Anionic polymerization of alkyl methacrylates and molecular weight distributions of the resulting polymers

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Anionic polymerizations of methyl methacrylate, n-butyl methacrylate and tert-butyl methacrylate with 1,1-diphenylhexyllithium in THF at 195 K were performed. By characterizing the resultant polymers, the controllable limits of molecular weight and molecular weight distribution were examined. Tert-butyl methacrylate gave a polymer with a high molecular weight (1.8×10^5) and narrow molecular weight distribution ($M_w/M_n = 1.0_7$). A well-defined block copolymer of tert-butyl methacrylate with styrene or α-methylstyrene was obtained by intermediate addition of 1,1-diphenylethylene.

(Keywords: poly(tert-butyl methacrylate); 1,1-diphenylhexyllithium; anionic polymerization; block copolymer; 1,1-diphenylethylene)

INTRODUCTION

Anionic polymerization offers a useful method to obtain a 'tailor-made polymer' having a definite molecular structure, predictable molecular weight and narrow molecular weight distribution[1–5]. In particular, anionic polymerization of a non-polar monomer such as styrene or α-methylstyrene is now fully established, while that for a polar monomer such as alkyl methacrylate is not so easy. This may be due to the following two reasons. (1) It is very difficult to completely remove impurities in the alkyl methacrylate monomer, since the monomer is too reactive to be purified by the reagents which are effective for non-polar monomers. (2) In the initiation or propagation process, the carbanion is involved not only in the conventional vinyl poly-addition but also in attacking the ester group. Various efforts have been made to overcome these difficulties[6–20].

From the viewpoint of macromolecular engineering, it is important to obtain a polymer having as high molecular weight and as narrow molecular weight distribution as possible. However, the reported values of molecular weights have been usually 2–3×10^4 and at most 1×10^5. In almost all cases, their molecular weight distributions were estimated by gel permeation chromatography (g.p.c.) on the basis of calibration with standard poly(styrenes). In some cases, standard poly(MMA)s were used[18]. This is, however, not satisfactory, since stereoregularity depends on the preparation conditions. Our opinion is that the molecular weight should be determined directly and the estimation of the molecular weight distribution by g.p.c. should be made on the basis of calibration with the polymers prepared under the same conditions.

The purpose of this study is to examine to what degree we can control the molecular weights and molecular weight distributions of alkyl methacrylates by anionic polymerization techniques. Block copolymerizations of alkyl methacrylates with styrene or α-methylstyrene are also studied.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA) and n-butyl methacrylate (NBMA) were obtained from Nakarai Tesque Inc. as GR grade and tert-butyl methacrylate (TBMA) from Tokyo Kasei Kogyo Co. Ltd as EP grade. They were treated with aqueous sodium hydroxide and then distilled under reduced pressure. Further purification of the monomers was carried out in all-glass apparatus equipped with break-seals under a pressure of 1×10^{-3} Pa or lower. After drying the monomers with calcium hydride, they were transferred into a vacuum apparatus and purified repeatedly with triethylaluminium[18]. Finally the monomers were redistilled in the presence of triethylaluminium and diluted to about 10 w/v% with purified tetrahydrofuran (THF) just prior to polymerization.

Styrene and α-methylstyrene were obtained from Nakarai Tesque Inc. as GR grade. They were first dried over calcium hydride under reduced pressure, then purified with octylbenzophenone sodium[21–23], and finally diluted to about 10 w/v% with purified THF.

An initiator, 1,1-diphenylhexyllithium (DPHL) was the reaction product between n-butyllithium (n-BuLi) and 1,1-diphenylethylene (DPE). n-BuLi was obtained from Nakarai Tesque Co. and diluted with purified n-heptane. DPE was purchased from Toyko Kasei Kogyo Co. Ltd and purified with triphenylmethyllithium.

