SHORT COMMUNICATIONS

Preparation of Uniform Stereoblock Poly(methyl methacrylate)

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Natural polymers such as nucleic acids and proteins are usually uniform with respect to molecular weight, sequence arrangement of constitutional units, stereoregularity and conformation. In contrast to them, synthetic polymers are usually inhomogeneous with respect to these structural features.

Uniform polymer is defined in an IUPAC document as "a polymer composed of molecules uniform with respect to relative molecular mass and construction."¹ Combining the synthetic utility of stereospecific living polymerizations^{2,3} and the high efficiency of separation given by supercritical fluid chromatography (SFC) technique, we recently obtained uniform poly(methyl methacrylate) (PMMA)s with high stereoregularities.⁴⁻¹⁰

End-functionalized PMMAs such as macromonomer are readily obtained by the stereospecific living polymerizations.¹¹ In the present work, we prepared hydroxyterminated stereoregular PMMAs (Scheme 1) and fractionated them by SFC into uniform end-functionalized PMMAs, which were further utilized as uniform building blocks to construct uniform stereoblock PMMA. The method shown here displays the first-step approach toward the construction of uniform polymer architecture such as block, star and comblike polymers through end-functionalized uniform polymers as a uniform building block.¹²⁻¹⁵ These materials will contribute to the explicit understanding of properties of multicomponent polymers such as phase separation behavior.

EXPERIMENTAL

Materials

Isotactic (*it*-) and syndiotactic (*st*-) poly(methyl methacrylate)s with terminal –OH group (*it*-PMMA-OH and *st*-PMMA-OH) were prepared by the procedure shown in Scheme 1. End-functionalities of the PMMA-OHs were determined by ¹H NMR spectroscopy as reported previously.¹¹ Details of the synthesis were reported in the literature.^{11,16}

Sebacoyl dichloride was purified by distillation and used as toluene solution. Coupling reaction of PMMA-OHs was carried out in a 5 mm (i.d.) glass ampoule filled with dried nitrogen at 25°C. The reaction mixture was recovered by evaporating the solvent and then dried in vacuo. Further details are described in the RESULTS AND DISCUSSION section.

SFC

The instrumental set-up of SFC is described elsewhere.⁶ SFC fractionations of PMMA-OHs were performed under the following conditions; flow rate of



¹ *N,N,N'N'*-Tetramethylethylenediamine ² 1,8-Diazabicyclo[5.4.0]undec-7-ene ³ 9-Borabicyclo[3.3.1]nonane ⁴ Tetrahydrofuran

Scheme 1. Preparation of hydroxy-terminated syndiotactic and isotactic PMMAs.

liquefied CO₂, 9.0 ml min^{-1} , flow rate of methanol as an entrainer, 1.8 ml min^{-1} , the fluid pressure, 200 kgf cm⁻², column temperature, 80° C to 40° C (rate of cooling, 1° C min⁻¹). SFC chromatograms were recorded using a UV-detector operated at a wavelength of 220 nm.

Purification of uniform stereoblock PMMA was also carried out using SFC operated under the following conditions; CO_2 flow, 7.0 ml min⁻¹, MeOH flow, 2.5 ml min⁻¹, column temperature, 90°C to 40°C (rate of cooling, 2°C min⁻¹).

Measurements

Gel permeation chromatography (GPC) was performed on a JASCO 880-PU chromatograph equipped with Shodex GPC columns KF803 (8.0 mm i.d. \times 300 mm, maximum porosity = 7×10^4) and KF802.5 (8.0 mm i.d. \times 300 mm, maximum porosity = 2×10^4) employing tetrahydrofuran (THF) as an eluent.

The flow rate was 1.0 ml min^{-1} and the column temperature was 40°C. GPC chromatograms were recorded using a UV-detector operated at a wavelength of 234 nm.

Differential scanning calorimetry (DSC) was performed on a Rigaku DSC-8230.

Mass spectra were recorded on a JEOL JMS-DX303HF operated at the field-desorption (FD) mode.

¹H NMR spectra were measured on a JEOL JNM-GX500 spectrometer.

