Preparation of α-hydroxy-ω-carboxy-poly(methyl methacrylate) by anionic polymerization: 1. Utilization of initiator derived from 1-[4-(2-tert-butyldimethylsiloxy)ethyl]phenyl-1-phenylethylene

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α-Hydroxy-ω-carboxy-poly(methyl methacrylate) was prepared by anionic polymerization with an initiator obtained by the reaction between 1-[4-(2-tert-butyldimethylsiloxy)-ethyl]phenyl-1-phenylethylene and n-butyllithium, followed by termination with carbon dioxide and hydrolysis of tert-butyldimethylsilyl ether. The resulting polymer was found to be pure and to have a fairly narrow molecular weight distribution.

(Keywords: telechelic polymer; anionic polymerization; 1-[4-(2-tert-butyldimethylsiloxy)ethyl]phenyl-1-phenylethylene; poly(methyl methacrylate); n-butyllithium)

Introduction

Anionic polymerization has offered various telechelic polymers having predictable molecular weights and sharp molecular weight distributions[1]. There have, however, been scarcely any reports on the preparation of telechelic polymers of polar monomers such as methyl methacrylate (MMA), except that prepared by group transfer polymerization[2]. Furthermore, all the telechelic polymers had the same functional groups at both chain ends. Thus the reported telechelic polymers have been limited to non-polar and symmetrical ones.

In this communication, we report the preparation of an unsymmetrical telechelic poly(methyl methacrylate) (PMMA), α-hydroxy-ω-carboxy–PMMA, by anionic polymerization. In preparing telechelic polymers, in general, it is important to confirm the existence of functional groups at both chain ends. Such a check is easy in the present polymer, because the successive introduction of the functional groups can be tested in a step-by-step fashion. Furthermore, the present polymer has the industrial advantage of the ability of direct coupling.

There are three problems in preparing the objective polymer: (a) suppression of an attack of the initiator onto the ester group of MMA; (b) introduction of the α-functional group; and (c) introduction of the ω-functional group. The first problem can be overcome by the use of a diphenylmethyl-type anion as initiator[3–6]. The second may be solved by the use of a protected functional group attached to the initiator[7–9]. As regards the third, we have experimentally confirmed that a carboxyl group can be introduced by the reaction between poly(methyl methacryloyl) anion and carbon dioxide[10]. Taking these facts and speculation into consideration, we use a diphenylhexyl lithium derivative having protected hydroxyl group as initiator and carbon dioxide as terminator. In this study, the protecting group is the tert-butyldimethylsilyl. The efficiency of other protecting groups will be discussed in a subsequent paper.

Experimental

1-[4-(2-tert-Butyldimethylsiloxy)ethyl]phenyl-1-phenylethylene (**1**) was prepared in the following way.

4-Bromobenzene (64.1 g, 0.408 mol) in tetrahydrofuran (THF) (200 ml) was added dropwise to magnesium turnings (10.9 g, 0.448 mol) at 337 K under N_2 gas and then stirred at the same temperature for 3 h to give the Grignard reagent. *p*-Bromoacetophenone (65.0 g, 0.327 mol) in THF (200 ml) was added to the Grignard reagent while cooling in an ice bath and then stirred at 313 K for 2 h. Hydrolysis of the product with 1 N HCl gave 1-(4-bromo)phenyl-1-phenylethanol, which was then dehydrated at 483 K under vacuum (1×10^2 Pa) in the presence of potassium hydrogen sulfate (5 g). Fractional distillation of the product gave 67.2 g (0.259 mol) of 1-(4-bromo)phenyl-1-phenylethylene (DPE-Br) at 393–394 K (1×10^2 Pa). The yield was 79% on the basis of *p*-bromoacetophenone.

DPE-Br (67.2 g) dissolved in THF (200 ml) was added dropwise to magnesium turnings (6.9 g, 0.284 mol) at 337 K and then refluxed for 2 h to give the Grignard reagent. Ethylene oxide ($\sim$25 ml) dissolved in THF (20 ml) was added dropwise to the Grignard reagent at 273 K and then stirred at 293 K for 3 h. After hydrolysis, the distillation of the product gave 37.2 g (0.166 mol) of 1-[4-(2-hydroxyethyl)]phenyl-1-phenylethylene (DPE-OH) under a pressure of $\leqslant 1$ Pa at a bath temperature of 483 K. The yield was 64% on the basis of DPE-Br.