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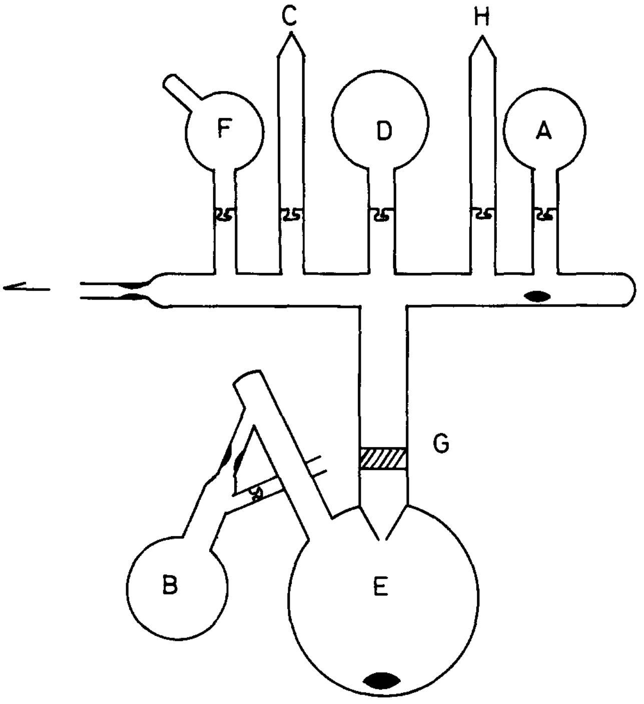

Figure 1 Schematic diagram of polymerization apparatus. Symbols are shown in the text

The reaction between n-BuLi and DPE was carried out in benzene at 273 K for 3 days in a glass-sealed apparatus under a pressure of 1×10^{-3} Pa. The concentration of the initiator was determined by titration with a standard HCl solution.

The THF used for the polymerization and the dilution of the alkyl methacrylate monomers was purified by distillation *in vacuo* (1×10^{-3} Pa) in the presence of the dipotassium salt of α-methylstyrene tetramer after the usual purification[24]. The benzene used for the dilution of the initiator and in the reaction between DPE and n-BuLi was purified by distillation *in vacuo* (1×10^{-3} Pa) in the presence of DPHL after the usual purification.

Polymerizations

Anionic polymerizations of various alkyl methacrylates were carried out in the apparatus shown in *Figure 1*. The apparatus was pumped to 1×10^{-3} Pa or lower and sealed. The whole apparatus was carefully washed with a benzene solution of DPHL in A, which can be recovered in vessel B. Any anion remaining on the glass wall was washed away with benzene which was directly distilled from the benzene solution of the washing reagent in B. Vessel B was then sealed off. Benzene solutions of DPHL in C and THF in D were introduced into the reaction vessel E. After the mixture had been kept at 195 K for about half an hour, THF solution of the monomer in F was added to the mixture in E. The diameter of the inlet nozzle was made small enough so that the monomer solution could be transferred in a shower-like manner. This was very effective for quick mixing. The glass filter G was included to prevent the nozzle from jamming with broken glass. Polymerization therefore starts homogeneously in the solution. After quenching with methanol in H, the polymers were precipitated into an excess of methanol. The purified polymers were freeze-dried from the benzene solution for 24 h.

Block copolymerizations of alkyl methacrylates with styrene or α-methylstyrene were carried out at 195 K in an apparatus similar to the one described above, in which styrene or α-methylstyrene was first allowed to polymerize. n-BuLi was used as an initiator and THF as the solvent. In the case of α-methylstyrene, the initiation reaction was made at 313 K. After the solution was kept at this temperature for 30 min, it was quickly moved into a dry ice–acetone bath. The reactions were continued for a few hours. The anionic polymerization of styrene or α-methylstyrene with n-BuLi has been confirmed to occur quantitatively[24–32], so an equimolar amount of DPE with n-BuLi was added to the solution of the living polymer. DPE was allowed to react with poly(styryl) or poly(α-methylstyryl) anion for 30 min, and then alkyl methacrylate monomer was added. The polymerization of alkyl methacrylate was carried out for a few hours and terminated with methanol. The purification procedures of the block copolymers were the same as in the poly(alkyl methacrylates).

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 an HLC type 803 instrument (Tosoh Ltd) with a refractive index detector and a set of two high-resolution columns GMH6 (600 mm length and 7.8 mm inner diameter). THF was used as eluent. The column set was calibrated with poly(alkyl methacrylates) having narrow molecular weight distributions which were obtained by fractionation of the polymers prepared in this study. Fractionation was carried out by g.p.c. at 298 K using an HLC type 837 fully automatic instrument (Tosoh Ltd) equipped with a set of three columns, two G4000H6 and one GMH6 (all of 600 mm length and 21.5 mm inner diameter). All runs for fractionation were carried out with chloroform. A sample amount of 1.5 g diluted into about 1 w/v% was normally used. All polymers in *Table 1* shown later were divided into three fractions and the central fraction was collected. The polymers thus obtained had narrow molecular weight distributions ($M_w/M_n \leq 1.0_3$). *Figure 2* shows an example of the g.p.c. chromatograms before and after fractionation. Steric regularity was determined from ^{1}H-n.m.r. spectra obtained at room temperature in $CDCl_3$ with a JEOL GX-270 FT n.m.r. spectrometer (270.05 MHz).

