS, PDMS, and PTBMA, respectively) were selected as the three components. PS is a non-polar polymer, PTBMA a polar polymer, and PDMS polymer contains no carbon atom in its main chain. These polymers are obtained using an anionic polymerization method that gives polymers exhibiting well-defined molecular structures, low compositional heterogeneities and narrow molecular weight distributions[40–42]. Furthermore, the present combination of polymers is favourable for structural studies, because the constituent polymers can be distinguishable by electron microscopy and small-angle X-ray scattering. Studies on the microphase separated structures and the properties of 3-arm star-shaped copolymers will be reported in subsequent papers.

EXPERIMENTAL

Materials

Styrene and hexamethylcyclotrisiloxane (D_3) were used as GR grade. Styrene was first dried over calcium hydride under reduced pressure, and purified with octylbenzophenone sodium[17,43,44] and finally with triphenylmethyllithium[18] at 273 K. It was then diluted to about 10 w/v% with purified benzene. D_3 dissolved in xylene (about 35 w/v%) was purified with sec-butylmagnesiumbromide in three stages after sublimation.

Tert-butyl methacrylate (TBMA) was purchased and used as EP grade. It was treated with aqueous sodium hydroxide and then distilled under reduced pressure.

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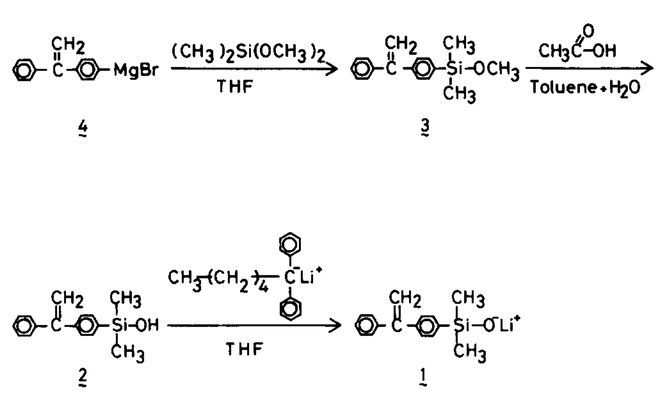


Scheme 1 Synthesis of lithium salt of *p*-(dimethylhydroxy)-silyl-α-phenylstyrene

After drying with calcium hydride, it was transferred into a vacuum apparatus and purified repeatedly with triethylaluminium[45]. TMBA was finally redistilled carefully in the presence of triethylaluminium and diluted to about 10 w/v% with purified THF just prior to polymerization. An initiator, the lithium salt of *p*-(dimethylhydroxy)silyl-α-phenylstyrene (**1**), used for the polymerization of D_3 was the reaction product of *p*-(dimethylhydroxy)silyl-α-phenylstyrene (**2**) with 1,1-diphenylhexyllithium (DPHL) as shown in *Scheme 1*. Sec-butyllithium (sec-BuLi) was prepared by the method of Smith *et al.*[46]. The concentrations of the initiators were determined by titration with standard HCl solution. THF and benzene were purified by distillation *in vacuo* in the presence of the dipotassium salts of α-methylstyrene tetramer and DPHL, respectively, after standard purification procedures. All the operations were carried out in reactors with breakseals under a pressure of $\leqslant 1 \times 10^{-3}$ Pa.

Lithium salt of p-(dimethylhydroxy)silyl-α-phenylstyrene (1)