DPE-OH was allowed to react with tert-butyldimethylsilyl chloride in the presence of imidazole[11] to give **1**. The crude product was purified in an all-glass apparatus equipped with breakseals under a pressure of $\leqslant 1 \times 10^{-3}$ Pa. After being transferred into a vacuum apparatus, the product was fractionally distilled in the presence of sec-butylmagnesium bromide at a bath temperature of 463 K to give pure **1** in 88% yield from DPE-OH: 270 MHz ^{1}H n.m.r. ($CDCl_3$) 0.09 (s, 6H, CH_3–Si), 0.93 (s, 9H, CH_3–C), 2.88 (t, 2H, $-CH_2-C_6H_4$), 3.88 (t, 2H, $-CH_2$–O), 5.43 (d, 2H, $CH_2{=}C$), 7.2 (m, 9H, C_6H_4, C_6H_5). The overall yield was 45%.

The product **1** was allowed to react with n-butyllithium

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(n-BuLi) in pure THF at 233 K for 1 h under a pressure of $\leqslant 1 \times 10^{-3}$ Pa to give the initiator (**2**). The reaction was carried out in a sealed-glass apparatus by essentially the same procedures as those reported previously[6,10].

Living anionic polymerization of MMA in THF was performed at 195 K for 1 h in a sealed-glass apparatus under a pressure of $\leqslant 1 \times 10^{-3}$ Pa by essentially the same procedures as those reported previously[6,10]. The carboxyl group at the chain end was introduced by the reaction of the living poly(methyl methacryloyl) anion with carbon dioxide at 195 K for 0.5 h. After being quenched with methanol, the PMMA sample was precipitated from THF solution into an excess of n-hexane. The polymer was purified by reprecipitation in benzene/n-hexane system, and then freeze-dried from benzene from 24 h. The lithium salt of the end-carboxylated PMMA was acidified with 0.1 N hydrochloric acid. Hydrolysis of the terminal tert-butyldimethylsilyl ether was carried out in acetone at 298 K for 2 h by bubbling hydrogen chloride gas.

The number average molecular weight, $\bar{M}_n$, and the molecular weight distribution, $\bar{M}_w/\bar{M}_n$, of the polymer were measured by gel permeation chromatography (g.p.c.) at 298 K using a Tosoh HLC-803D instrument equipped with refractive index (r.i.) and ultraviolet (u.v.) absorption detectors. The column was a Tosoh G3000H8. THF was used as an eluent. The column was calibrated with standard polystyrenes. The absolute values of $\bar{M}_n$ were determined by vapour pressure osmometry (v.p.o.) in toluene at 343 K with a Corona type 117 instrument; the apparatus constant was determined with a standard polystyrene ($\bar{M}_n = 1.04 \times 10^4$, $\bar{M}_w/\bar{M}_n = 1.02$). It was experimentally confirmed that association between carboxyl groups at chain ends hardly took place under our measurement conditions[10].

Potentiometric titration was carried out to estimate the number of the carboxyl group at the chain end, using a Hiranuma Comtite-8 electrometer with glass and Ag–AgCl electrodes. The sample was dissolved in a mixture of methylisobutylketone/methanol in 4/1 volume ratio[12]. A titrant was potassium methoxide dissolved in a mixture of benzene/methanol in 9/1 volume ratio, (Wako Pure Chemicals).

^{1}H n.m.r. 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) in $CDCl_3$ and methylene chloride (5.35 ppm) in CD_2Cl_2.

Results and discussion

The result of the polymerization of MMA is shown in *Table 1*. The tacticity of the resulting polymer was estimated from its ^{1}H n.m.r. spectrum to be 3% isotactic, 13% heterotactic, and 84% syndiotactic, consistent with the values reported previously[6,10]. When **1** was added to n-BuLi dissolved in THF at 233 K, the solution showed a dark red colour which remained unchanged for 1 h at that temperature but disappeared immediately upon addition of MMA. The living end of the PMMA was allowed to react with carbon dioxide before quenching. The polymer yield was quantitative. The $\bar{M}_n$ was close to the kinetic molecular weight, $\bar{M}_k$, which is calculated from the polymer yield, the molar ratio of monomer to n-BuLi, and the average number of **1** units per molecule, as will be mentioned later. This means that addition of n-BuLi on the double bond of **1** proceeded quantitatively. This result is consistent with that observed in the reaction between n-BuLi and 4-[2-(tert-butyldimethylsiloxy)ethyl]-α-methylstyrene[10]. Under our experimental conditions, therefore, there is no side-reaction such as cleavage of the trialkylsily group as reported by Hirao *et al.*[13].