RESULTS AND DISCUSSION

Calibration of g.p.c. columns

Figure 3 shows the calibration curves for poly(MMA), poly(NBMA) and poly(TBMA). The curve for poly(TBMA) is higher than those for poly(MMA) and poly(NBMA). This may be because poly(TBMA) has a larger characteristic ratio than the others due to the steric effect of the tert-butyl group. In *Figure 3*, the calibration curve for standard poly(styrenes) is also shown by the fine line. This is entirely different from the others. It confirms that we must estimate average molecular weight or molecular weight distribution on the basis of calibration with the corresponding polymers, though this fact is well known. In this study, the molecular weight heterogeneity factor, M_w/M_n, listed in *Table 1* was estimated with the corresponding calibration curve in *Figure 3*.

Table 1 Anionic polymerization of methyl, n-butyl, and tert-butyl methacrylates with 1,1-diphenylhexyllithium in THF at 195 K

No.	DPHL (mmol)	Monomer Name	Monomer (mmol)	Conc. (%)	Time (min)	Conv. (%)	$10^{-4}M_k$[a]	$10^{-4}M_n$[b]	M_w/M_n[c]	f[d]
1	0.076	MMA[e]	75	2.7	13	100	9.9	12	1.0_9	0.83
2	0.076	MMA	75	4.7	13	96	9.5	11	1.0_8	0.83
3	0.059	MMA	87	4.1	13	100	14.7	23	1.2_8	0.64
4	0.16	NBMA[f]	49	2.9	60	100	4.3	4.5	1.2_3	0.96
5	0.11	NBMA	60	4.5	60	100	7.8	9.8	1.2_8	0.80
6	0.069	NBMA	53	3.1	80	100	10.9	15	1.1_9	0.73
7	0.13	TBMA[g]	57	4.0	150	100	6.2	6.8	1.0_8	0.91
8	0.043	TBMA	42	2.3	330	100	13.9	17	1.0_7	0.82
9	0.057	TBMA	57	3.8	40	98	13.9	18	1.0_7	0.77

[a] M_k was estimated from the polymer yield and the ratio of amounts of monomer to initiator
[b] M_n was determined by osmometry
[c] M_w/M_n was estimated from the g.p.c. peak on the basis of calibration with fractionated poly(alkyl methacrylate)
[d] Initiation efficiency f was estimated from the ratio of M_k to M_n
[e] MMA; methyl methacrylate
[f] NBMA; n-butyl methacrylate
[g] TBMA; tert-butyl methacrylate

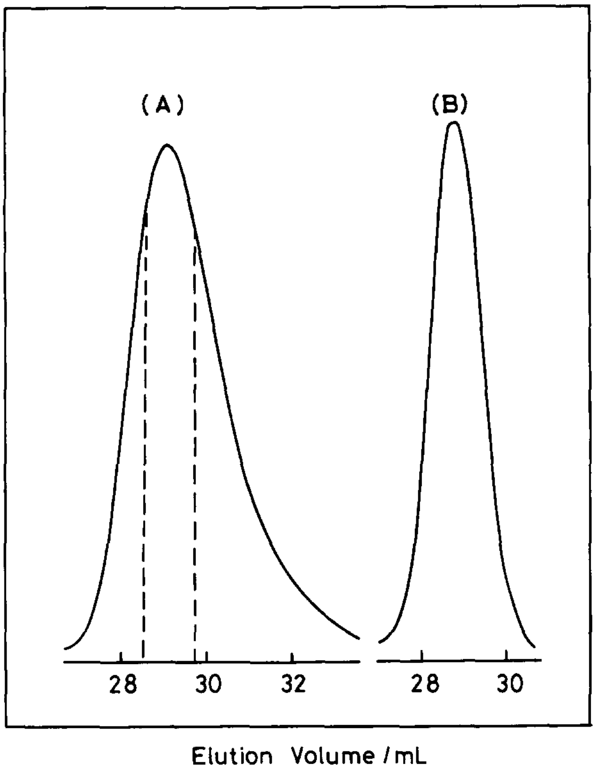

Figure 2 Comparison of g.p.c. chromatograms of the samples before and after fractionation. Sample was poly(MMA) (no. 3). (A) as-polymerized, $M_n = 2.3 \times 10^5$, $M_w/M_n = 1.2_8$, and (B) after fractionation, $M_n = 2.5 \times 10^5$, $M_w/M_n = 1.0_3$. Columns were two GMH6 combined in series. Carrier was THF at 298 K. Flow rate, 1 ml min^{-1}; concentration, 0.1 g dl^{-1}