Scheme 1 describes a synthetic route for initiator (**1**). 1-Phenyl, 1-*p*-bromo-phenylethylene (PBPE) was synthesized from *p*-bromoacetophenone and the Grignard reagent of bromobenzene through hydrolysis and dehydration. The starting compound PBPE (80.0 g, 0.308 mol) in THF (200 ml) was added dropwise to magnesium turnings (8.2 g, 0.34 mol) under nitrogen gas, and then stirred at 298 K for 1.5 h to give the Grignard reagent (**4**). This Grignard reagent was added dropwise to dimethyldimethoxysilane (44.4 g, 0.370 mol) dissolved in THF (200 ml) and then stirred at 323 K for 2 h. Fractional distillation of the product gave 36.0 g (0.134 mol, 36%) of ether **3** at 433–437 K (133 Pa). Ether **3** (30.0 g, 0.112 mol) dissolved in toluene (60 ml) was allowed to react with acetic acid (6.15 N, 20 ml) under vigorous stirring at 300 K for 16 h to give 20.8 g (0.0819 mol, 73%) of **2**. Silanol **2** (10.0 g, 0.0394 mol) dissolved in hexane (60 ml) was allowed to react with potassium hydroxide (3.4 g, 0.061 mol) at 300 K for 2 h to give the potassium salt of **2**, which was insoluble in hexane. This potassium salt of **2** was neutralized with acetic acid to give 5.4 g (0.0213 mol, 54%) of pure **2**: 270 MHz ^{1}H-n.m.r. ($CDCl_3$) 0.58 (6H, s, CH_3–Si), 2.53, 3.50 (1H, 2s, HOSi), 5.67 (2H, s, $H_2C{=}C$), 7.30–7.78 (9H, m, C_6H_4, C_6H_5). The overall yield was 14%.

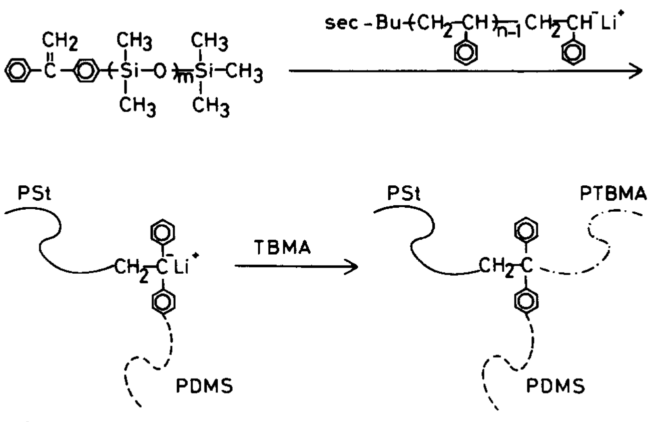
Metallation of **2** with DPHL was carried out in all-glass apparatus equipped with breakseals under a pressure of $\leqslant 1 \times 10^{-3}$ Pa. DPHL does not react with the double bond but with the hydroxyl group in **2**. THF solution of DPHL (0.12N) was carefully added dropwise to THF solution of **2** (about 0.8 w/v%). The addition of DPHL was stopped when a slight red coloration indicated the presence of DPHL.

Preparation of 3-arm star-shaped copolymer

3-Arm star-shaped copolymer was prepared by coupling of the poly(styryl) anion with end-reactive poly(dimethylsiloxane), followed by anionic propagation of tert-butyl methacrylate as outlined in *Scheme 2*. All the operations were performed in a sealed glass apparatus under $\leqslant 1 \times 10^{-3}$ Pa, using essentially the same procedure as has been reported previously[40,41,47–49]. Anionic polymerization of D_3 with initiator **1** was performed in THF at 298 K for 5–8 h, after the initiation reaction was made at 318 K. The polymerization was terminated with excess amounts of trimethylchlorosilane. Living poly(styryl) anion was made by anionic polymerization of styrene with sec-BuLi in benzene at 303 K. Three-component, star-shaped copolymer with three different branches was prepared via two steps, the first of which was the addition of living poly(styryl) anion onto end-reactive PDMS to yield diphenylmethyl anion, and the second was the anionic propagation of TBMA from the diphenylmethyl anion. At first, about two-thirds of the benzene solvent that dissolved the poly(styryl) anion was evaporated and a large amount of THF was added. After the temperature was decreased to 195 K, a THF solution of end-reactive PDMS was added and reacted with the poly(styryl) anion for a few hours. Finally TBMA monomer was added quickly and polymerized. The polymerization was terminated with methanol.