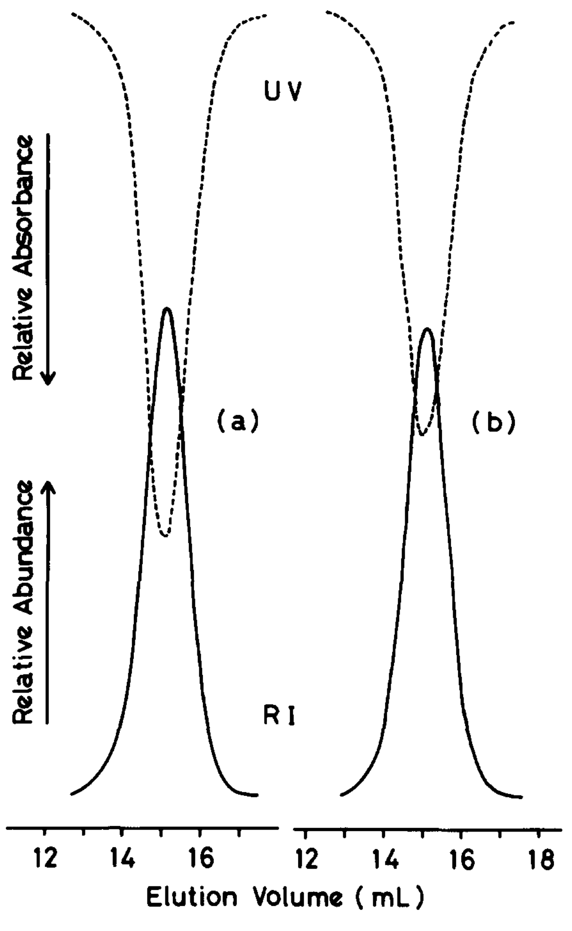

Figure 1 G.p.c. chromatograms of the telechelic PMMA: (a) before and (b) after deprotection. Column, G3000H8; carrier, THF at 298 K; flow rate, 1 ml min^{-1}; concentration, 0.1 g dl^{-1}; detector, r.i. (——) and u.v. (---, 254 nm)

Table 1 Polymerization of MMA with **2** in THF[a]

n-BuLi (mmol)	**1** (mmol)	MMA (mol)	Conversion (%)	$10^{-3} \times M_k$	V.p.o. $10^{-3} \times M_k$	G.p.c. $10^{-3} \times M_n$	G.p.c. M_w/M_n	N_1 Si–CH_3[b]	N_1 Phenyl[c]	N_c
2.2_6	4.1_3	0.10_6	100	5.1	4.6	5.2	1.2_9	1.0_7	0.9_5	1.01 ± 0.04

[a] Condition of polymerization: temperature 195 K; time 1 h; concentration of monomer 6.5%
[b] Estimated from the ^{1}H n.m.r. signal intensity ratio of the Si–CH_3 to the methoxy protons
[c] Estimated from the ^{1}H n.m.r. signal intensity ratio of the phenyl to the methoxy protons

The g.p.c. chromatogram of the polymer (*Figure 1a*) shows a single and fairly narrow peak, indicating a successful living polymerization of MMA with initiator **2**.

Figure 2a shows the ^{1}H n.m.r. spectrum of the polymer. The signals at 0, 3.6 and 7.0–7.5 ppm are assigned to the CH_3–Si, methoxy and phenyl protons, respectively. The weak signal appearing near 2.7 ppm is due to the CH_2–C_6H_4 in **1**. The signals at 0.91, 1.05 and 1.22 ppm are assigned to the α-methyl protons of the syndiotactic, heterotactic and isotactic triads in PMMA, respectively[14].