Anionic polymerizations of alkyl methacrylates

Purification of three types of monomer, MMA, NBMA, TBMA, was carried out with triethylaluminium, which has been reported to be most effective for elimination of impurities in the monomers[18].

In anionic polymerizations of alkyl methacrylates, as already mentioned, the main unfavourable side-reaction is the attack of carbanion on the ester group of the monomer yielding a vinylketon[5]. To prevent this side reaction, an initiator having a bulky side group is desirable. So we selected 1,1-diphenylhexyllithium as an initiator. The polymerization temperature was set at 195 K to make the carbanion of alkyl methacrylate as stable as possible.

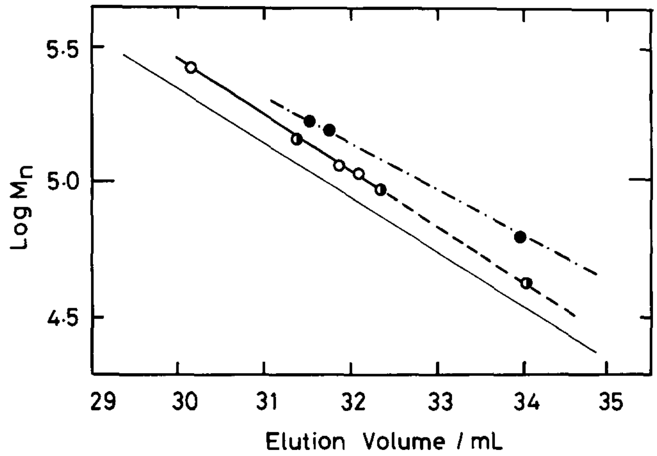

Figure 3 Calibration curves for poly(alkyl methacrylates) and standard poly(styrene). —— and ○, poly(MMA); — — — and ◑, poly(NBMA); — · — and ●; poly(TBMA); ——, standard poly(styrene)

The results of anionic polymerizations of alkyl methacrylates are summarized in *Table 1*. The g.p.c. chromatograms for poly(MMA), poly(NBMA) and poly(TBMA) are shown in *Figures 4–6*, respectively, where the chromatograms for samples 1 and 8 were omitted because of overlapping. The polymer yields were all quantitative. However, the initiation efficiency was less than one in all cases. So side reactions in the initiation step do not seem to be completely suppressed, if DPHL was used as initiator. The initiation efficiency for poly(NBMA) or poly(TBMA) is higher than that for poly(MMA). This may be due to the bulkiness of the ester group. By comparing the data for 1 and 2, we find that the initiation efficiency of DPHL towards MMA and the molecular weight distribution of poly(MMA) are independent of monomer concentration.