Fractionation

The end-reactive PDMS obtained by anionic polymerization with initiator **1** had a fairly broad molecular weight distribution ($M_w/M_n \simeq 1.3$–1.4). This was fractionated by g.p.c. at 298 K using an HLC Type 837 fully automatic instrument equipped with a set of three columns, two G4000H6 and one GMH6 (all of them were 600 mm in length and 21.5 mm i.d.). Isolation of the star-shaped copolymer was also carried out with the same instrument. All runs for fractionation were made with chloroform as an eluent. The concentration of the



Scheme 2 Synthesis of star-shaped copolymer having three different branches, poly(styrene), poly(dimethylsiloxane) and poly(tert-butyl methacrylate)

Table 1 Preparation of end-reactive poly(dimethylsiloxane) with lithium salt of p-(dimethylhydroxy)silyl-α-phenylstyrene in THF at 298 K[a]

Sample code	Initiator (mmol)	D_3 (mmol)	Time (h)	As-polymerized			After fractionation		
				$10^{-4}M_k$[b]	$10^{-4}M_{n,OSM}$[c]	M_w/M_n[d]	$10^{-4}M_{n,n.m.r.}$[e]	$10^{-4}M_{n,OSM}$[c]	M_w/M_n[d]
PDMS(2)	0.73	63	4.0	1.9	1.9	1.2_9	2.1 ± 0.2	2.0	1.1_3
PDMS(3)	0.56	82	7.5	3.3	3.2	1.3_5	3.3 ± 0.3	3.2	1.1_2
PDMS(4)	0.57	80	8.5	3.1	3.3	1.3_6	3.3 ± 0.3	3.2	1.1_4

[a] Monomer concentration was about 7 w/v%

[b] M_k was calculated from the polymer yield and the ratio of amounts of monomer to initiator

[c] $M_{n,OSM}$ was determined by osmometry

[d] M_w/M_n was estimated from the g.p.c. peak on the basis of calibration with fractionated poly(dimethylsiloxane)

[e] $M_{n,n.m.r}$ was determined by ^{1}H-n.m.r. spectrum

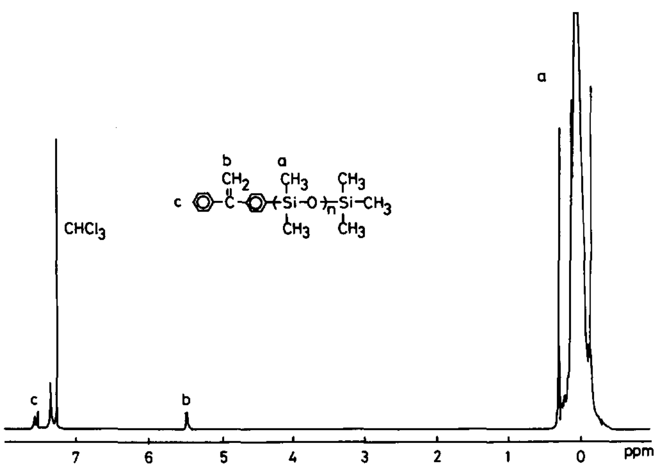


Figure 1 ^{1}H-n.m.r. spectrum of poly(dimethylsiloxane) initiated with lithium salt of *p*-(dimethylhydroxy)silyl-α-phenylstyrene and terminated with trimethylchlorosilane. Sample was PDMS(4)

polymer solution for fractionation was adjusted to 0.8–1.6 w/v%, depending on the molecular weight of the sample.

Characterization

Number-average molecular weights, M_n, were determined by osmometry in toluene at 303 K with a Hewlett-Packard type 502 high-speed membrane osmometer. Molecular weight heterogeneities were tested by g.p.c. at 298 K using a HLC type 803 instrument with a refractive index detector and a set of two high-resolution columns GMH6 (600 mm in length and 7.8 mm i.d.). THF was used as an eluent. The column set was calibrated with standard poly(styrene)s and also PDMS with narrow molecular weight distributions. ^{1}H-n.m.r. spectra were obtained at room temperature in $CDCl_3$ with a JEOL GX-270 FT-n.m.r. spectrometer (270.05 MHz). Chemical shifts were referred to $CHCl_3$ (7.25 ppm) in $CDCl_3$.

