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Preparation and Characterization of Telechelic Poly(methyl methacrylate). 1. Anionic Polymerization with an Initiator Derived from 4-[2-(*tert*-Butyldimethylsiloxy)ethyl]-α-methylstyrene

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ABSTRACT: Telechelic poly(methyl methacrylate) having a terminal OH and COOH group was prepared by anionic polymerization with the initiator made by the reaction between 4-[2-(*tert*-butyldimethylsiloxy)-ethyl]-α-methylstyrene and *n*-butyllithium, followed by termination with carbon dioxide and hydrolysis of the *tert*-butyldimethylsiloxy group. The resulting polymer was characterized by osmometry, GPC, ^{1}H NMR, and potentiometric titration. It was confirmed that the polymer was pure and had a fairly narrow molecular weight distribution.

Introduction

Acryl polymers such as poly(methyl methacrylate) [abbreviated poly(MMA)] have been used widely as resin for paint and varnish. This is because the polymers have high weathering resistance and high transparency.

Now, solvent-based paint is being replaced with a solvent-free powder one,[2,3] since organic solvents cause the serious problem of air pollution. The important factors of powder paints are the pour point and the glass-transition temperature of the resin, both of which depend on molecular weight.[4,5] Hence the polymers for powder paint should have narrow molecular weight distributions. To obtain a hard coating, we need polymers having reactive groups. In particular, α,ω-difunctional polymers, so-called telechelic polymers, are effective, since they can form a network structure through end-cross-linking.

The present objective is to prepare telechelic poly(MMA) having as narrow a molecular weight distribution as possible. We think the best way is to carry out an anionic polymerization of MMA using an initiator having a protected functional group followed by functional termination.[6,7] There are scarcely any reports on preparation of telechelic poly(MMA), though numerous telechelic polymers have been investigated.[6–14]

It is well-known that anionic initiators such as *n*-butyllithium (*n*-BuLi) make an attack not only on the vinyl group of MMA but also on the ester group.[15,16] The latter, unfavorable side-reaction is suppressed by using bulky carbanion instead of small one.[17–20] It is very interesting that the addition of lithium chloride has a beneficial effect on the living character of the poly(methyl methacrylate) anion.[21] From a practical point of view, however, this method may be unprofitable for our purpose, since it is not so easy to remove the added salt from the resulting polymer–salt mixture, and the residual salt, especially chlorine, may have an adverse influence upon coating. Incidentally, the α-methylstyrene derivative can be quantitatively metalized by alkyllithium through equilibrium oligomerization near or above the ceiling temperature.[22–28] It is relatively easy to purify monomers of the α-methylstyrene type because of their low ability to undergo thermal polymerization.[28] The *tert*-butyldimethylsilyl group has been found to be effective for the protection of the hydroxyl group in anionic polymerization.[29] Taking these facts and speculations into consideration, we have synthesized a new monomer, 4-[2-(*tert*-butyldimethylsiloxy)ethyl]-α-methylstyrene (I) which can react with *n*-BuLi to give an initiator (II).

The telechelic poly(MMA) is prepared through three steps: The first is an anionic polymerization of MMA with the initiator II. The second is introduction of a carboxyl group by the reaction between the living poly(methyl methacrylate) anion and carbon dioxide. The third is hydrolysis of *tert*-butyldimethylsiloxy group. Prior to preparation of the telechelic poly(MMA), α-methylstyrene (α-MeSt) was polymerized with the initiator II to check the initiation ability of II. In every step for the preparation of the telechelic poly(MMA), the resulting polymer and the number of end-functional groups were characterized.