The g.p.c. chromatograms of these polymers were

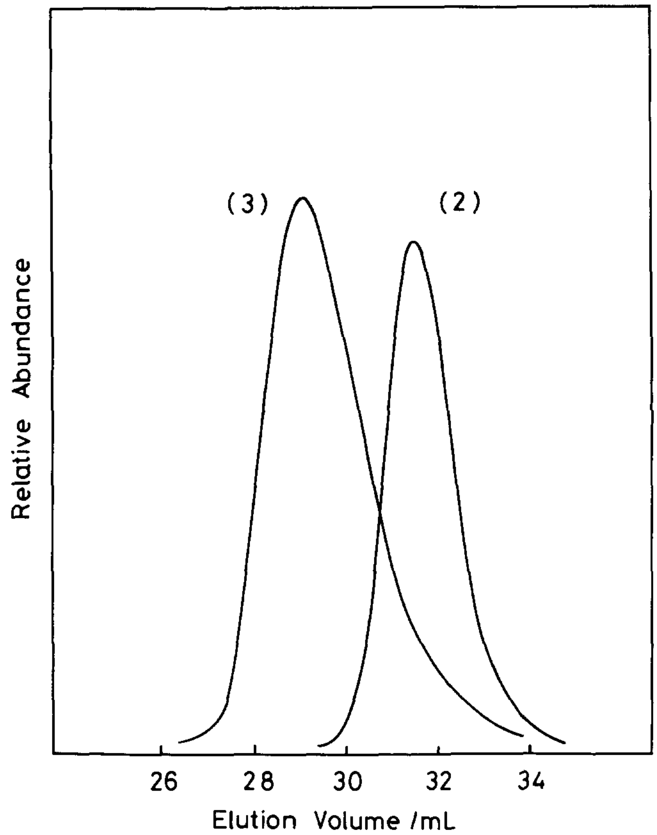

Figure 4 G.p.c. chromatograms of poly(MMA)s. (2) sample no. 2, $M_n = 1.1 \times 10^5$, $M_w/M_n = 1.0_8$, and (3) sample no. 3, $M_n = 2.3 \times 10^5$, $M_w/M_n = 1.2_8$ (see *Table 1*). Measurement conditions were the same as in *Figure 2*

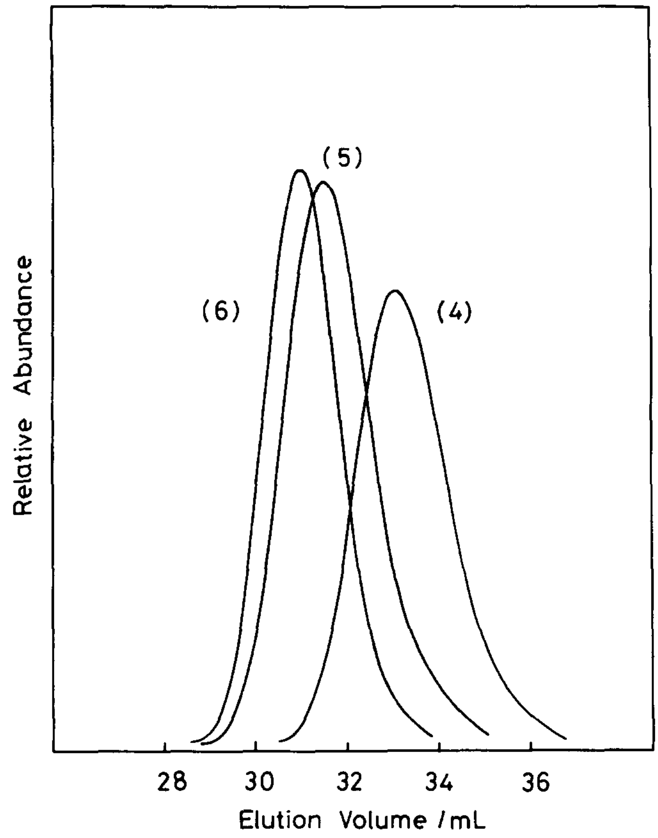

Figure 5 G.p.c. chromatograms of poly(NBMA)s. (4) sample no. 4, $M_n = 4.5 \times 10^4$, $M_w/M_n = 1.2_3$, (5) sample no. 5, $M_n = 9.8 \times 10^4$, $M_w/M_n = 1.2_8$, and (6) sample no. 6, $M_n = 1.5 \times 10^5$, $M_w/M_n = 1.1_9$ (see *Table 1*). Measurement conditions were the same as in *Figure 2*