RESULTS AND DISCUSSION

Preparation of poly(dimethylsiloxane) having a diphenylethylene type double bond at one end

End-reactive PDMS used in this study must have a diphenylethylene type double bond at one end only and must also have a narrow molecular weight distribution. It has been reported[50] that D_3 can be initiated by silanol lithium salt. In this work, a silanol lithium salt of monofunctional initiator **1** was used. The results of the polymerization of D_3 with **1** are summarized in *Table 1*. The conversions were all 100%, within experimental error. There is fine agreement between the values of M_n for the polymers determined by osmometry and the values expected from the amounts of monomer and initiator used. These facts indicate clearly that the present compound **1** can be used as a new initiator for the anionic polymerization of D_3.

Figure 1 shows an example of the ^{1}H-n.m.r. spectrum of end-reactive PDMS. The signal due to $H_2C{=}C$ appears at around 5.48 ppm. Furthermore, the values of M_n estimated from the relative intensity of the vinylidene to methyl protons in siloxane are in fair agreement with those obtained by osmometry. These facts indicate that a diphenylethylene type double bond remains quantitatively at one end of PDMS. However, the polymers obtained have rather broad molecular weight distributions. Hence these polymers were fractionated by g.p.c. Taking the middle of the three fractions, their molecular weight distributions were made narrower as shown in *Figure 2*. The values of M_n and M_w/M_n of the fractionated polymers were also listed in *Table 1*. These polymers were purified thoroughly in the following manner. After precipitation into an excess of methanol and freeze-drying, they were further dried under high vacuum (1×10^{-3} Pa) for 12 h. PDMS exists, however, in a liquid state at room temperature. The polymer therefore still contains a small amount of impurities, probably methanol. The volatile impurities can be removed under high vacuum in a sealed glass apparatus which has two compartments connected with a tube for distillation. The polymer dissolved in THF was put into one compartment (A), and the THF solution of a purification reagent, disodium salt of α-methylstyrene tetramer in the other, (B). First, about half the amount of THF in compartment (A) was distilled into (B). In this process, part of the volatile impurities were distilled into (B), followed by trapping with the purification reagent. Then pure THF was distilled back from (B) to (A). Such a procedure was repeated at least three times. Finally, DPHL dissolved in THF was added dropwise to the THF solution of PDMS in (A). The addition of DPHL was stopped when a red colour appeared, indicating the presence of DPHL. The polymers used thus have sufficient purity for the subsequent anionic polymerizations.

Preparation of living polystyryl anion

For our purposes, we need constituent polymer blocks having as narrow molecular weight distributions as possible. The preliminary experiments on the anionic polymerization of styrene showed that we can obtain polymers having narrower molecular weight distributions in benzene rather than in THF. Benzene and