Experimental Section

Initiators. Scheme I shows a synthetic route for the precursor of the initiator, 4-[2-(*tert*-butyldimethylsiloxy)ethyl]-α-methylstyrene (I). 4-Bromo-α-methylstyrene was synthesized from 4-bromoacetophenone and the Grignard reagent of methyl iodide through hydrolysis and dehydration in 92% yield.[28] 4-Bromo-α-methylstyrene (135 g, 0.685 mol) dissolved in tetrahydrofuran (THF, 400 mL) was added dropwise to magnesium turnings (24.9 g, 1.02 mol) under nitrogen gas and then stirred at 337 K for 3 h to give the Grignard reagent. Ethylene oxide (ca. 100 mL, 2.0 mol) dissolved in THF (100 mL) was added dropwise to the Grignard reagent of 4-bromo-α-methylstyrene and then stirred at 273 K for 3 h. 4-(2-Hydroxyethyl)-α-methylstyrene (56.3 g, 0.347 mol) obtained by hydrolysis was allowed to react with excess amounts of *tert*-butyldimethylchlorosilane (62.8 g, 0.417 mol) in dimethylformamide (500 mL) in the presence of imidazole (30.7 g, 0.451 mol) at 313 K for 5 h.[30] Fractional distillation of the product gave 85.0 g (0.307 mol, 45%) of I at 383–385 K (1.3×10^{-2} Pa). The overall yield was 41%. From the ^{1}H NMR spectrum, the final product was confirmed to be I: 270-MHz ^{1}H NMR ($CDCl_3$): δ 0.09 (s, 6 H, CH_3Si), 0.93 (s, 9 H, $(CH_3)_3CSi$), 2.20 (s, 3 H, $CH_3C{=}$), 2.28 (t, 2 H, $CH_2C_6H_4$), 3.87 (t, 2 H, CH_2O), 5.10, 5.40 (ss, 2 H, $CH_2{=}C{<}$), 7.21–7.44 (m, 4 H, C_6H_4).

The purification of I was carried out in an all-glass apparatus equipped with breakseals under a pressure of 1×10^{-3} Pa or lower. After being dried over calcium hydride, I was transferred into a vacuum apparatus and purified with *sec*-butylmagnesium bromide in three stages by distillation in vacuo.

The initiator II having a protected hydroxyl group was the reaction product between I and *n*-butyllithium (*n*-BuLi) in THF, as shown in Scheme II. In the case of the polymerization of

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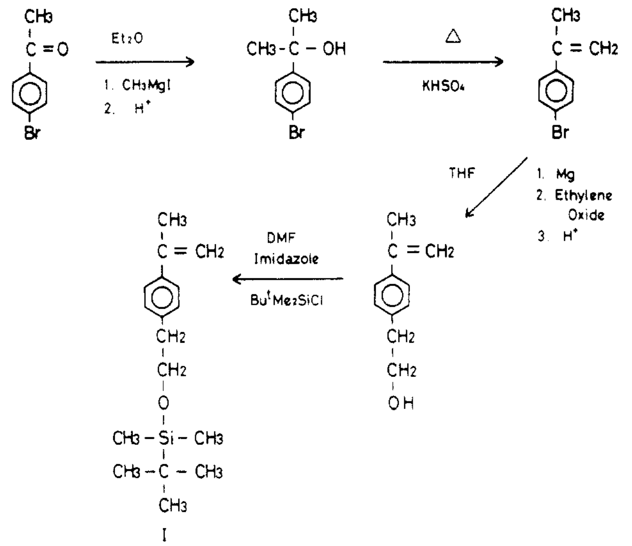
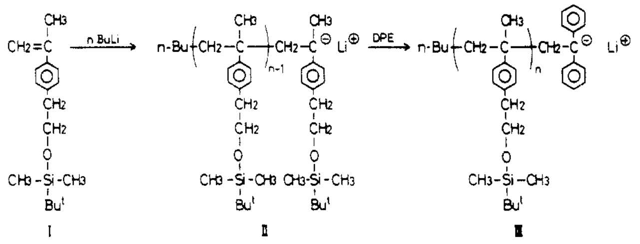
Scheme I
Synthetic Route for I



Scheme II
Preparation of Monofunctional Initiators II and III



MMA, initiator II was further allowed to react with 1,1-diphenylethylene (DPE) to give initiator III.

Monomers and Solvents. THF used for the preparation of the initiators and the polymerizations was purified in the same way as has been reported previously.[24,25]

Methyl methacrylate (MMA) and α-methylstyrene (α-MeSt) were obtained from Nakarai Tesque, Inc. as GR grades. These were purified by distillations with calcium hydride and the sodium salt of *n*-octylbenzophenone, respectively, after standard purification procedures.[28,31] The monomers were redistilled finally and diluted to about 10–20% v/v with purified THF just prior to polymerization. Carbon dioxide having a purity of 99.99% or higher was obtained from Takachiho Syoji Co. Ltd. The gas was packed in a glass ampule equipped with a breakseal.

n-BuLi was obtained from Nakarai Tesque, Inc. and diluted with purified *n*-hexane. DPE obtained from Tokyo Kasei Kogyo Co., Ltd. was first dried over calcium hydride and then purified in vacuo with the sodium salt of *n*-octylbenzophenone.