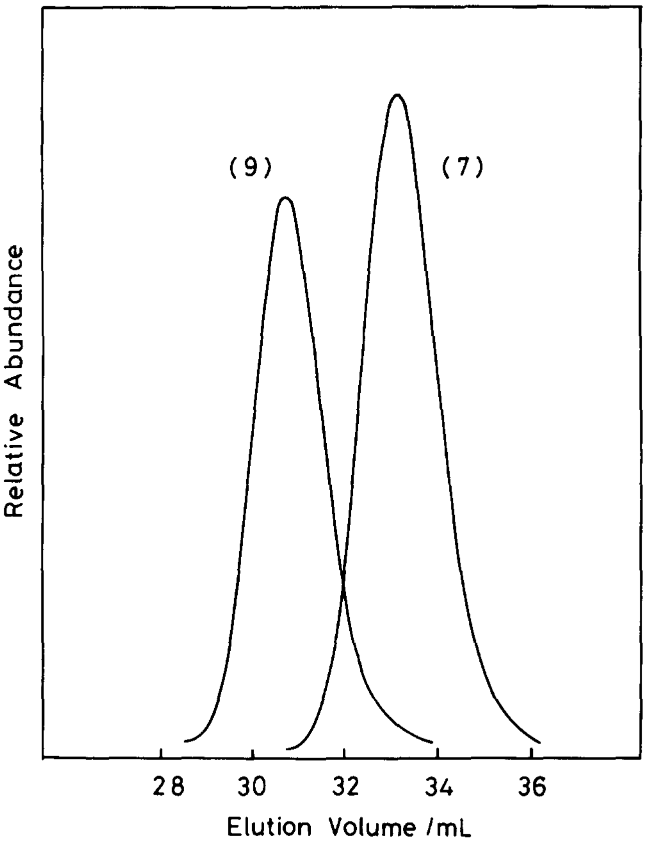

Figure 6 G.p.c. chromatograms of poly(TBMA)s. (7) sample no. 7, $M_n = 6.8 \times 10^4$, $M_w/M_n = 1.0_8$, and (9) sample no. 9, $M_n = 1.8 \times 10^5$, $M_w/M_n = 1.0_7$ (see *Table 1*). Measurement conditions were the same as in *Figure 2*

found to be fairly symmetric, though small tailing on the lower molecular weight side was observed. The values of the index M_w/M_n for these polymers were less than 1.1. However, we could not trace the result reported by Allen *et al.*[18] whose index was 1.0_5, though our estimation of the index is based on carefully fractionated poly(MMA)s having the same origin. When the monomer to initiator ratio was made large (sample 3), the g.p.c. chromatogram showed tailing on the lower molecular weight side. This may be because the polymerization rate of MMA is so fast that initiation or polymerization does not proceed homogeneously. So we can say that M_w/M_n for poly(MMA) can be controlled to be less than 1.1, if the molecular weight is less than 1×10^5.

In the case of NBMA (samples 4–6), their molecular weight distributions were rather broad, though their g.p.c. chromatograms were fairly symmetric. As a result, the n-butyl group does not seem to have such an effective protection effect on the side reactions.

In the case of TBMA, it can be expected that the rate of polymerization is fairly slow and attack by the active end on the ester group is suppressed, because of the bulkiness of the tert-butyl group. As expected, the g.p.c. chromatograms showed symmetric peaks. The values of M_w/M_n of poly(TBMA) could be controlled to be 1.0_7–1.0_8 up to a molecular weight of 1.8×10^5. In TBMA monomer, the rate of polymerization is not as fast. Therefore part of the initiator may be consumed by reaction with a small amount of impurities in the monomer during the spread of monomer into the THF solution of the initiator and the residual initiator may cause the polymerization. This may be why initiation efficiency decreases with increasing molecular weight but the value of M_w/M_n is still constant, 1.0_7–1.0_8.

Stereoregularity of poly(MMA) and poly(TBMA) is listed in *Table 2*. In this study, the polymerization solvent was THF, so the isotacticity of the polymers is very small. The syndiotacticity was very high in poly(MMA) but as low as about 50% in poly(TBMA). These values are consistent with those reported by Long *et al.*[19].

Block copolymerizations

The synthesis of block copolymers of TBMA and non-polar monomers such as styrene (St) or α-methylstyrene (α-MeSt) is very interesting from the following viewpoints. (1) This block copolymer is expected to exhibit controlled molecular weight, low compositional heterogeneity and narrow molecular weight distribution. (2) Upon saponification, the poly(TBMA) block may be converted into a polyacid and a resultant block copolymer becomes amphiphilic, consisting of hydrophilic and hydrophobic block chains. In the combination of TBMA and non-polar monomer, the latter monomer must be polymerized prior to TBMA. However, this could lead to side reactions. To avoid these side reactions, the excellent idea of intermediate addition of 1,1-diphenyl-ethylene has been proposed by Freyss *et al.*[33].

The results are summarized in *Table 3* and the g.p.c. chromatograms of the resultant block copolymers are shown in *Figure 7*. The block copolymerization products possess unimodal narrow molecular weight distributions. The compositions of block copolymers determined by ^{1}H-n.m.r. were almost the same as those calculated from the amounts of both monomers. The molecular weights of the polymers determined by osmometry were in agreement with those calculated from the ratio of monomer to initiator. These results show that the block copolymerizations proceed efficiently without termination reaction. If we compare poly(St-b-TBMA) and poly(α-MeSt-b-TBMA), the latter had a narrower molecular weight distribution than the former. This may be because poly(α-MeSt) has a narrower molecular weight distribution than poly(St), as is usually found[24–26].