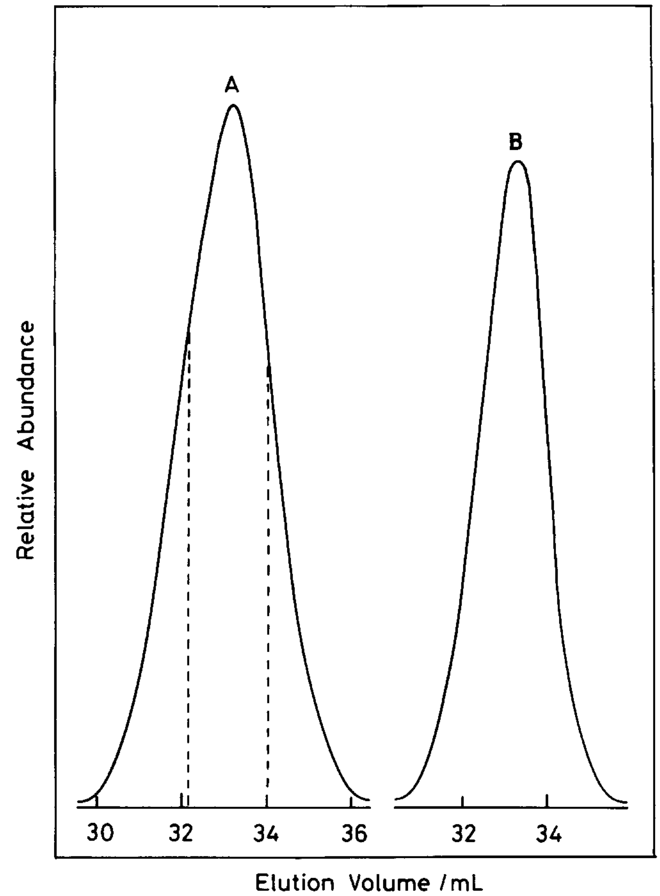


Figure 2 G.p.c. chromatograms of end-reactive PDMS before and after fractionation. Sample was PDMS(4). (A) As-polymerized, $M_n = 3.3 \times 10^4$, $M_w/M_n = 1.3_6$; (B) after fractionation, $M_n = 3.2 \times 10^4$, $M_w/M_n = 1.1_4$. Columns were two GMH6 combined in series. Carrier was THF at 298 K. Flow rate, 1 ml min^{-1}; concentration, 0.3 g dl^{-1}

Table 2 Preparation of living poly(styrene) with sec-butyllithium in benzene at 308 K[a]

Sample code	sec-BuLi (mmol)	St (mmol)	$10^{-4}M_k$[b]	$10^{-4}M_n$[c]	M_w/M_n[d]
PSt(2)	0.67	92	1.4	1.4	1.0_5
PSt(3)	0.34	104	3.2	3.1	1.0_4
PSt(4)	0.13	55	4.4	4.5	1.0_5

[a] Monomer concentration was about 6 w/v%

[b] M_k was calculated from the polymer yield and the ratio of amounts of monomer to initiator

[c] M_n was determined by osmometry

[d] M_w/M_n was estimated from the g.p.c. peak on the basis of standard poly(styrene) calibration curve

sec-BuLi[51,52] were used as solvent and initiator, respectively. The initiation reaction was carried out at 313 K, followed by propagation at 303 K. About one-third of the sample was removed for sample characterization and estimation of polymer yield, and the remainder was used for coupling with end-reactive PDMS. The results and the g.p.c. curves are shown in *Table 2* and *Figure 3*, respectively. The polymer yields were all quantitative. There is good agreement between M_n values determined by osmometry and those calculated from the monomer to initiator ratio. The g.p.c. curves indicate that all the polystyrene samples possess narrow molecular weight distributions.

Preparation of 3-component, 3-arm star-shaped copolymer

The conditions for the preparation of 3-component, 3-arm star-shaped copolymers are summarized in *Table 3*. To avoid production of poly(styrene-b-tert-butyl methacrylate), an excess amount of end-reactive PDMS was used in all runs. THF solution of poly(styryl) lithium showed as a yellow colour. When a THF solution of end-reactive PDMS was added, the colour changed immediately from yellow to deep red, showing the presence of diphenylmethyl anion. When the third monomer, TBMA, was added, the deep red colour disappeared immediately, showing an initiation reaction of TBMA. Such processes can be monitored clearly by g.p.c. chromatograms as shown in *Figure 4*. The three curves correspond to each of the first, second and third products. As the reaction stage proceeds, the main peak moves to the higher molecular weight side while the shoulder or small peak remains at the same position. These correspond to the residual, unreacted PDMS, which can be removed by fractionation using g.p.c. The third product was fractionated into three parts, and the middle fraction which contains the main peak was collected. The g.p.c. curve for the resultant polymer, S-ZH(444), fractionated from Star(4), is shown on the left in *Figure 5*. In the present synthetic method, a