Polymerization. Anionic polymerizations of α-MeSt and MMA were carried out at 195 K in a sealed-glass apparatus under 1×10^{-3} Pa or lower, using essentially the same procedures as have been reported previously.[20] The carboxyl group at the chain end was introduced by the reaction of the living poly(MMA) with carbon dioxide at 195 K for 0.5 h. After being quenched with methanol, the poly(α-MeSt) and the poly(MMA) samples were precipitated from THF solutions into an excess of methanol and *n*-hexane, respectively. After being dried in vacuo, the samples dissolved in benzene were precipitated again for purification. The purified polymers were freeze-dried from the benzene solutions for 24 h.

Introduction of Carboxyl and Hydroxyl Groups. The lithium salt of the end-carboxylated poly(MMA) dissolved in benzene was acidified by being shaken with hydrochloric acid (0.1 N). The end-carboxylated poly(MMA) (abbreviated as C-PMMA) dissolved in acetone was purified by being precipitated into a mixture of methanol/water 1/2 in volume ratio).

Hydrolysis of the *tert*-butyldimethylsiloxy group of C-PMMA was carried out by hydrogen chloride bubbled in acetone for 2 h. Purification procedures were the same as for C-PMMA.

Molecular Characterization. Number average molecular weights, $\bar{M}_n$, and molecular heterogeneities, $\bar{M}_w/\bar{M}_n$, were tested by gel permeation chromatography (GPC) at 298 K using an HLC-803D instrument (Tosho Ltd.) equipped with refractive index (RI) and ultraviolet absorption (UV) detectors. The column was G3000H8 or GMH6 (Tosoh Ltd.). THF was used as an eluent. The columns were calibrated with standard poly(styrene)s.

The absolute values of $\bar{M}_n$ of poly(MMA), C-PMMA, and resulting telechelic poly(MMA) were determined by vapor pressure osmometry (VPO) in toluene at 343 K with a Corona type 117 instrument. In the measurement of VPO, the apparatus constant was determined with benzil and a standard poly(styrene) ($\bar{M}_n = 1.04 \times 10^4$, $\bar{M}_w/\bar{M}_n = 1.02$). When a polymer has carboxyl groups, a value of $\bar{M}_n$ determined by VPO might be higher than the real value due to association between carboxyl groups. To check the possibility of association between carboxyl groups, the molecular weight of 1-naphthylacetic acid was measured by VPO under the same conditions as above. The molecular weight was found to be 189, which was close to the formula weight of 186. This implies that the association between carboxyl groups at the chain ends hardly takes place under our conditions of measurement.

The average number of carboxyl groups at the chain end was estimated by potentiometric titration, using an electrometer (HIRANUMA COMTITE-8) with glass and Ag–AgCl electrodes. The sample was dissolved in a mixture of methyl isobutyl ketone/methanol 4/1 in volume ratio).[32] A titrant was potassium methoxide dissolved in a mixture of benzene/methanol (9/1 in volume ratio), obtained from WAKO Pure Chemicals Inc. Ltd.

^{1}H NMR spectra were obtained at room temperature in $CDCl_3$ or CD_2Cl_2 with a JEOL GX-270 FT-NMR spectrometer (270.05 MHz). Chemical shifts were referred to chloroform (7.25 ppm) or methylene chloride (5.35 ppm) in $CDCl_3$ or CD_2Cl_2, respectively. Steric regularity of the poly(MMA) samples was determined by the ^{1}H NMR spectra.