The average number of **1** units per molecule, N_1, can be estimated from the signal intensity ratio, i.e. the intensity ratio of the phenyl to the methoxy protons or that of the CH_3–Si to the methoxy protons, and the value of $\overline{M}_n$ by v.p.o. We have employed double molar amounts of **1** to n-BuLi with the expectation that **1** is not dimerized in our experimental conditions. This is due to the following reasons. From a technical point of view, it is not easy to establish the 1:1 stoichiometry of **1** with n-BuLi. If the amount of **1** is less than that of n-BuLi, we cannot obtain the desired telechelic PMMA. DPE and its derivatives can scarcely be dimerized by an anionic method[15,16]. The estimated values of N_1 (see *Table 1*) were both close to unity, as expected. The remaining **1** does not influence the subsequent polymerization of MMA, because a poly(methyl methacryloyl) anion, as well as a polystyryl anion[17], may not react with **1**. In *Figure 1a*, the g.p.c. curve detected by u.v. at 254 nm appeared almost in the same range of elution volume as that by r.i., showing the existence of the units derived from **1** in all the PMMA chains. From these results, we may consider that the polymer has the residue of **1** at one end.

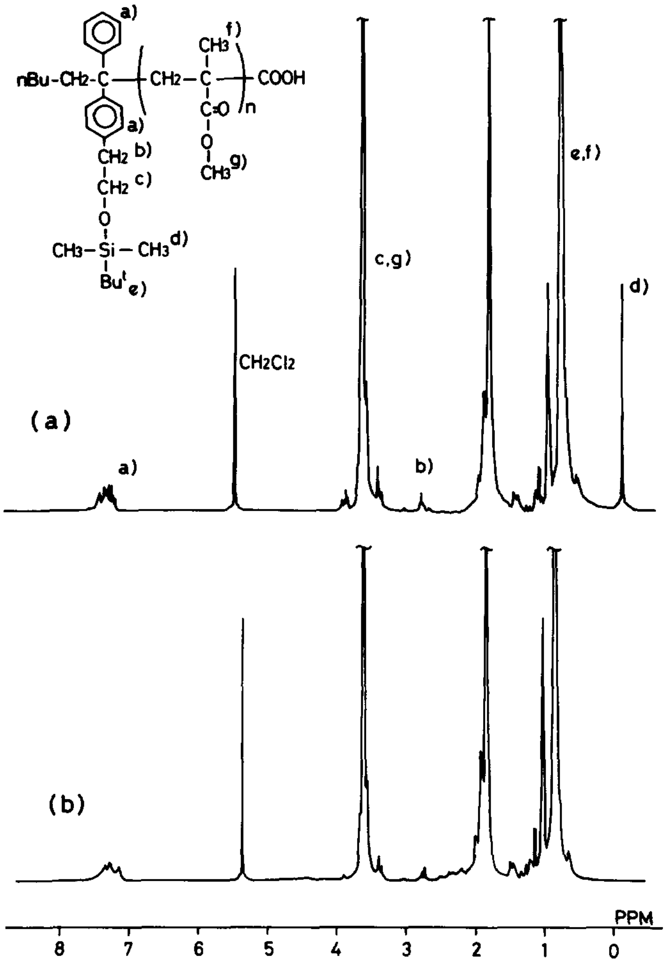

Figure 2 ^{1}H n.m.r. spectra of the PMMA: (a) acidified and (b) deprotected. Solvent, CD_2Cl_2

The average number of carboxyl groups per molecule, N_c, was estimated from the $\overline{M}_n$ by v.p.o. and the number of carboxyl groups per unit weight of the sample, which was obtained by potentiometric titrimetry. The N_c was unity within experimental error, as shown in *Table 1*.

Figure 2b shows the ^{1}H n.m.r. spectrum of the sample after the deprotection of the blocking group in **1**. Only the signal at 0 ppm, assigned to CH_3–Si, disappeared, showing a complete elimination of the tert-butyldimethylsilyl group. The g.p.c. curve after deprotection (*Figure 1b*) is similar in shape to that before deprotection (*Figure 1a*). The $\overline{M}_n$ of the deprotected sample was 4.3×10^3 by v.p.o., showing no change in degree of polymerization within experimental error. These facts suggest that no cleavage took place in the main chain during the removal of the protecting group.

These results confirm that the resulting polymer has a hydroxyl group at one end of the chain and a carboxyl group at the other.

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