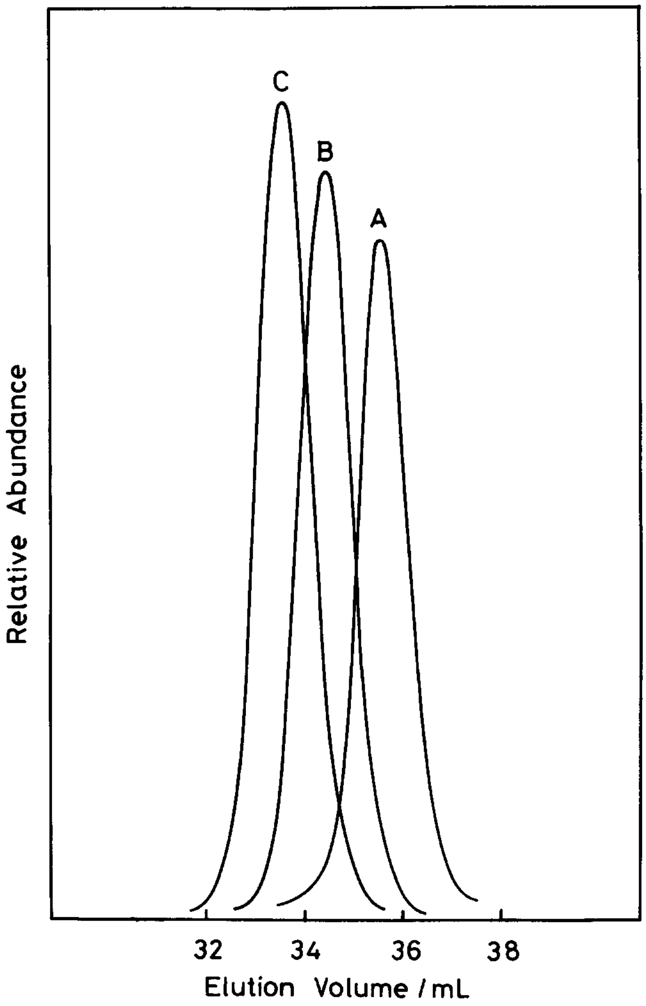


Figure 3 G.p.c. chromatograms of poly(styrene)s. (A) PS(2), $M_n = 1.4 \times 10^4$, $M_w/M_n = 1.0_5$; (B) PS(3), $M_n = 3.1 \times 10^4$, $M_w/M_n = 1.0_4$; (C) PS(4), $M_n = 4.5 \times 10^4$, $M_w/M_n = 1.0_5$ (see *Table 2*). The measurement conditions were the same as in *Figure 2*, except concentration was 0.1 g dl^{-1}

Table 3 Preparation of three-component, three-arm star-shaped copolymer in THF at 195 K[a]

Sample code	Living PSt[b]		Reactive PDMS[c]		TBMA[d] monomer		
	$10^{-4}M_n$[e]	(mmol)	$10^{-4}M_n$[e]	(mmol)	(mmol)	Conv. (%)	$10^{-4}M_k$[f]
Star(2)	1.4	0.13	2.0	0.14	18	100	2.0
Star(3)	3.1	0.063	3.2	0.069	12	100	2.7
Star(4)	4.5	0.13	3.2	0.16	42	100	4.6

[a] Initial concentration of living poly(styrene) was about 6 w/v%
[b] PSt; poly(styrene)
[c] PDMS; poly(dimethylsiloxane)
[d] TBMA; tert-butyl methacrylate
[e] M_n was determined by osmometry
[f] M_k of poly(TMBA) was calculated from the ratio of amounts of TBMA monomer to living poly(styrene)