^{1}H NMR Measurements for the Thermodynamic Study. The sample solution used for the ^{1}H NMR measurements was prepared in a sealed-glass apparatus under 1×10^{-3} Pa or lower, using essentially the same procedures as have been reported previously.[28] Equilibrium concentrations of monomer I were measured at various temperatures ranging from 206 to 241 K with a Bruker AM-360 FT-NMR spectrometer (360.13 MHz): pulse repetition time, 13 s; accumulated scans, 16. Chemical shifts were referred to THF (3.60 ppm) in THF-d_8. The density of THF-d_8 at various temperatures was estimated in the same way as has been described in the preceding paper.[28]

Results

The result of the polymerization of α-MeSt with II is listed in Table I. The initiator used here was prepared at 298 K by transferring *n*-BuLi diluted with *n*-hexane and then THF into the polymerization vessel with stirring, followed by immediate addition of I. When I was added to *n*-BuLi dissolved in THF, the solution showed a red color, which remained unchanged. After being kept for 30 min at the given temperature, the apparatus was moved into a bath at 195 K, followed by addition of α-MeSt. The polymer yield was quantitative. The GPC peak of sample S-1 was single and very narrow, as shown in Figure 1. The molecular heterogeneity index, $\bar{M}_w/\bar{M}_n$ was estimated to be 1.0_4. The value of $\bar{M}_n$ was, however, considerably larger than that of the kinetic molecular weight, M_k, which is calculated from the ratio of the amounts of monomer to initiator. It is well-known that the initiation reaction proceeds quantitatively in α-MeSt/*n*-BuLi system.[24,25] Hence part of *n*-BuLi may be consumed wastefully. Two reasons may be considered for the consumption; (a) instability of *n*-BuLi in THF[33] and (b) a side-reaction such as cleavage of trialkylsilyl ether.[29] In the present work, the initiator II was prepared right after the *n*-BuLi was mixed with THF. Hence we consider that the latter is the main reason. If we take the values of $\bar{M}_n$ and M_k into consideration, about 80% of *n*-BuLi was estimated to be

Table I
Polymerization of α-MeSt with II in THF at 195 K

sample code	amt of *n*-BuLi, mmol	amt of I,[a] mmol	amt of α-MeSt, mmol	time, h	conc, %	conv, %	$10^{-4}M_k$	GPC $10^{-4}\bar{M}_n$	GPC $\bar{M}_w/\bar{M}_n$
S-1	0.27_0	0.40_5	$66._0$	1	4.7	100	2.9	16	1.0_4

[a] Reaction between *n*-BuLi and I was carried out at 298 K for 0.5 h.

Table II
Polymerization of MMA with II and III in THF[a]

sample code	amt of *n*-BuLi, mmol	amt of I,[b] mmol	amt of DPE,[c] mmol	amt of MMA, mmol	amt of THF, L	conv, %	$10^{-3}M_k$[d]	$10^{-3}\bar{M}_n$	GPC $10^{-3}\bar{M}_n$	GPC $\bar{M}_w/\bar{M}_n$	f[e]	tacticity[f] I	tacticity[f] H	tacticity[f] S
M-1	2.0_9	$10._0$		$87._9$	0.11	100	4.7		14	3.2_4				
MD-1	2.0_3	$10._5$	$11._3$	$97._2$	0.13	98	6.3	8.6	6.8	1.1_7	0.63	3	16	81
MD-2[g]	4.1_3	7.8_5	6.2_0	187	0.28	100	5.1	6.6	5.9	1.2_4	0.77	2	18	80

[a] Conditions of polymerization: temp, 195 K; time, 1–2 h. [b] Conditions of reaction: temp, 233 K (MD-1), 228 K (MD-2); time, 1 h. [c] Conditions of reaction: temp, 228–233 K; time, 0.5 h. [d] M_k was calculated from the polymer yield, the ratio of the amounts of MMA to *n*-BuLi, and the average numbers N_I and N_{DPE} in Table III. In estimating M_k of M-1, N_I was assumed to be the same as in MD-1. [e] Initiation efficiency: $f = M_k/\bar{M}_n$. [f] I, isotactic; H, heterotactic; S, syndiotactic. [g] End-carboxylated poly(MMA).