The result for poly(α-MeSt-b-MMA) and the g.p.c. curve are also shown in *Table 3* and *Figure 7*, respectively. Here, the polymer yield was quantitative and the value of M_n of the polymer was in agreement with that of M_k. However, the g.p.c. curve was not symmetric and showed tailing on the lower molecular weight side. This tendency was consistent with that for homopolymerization of MMA.

CONCLUSION

The stabilized diphenylmethyl anion and bulky tert-butyl group was confirmed to be very effective in suppressing unwanted side-reactions. The controllable limits of

Table 2 Stereoregularity of poly(methyl methacrylate) and poly(tert-butyl methacrylate)

Polymer	Run no.	Tacticity^a (%) I	H	S
Poly(MMA)	2	0.3	19	80.7
Poly(TBMA)	8	3	49	48

^{a}Tacticity was calculated from ^{1}H-n.m.r. spectrum

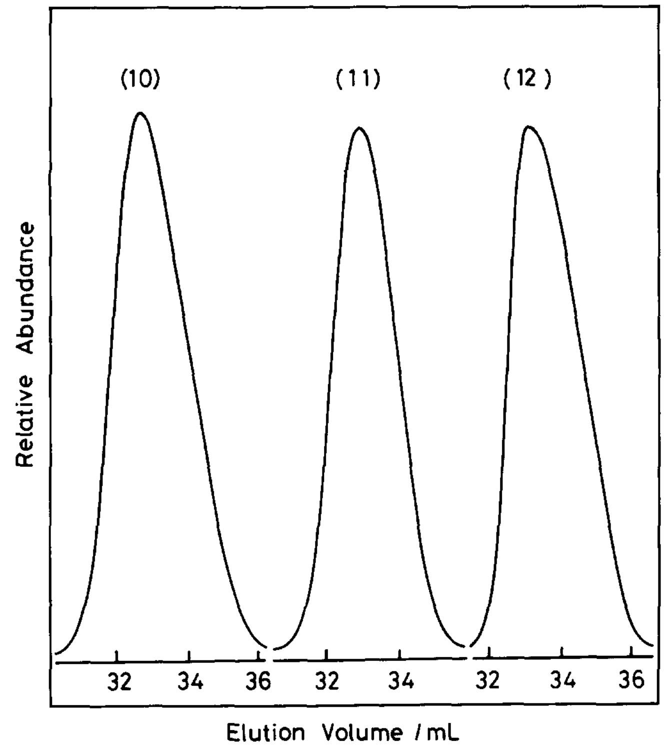

Figure 7 G.p.c. chromatograms of block copolymers. (10) sample no. 10, poly(St-b-TBMA), $M_n = 5.0 \times 10^4$, (11) sample no. 11, poly(α-MeSt-b-TBMA), $M_n = 4.3 \times 10^4$, and (12) sample no. 12, poly(α-MeSt-b-MMA). $M_n = 3.9 \times 10^4$ (see *Table 3*). Measurement conditions were the same as in *Figure 2*

Table 3 Block copolymerization of alkyl methacrylates with styrene or α-methylstyrene in THF at 195 K^a

	Monomer 1		Monomer 2		n-BuLi	Conv.		
No.	Name	(mmol)	Name	(mmol)	(mmol)	(%)	$10^{-4}M_k$^{b}	$10^{-4}M_n$^{c}
10	St^d	73	TBMA^f	51	0.29	100	5.1	5.0
11	α-MeSt^e	61	TBMA	51	0.35	100	4.1	4.3
12	α-MeSt	110	MMA^g	85	0.56	100	3.8	3.9

^{a}Initial concentration of monomer 1 was about 5 w/v%
^{b}M_k was estimated from the polymer yield and the ratio of amounts of monomer to initiator
^{c}M_n was determined by osmometry
^{d}St; styrene
^{e}α-MeSt; α-methylstyrene
^{f}TBMA; tert-butyl methacrylate
^{g}MMA; methyl methacrylate

molecular weight and molecular weight distribution in the anionic polymerization of MMA initiated with DPHL are 1×10^5 and 1.1, respectively. Those of poly(TBMA) are at least 2×10^5 and 1.0_7, respectively. Block copolymerization of TBMA with styrene or α-methylstyrene proceeds quantitatively by intermediate addition of 1,1-diphenylethylene.

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