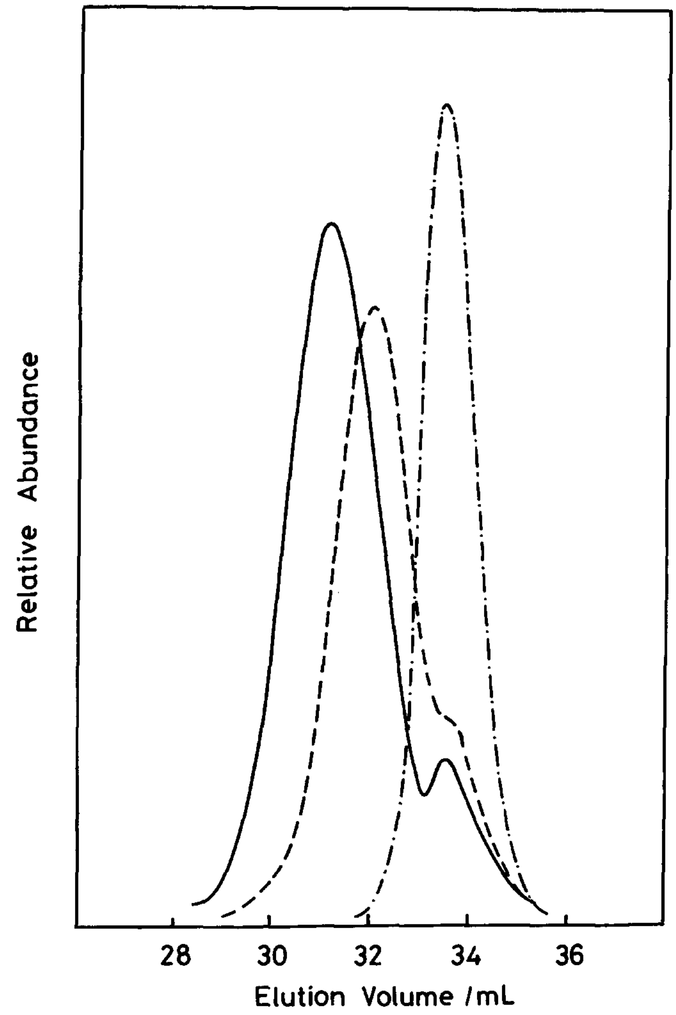


Figure 4 G.p.c. chromatograms of the first, second, and third products during preparation of 3-arm star-shaped copolymer. —·— PS(4); --- coupling product between PS(4) and end-reactive PDMS(4); —— product Star(4) after propagation of TBMA (see text). The measurement conditions were the same as in *Figure 2*, except concentration was 0.1 g dl^{-1}

star-shaped polymer having four or more than four branches can not be prepared. In the solid curve, furthermore, there is no peak or shoulder at the range of elution volume corresponding to PDMS (see curve B in *Figure 2*). The solid curve therefore corresponds to the objective, 3-arm star-shaped copolymer. The g.p.c. curve is fairly sharp and symmetrical, showing a fairly narrow molecular weight distribution. Similar curves were obtained for other samples as shown in *Figure 5*.