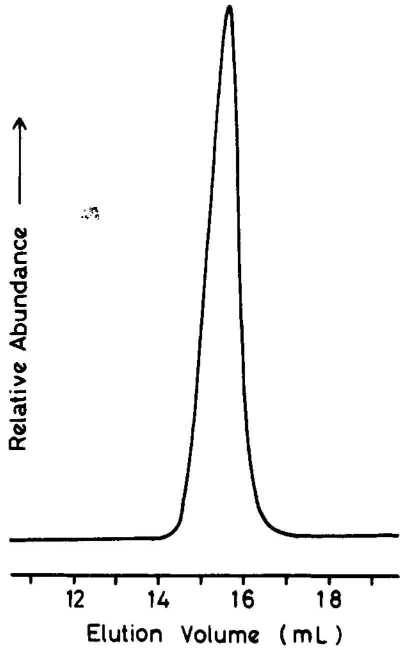


Figure 1. GPC chromatogram of poly(α-MeSt), S-1. Conditions: GMH6 column; carrier, THF at 298 K; flow rate, 1 mL/min; concentration, 0.1 g/dL; RI detector.

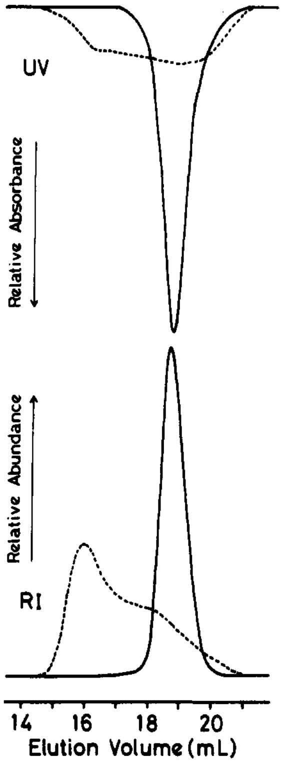


Figure 2. GPC chromatograms of poly(MMA)s: M-1 (broken curve) and MD-2 (solid curve). Conditions: GMH6 column; RI and UV (254-nm) detectors. Other measurement conditions were the same as in Figure 1.

consumed. Therefore the side-reaction may be suppressed at a lower temperature. In preparing poly(MMA), we made the reaction between *n*-BuLi and I at a lower temperature.

The results of the polymerization of MMA with II and III are shown in Table II. The values in stereoregularity of the resulting poly(MMA)s are also listed in Table II. When I was added to *n*-BuLi dissolved in THF at 228 K, the solution immediately showed a deep red color. The color remained unchanged, even after the temperature of the solution was maintained at 228 K for 1 h. When the monomer MMA was added to the solution at 195 K, the color immediately disappeared. The polymer yield of M-1 was quantitative, but the value of $\bar{M}_n$ was very large in comparison with that of M_k. Although the GPC chromatogram of M-1 was broad, as shown by the broken curve in Figure 2, the signals by refractive index and UV absorption at 254 nm were observed in the same range of elution volume. This shows the existence of the unit of monomer I in the sample M-1. Possibly, the carbanion of II was involved not only in the vinyl addition but also in attacking the ester group.[15,16] It is well-known that such an unfavorable side-reaction is fairly prevented by the use of (1,1-diphenylhexyl)lithium.[18,20]

In the cases of MD-1 and -2, DPE was allowed to react with II prior to polymerization of MMA. When DPE was added to a THF solution of II at 233 or 228 K, the deep red color became dark red. The polymer yields of MD-1 and -2 were quantitative. The values of $\bar{M}_n$ determined by VPO were larger than those of M_k, indicating the initiation efficiency, f, was less than 1. However, the values of f, 0.63–0.77, were consistent with the values obtained for the MMA/(1,1-diphenylhexyl)lithium system, 0.64–0.83.[20] Furthermore, the GPC chromatogram of MD-2 showed a single and fairly narrow peak, as shown by solid curve in Figure 2. MD-1 also showed a similar peak. We can say that MMA is polymerized successfully using the initiator III, as expected.

Figure 3a shows the ^{1}H NMR spectrum of sample MD-2. MD-1 also showed a similar spectrum. Signals at 0 and 3.6 ppm are assigned to the protons in CH_3–Si and CH_3–O, respectively. The average number of I units per

Table III
Characterization of Poly(MMA) Prepared with III

sample code	no. of I per molecule, N_I theor	no. of I per molecule, N_I found[b]	no. of DPE[a] per molecule, N_{DPE} theor	no. of DPE[a] per molecule, N_{DPE} found[b]	no. of carboxyl groups per molecule, N_C[c]
MD-1	5.2	1.6_6	5.6	1.0_0	
MD-2	1.9	1.0_9	1.5	0.9_8	0.97 ± 0.04

[a] 1,1-Diphenylethylene. [b] Determined by ^{1}H NMR. [c] Estimated from the total number of carboxyl groups measured by potentiometric titration, the value of $\bar{M}_n$ determined by VPO, and the weight of the sample.

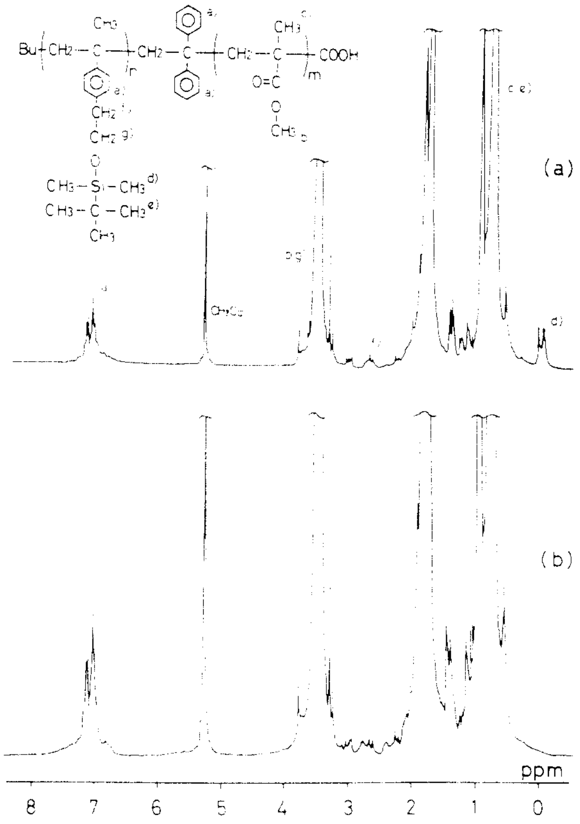


Figure 3. ^{1}H NMR spectra of poly(MMA), MD-2: (a) acidified and (b) deprotected. The solvent was CD_2Cl_2.

molecule, N_I, can be estimated from the relative intensity of these signals and the value of $\bar{M}_n$ determined by VPO. The number of DPE units per molecule, N_{DPE}, also can be estimated by the use of the relative intensity of the signals at 6.5–7.5 ppm due to phenyl protons, the values of $\bar{M}_n$ by VPO, and N_I. These values are listed in Table III. The values of N_I were larger than unity but smaller than the values expected from the ratio of amounts of I and *n*-BuLi. Hence, part of monomer I remained in the solution. This is, however, not a serious problem, because the poly(methyl methacrylate) anion is known not to react with styrene or α-MeSt derivatives.[34,35] Important is the existence of I in the polymer. The values of N_{DPE} were unity in the experimental error as expected.

In sample MD-2, the poly(methyl methacrylate) anion was allowed to react with carbon dioxide before quenching. The average number of carboxyl groups per molecule, N_C, was estimated from the total number of carboxyl groups determined by potentiometric titration, as shown in Figure 4, the value of $\bar{M}_n$ by VPO, and the weight of the sample. The value of N_C was unity in the experimental error as shown in Table III.

Figure 3b shows the ^{1}H NMR spectrum of sample MD-2 after deprotection of the blocking group in I. It is clear that only the signal at 0 ppm assigned to CH_3–Si disappears, showing complete elimination of the *tert*-butyldimethylsilyl group. Parts a and b of Figure 5 show the GPC chromatograms of MD-2 before and after deprotection, respectively. The shape of the curve of the sample after deprotection was not different from that before deprotection. Furthermore, the value of $\bar{M}_n$ of deprotected MD-2 was determined to be 6.7 × 10^3 by VPO, showing no change in the degree of polymerization within experimental error. These facts suggest that no cleavage occurred in the main chain through the hydrolysis of the *tert*-butyldimethylsiloxy group.