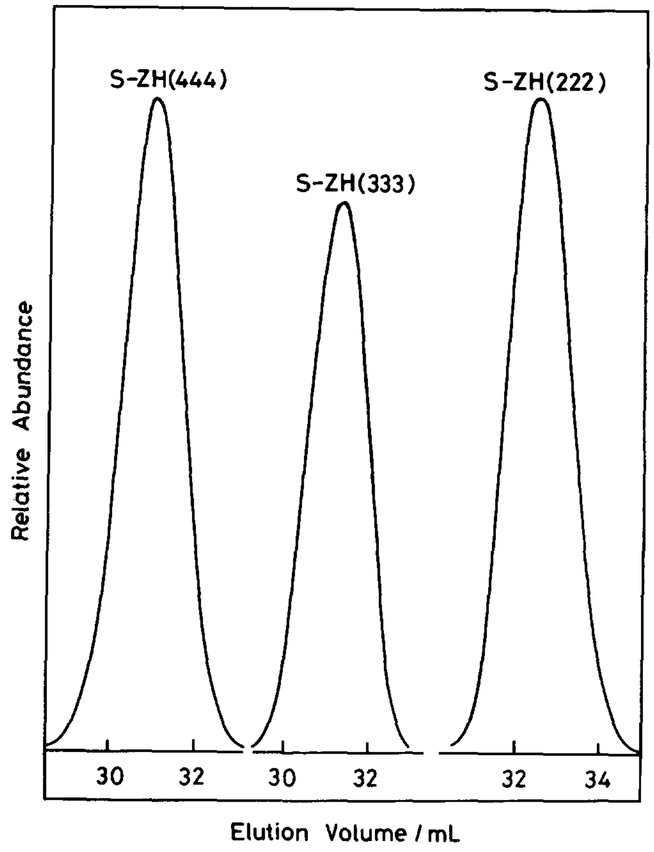


Figure 5 G.p.c. chromatograms of 3-component, 3-arm star-shaped copolymers S-ZH(444), S-ZH(333), and S-ZH(222) from left to right, respectively. The measurement conditions were the same as in *Figure 2*, except concentration was 0.1 g dl^{-1}

Figure 6 shows a ^{1}H-n.m.r. spectrum of S-ZH(444). All the peaks were assigned quantitatively. Other star-shaped samples showed similar spectra. The number-average molecular weight values of the samples were determined (by osmometry) to be 5.9×10^4, $1.0_0 \times 10^5$ and $1.3_5 \times 10^5$ for S-ZH(222), S-ZH(333) and S-ZH(444), respectively, which were obtained from Star(2), Star(3), and Star(4), respectively, by fractionation. The molecular weight of each constituent branch was estimated from the M_n value of star-shaped copolymer and the signal intensity ratio in ^{1}H-n.m.r. spectrum. Values thus determined are listed in *Table 4*. These values are in fairly good agreement with those of the starting poly(styrene), PDMS and M_k of PTBMA, respectively. This indicates that the reactions proceeded

Table 4 Characterization of three-component, three-arm star-shaped copolymers

Sample code	$10^{-4}M_n$(PSt)[a]	$10^{-4}M_n$(PDMS)[a]	$10^{-4}M_n$(PTBMA)[a]	$10^{-4}M_n$(Star)[b]
S-ZH(222)	1.6	2.2	2.1	5.9
S-ZH(333)	3.4	3.5	3.1	10_0
S-ZH(444)	4.9	3.5	5.1	13_5

[a] M_n of constituent branch was estimated from the M_n value of star-shaped copolymer and the signal intensity ratio in ^{1}H-n.m.r. spectrum
[b] M_n of star-shaped copolymer was determined by osmometry

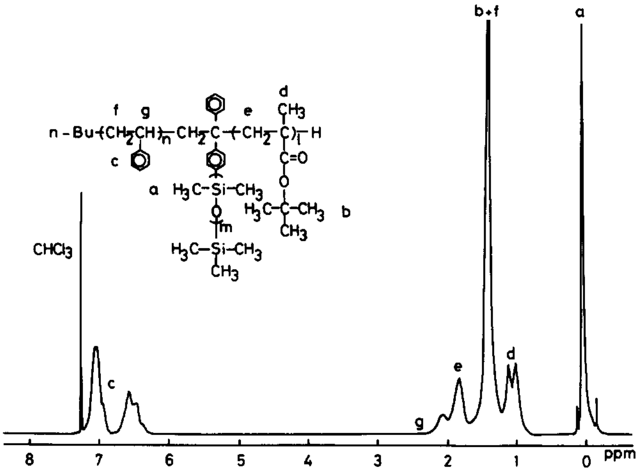


Figure 6 ^{1}H-n.m.r. spectrum of 3-component, 3-arm star-shaped copolymer S-ZH(444)

quantitatively. However, the M_n values of the branches are larger than those of the starting materials and PTBMA. This may be because the fractionation was carried out at a relatively higher molecular weight in order to remove the residual, unreacted PDMS completely.

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