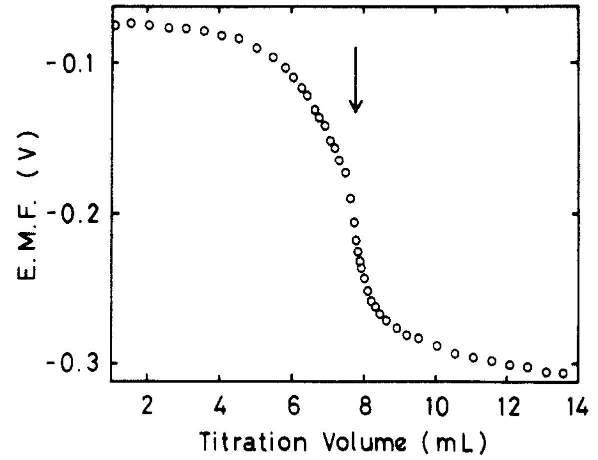


Figure 4. Potentiometric titration curve. The sample was end-carboxylated poly(MMA), MD-2. The conditions of measurement are described in the text. The arrow shows the equivalence point.

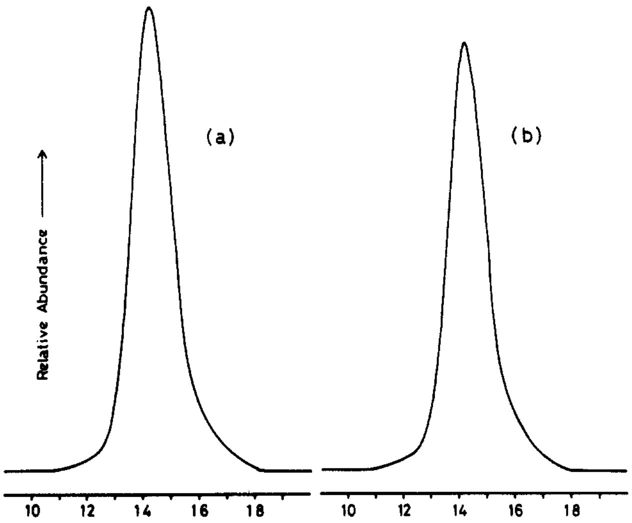


Figure 5. GPC chromatograms of telechelic poly(MMA), MD-2; (a) before and (b) after deprotection. Conditions: G3000H8 column; RI detector. The measurement conditions were the same as in Figure 2.

These results confirm that the resulting polymer has a hydroxyl group at one end of the chain and a carboxyl group at the other end. It may be concluded that we have prepared successfully a telechelic poly(MMA) having carboxyl and hydroxyl groups.

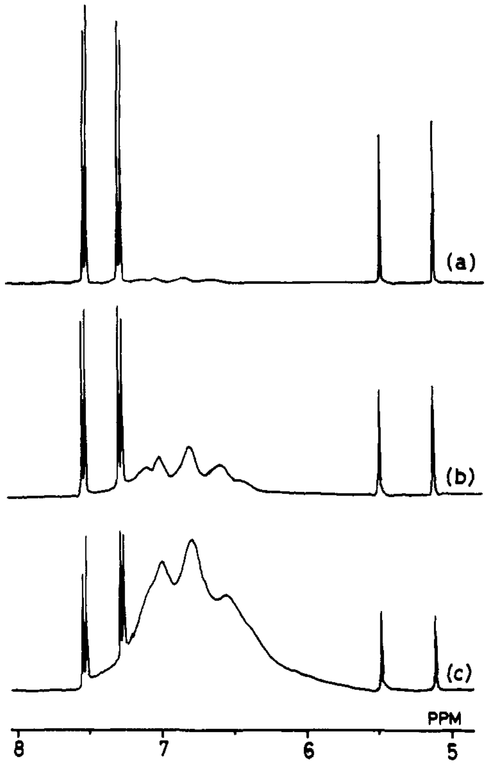


Figure 6. Examples of ^{1}H NMR spectra of the living poly(I) in THF-d_8 at the equilibrium states: (a) 241 K; (b) 226 K; (c) 206 K.

Discussion

A number of studies have been reported on the equilibrium polymerization of α-MeSt[22-25] or α-MeSt type monomers,[26-28] where no propagation reaction occurred at a temperature above the ceiling temperature, T_c. Monomer I is an α-MeSt type of monomer. Hence, I may have a nature of equilibrium polymerization. Figure 6 shows examples of the ^{1}H NMR spectra at equilibrium states of the THF-d_8 solution of living poly(I) initiated with n-BuLi. Signals at 5.1 and 5.4 ppm are assigned to olefin protons in the monomer, split ones at 7.2–7.4 ppm to phenyl protons in the monomer, and broad ones at 6.0–7.5 ppm to phenyl protons in the polymer. The relative intensity changes with the temperature. The broad signals of the phenyl protons became smaller and the sharp ones of the olefin protons became larger with increasing temperature. This suggests equilibrium polymerization of I, which may control N_I of the telechelic PMMA.

The equilibrium concentration of monomer I, $[I]_e$, is given by

$$[I]_e = (2I_o/I_p)[I]_0 \qquad (1)$$

where I_0 and I_p are the relative intensity of the signals of olefin and phenyl protons, respectively, and $[I]_0$ is the initial concentration of the monomer I. Plots of ln $[I]_e$ vs the reciprocal temperature are shown in Figure 7,where a good linear relationship is observed. The relationship between $[I]_e$ and thermodynamic parameters can be expressed by

$$\ln [I]_e = \Delta H_{ss}/RT - \Delta S_{ss}/R \qquad (2)$$

where ΔH_{ss} is the heat of polymerization, ΔS_{ss} the corresponding entropy for a 1 mol L^{-1} solution, and R the gas constant. Hence, ΔH_{ss} and ΔS_{ss} in THF-d_8 are estimated to be -7.8_8 kcal mol^{-1} and $-2.8_1 \times 10$ cal mol^{-1} K^{-1}, respectively. The ceiling temperature, T_c (=$\Delta H_{ss}/\Delta S_{ss}$), for a 1 mol L^{-1} solution in monomer is calculated to be 278 K.

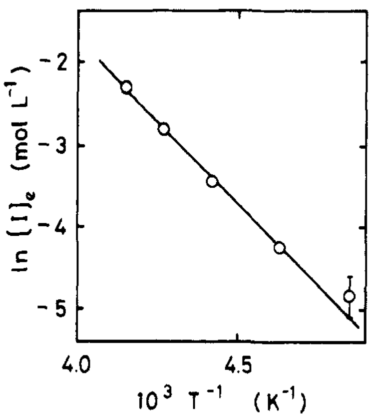


Figure 7. Semilogarithmic plots of the equilibrium monomer concentration $[I]_e$ against T^{-1} for the polymerization of I with n-BuLi in THF-d_8.

Initiator III for sample MD-1 was prepared at 233 K. If we assume the values of thermodynamic parameters in THF are equal to those in THF-d_8, the value of N_I is estimated to be 1.6, which agrees well with the value observed, 1.6_6. When initiator III for MD-2 was prepared, the initial concentration of I was 0.028 mol L^{-1}. The corresponding T_c for the solution is estimated to be 224 K. Thus the reaction between n-BuLi and I for MD-2 was carried out above the corresponding T_c. This is the reason for N_I of MD-2 being nearly 1. Therefore we may conclude that the values of N_I much smaller than the theoretical ones are due to the nature of the equilibrium polymerization of I.

The values of ΔH_{ss} and ΔS_{ss} for α-MeSt derivatives having a bulky substituent such as isopropyl,[26] *tert*-butyl,[27] and bis(diethylamino)phosphino groups[28] have been reported to be smaller than those for α-MeSt[23] (typically, $\Delta H_{ss} = -8.0_2$ kcal mol^{-1} and $\Delta S_{ss} = -28._8$ cal mol^{-1} K^{-1}). This has been attributed to a steric effect of the bulky substituent. The corresponding values for I are close to those for α-MeSt, though I has a bulky substituent, *tert*-butyldimethylsilyl. This may be because the steric effect of the *tert*-butyldimethylsilyl group is diminished by the spacer of the oxyethylene group.

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Registry No. I, 120848-81-9; II, 143106-00-7; α-MeSt (homopolymer), 25014-31-7; BrC_6H_4-*p*-$C(CH_3)=CH_2$, 6888-79-5; $HO(CH_2)_2C_6H_4$-*p*-$C(CH_3)=CH_2$, 116656-77-0; $Me_2ClSiBu$-*t*, 18162-48-6; BuLi, 109-72-8; ethylene oxide, 75-21-8.