RESULTS AND DISCUSSION

SFC Separation of Hydroxy-Terminated PMMAs

18 mer

20

30

20

25

(b)

5

10

0

Figure 1a shows an SFC chromatogram of *it*-PMMA-OH (\overline{DP} =31.6, $\overline{M}_w/\overline{M}_n$ =1.18, end functionality=0.98, mm: mr: rr=97:2:1). The chromatogram consists well-separated peaks due to the homologous *it*-PMMA-OHs from 10 mer to 36 mer. The higher oligomers over 36 mer were purged out to facilitate repeated fractionations. The fractions from 14 mer to 34 mer were collected separately for several times. Each fraction was subjected to purification by SFC to remove a small amount of lower DP contaminants. One of the lower DP components thus purified was subjected to FD mass

Figure 1. SFC traces of *it*-PMMA-OH ($\overline{\text{DP}}$ = 31.6, $\overline{M}_w/\overline{M}_n$ = 1.18, end functionality = 0.98) (a) and the 18 mer isolated from the *it*-PMMA-OH (b).

15

Elution time (min)

spectrometric analysis and DP value was determined to be 9. DP values of other fractions were determined from the elution order in the SFC chromatogram. An SFC trace of the 18 mer is shown in Figure 1b, as an example.

The ¹H NMR spectrum of the fractionated uniform *it*-PMMA-OH (18 mer) is shown in Figure 2. From the intensity ratio of the signals due to $-OCH_3$ and terminal $t-C_4H_9$ - groups, DP of the uniform *it*-PMMA-OH was calculated to be 17.8, which agreed well with the value (DP=18) determined from the elution order in the SFC chromatogram. *st*-PMMA-OH $(\overline{DP}=32.7, \overline{M}_w/\overline{M}_n=1.04, \text{ end functionality}=1.00, mm:mr:rr=1:11:88)$ was also separated into uniform *st*-PMMA-OH in a similar manner.

Preparation of Uniform Stereoblock PMMA

Reaction of uniform 18 mer of it-PMMA-OH (21.88 mg, hydroxy end-group = $11.41 \,\mu$ mol) and uniform 30 mer of st-PMMA-OH (33.14 mg, hydroxy end-group = $10.63 \,\mu$ mol) with sebacoyl dichloride (2.70 mg, 11.30 μ mol) was carried out in toluene (0.511 ml) at 25° C in the presence of pyridine (3.57 mg, 45.11 μ mol) for 3 days. It has been known that it- and st-PMMA chains associate to form a stereocomplex in certain solvents including toluene.¹⁷ Our previous study on the minimum length necessary for the complex formation in THF showed that 40 mers of uniform it- and st-PMMA did not form a stereocomplex.^{6,18} Thus, we used 18 mer of it-PMMA-OH and 30 mer of st-PMMA-OH to avoid stereocomplex formation during the coupling reaction. The reason why we used it- and st-PMMA-OHs of different chain lengths is to facilitate the separation of the uniform stereoblock PMMA (it-st-) from it-it- and st-st-block polymers formed concomitantly.

Figure 3a shows a GPC chromatogram of the reaction mixture. Five peaks corresponding to *it-it-*, *it-st-*, *st-st*block polymers and two unreacted starting PMMA-OHs were observed separately. Each component was first fractionated by GPC and then by SFC. An SFC chromatogram of the purified uniform stereoblock polymer is shown in Figure 4 together with those of *it-it-* and *st-st-*block polymers. Figures 3b and 4b clearly showed that the *it-st*-stereoblock polymer thus obtained was uniform with respect to molecular weight.

500 MHz ¹H NMR spectra of the uniform *it-it-*, *it-st-*,



Figure 2. 500 MHz ¹H NMR spectrum of 18 mer of *it*-PMMA-OH measured in nitrobenzene- d_5 at 110°C.



Figure 3. GPC curves of the reaction mixture of the 18 mer of *it*-PMMA-OH and the 30 mer of *st*-PMMA-OH with sebacoyl dichloride (a) and the stereoblock PMMA isolated from the mixture (b).



Figure 4. SFC traces of uniform *st-st-* (a), *it-st-* (b), and *it-it-* (c) block PMMAs.

and *st-st*-block polymers were measured in benzene- d_6 at 55°C. The spectrum of the stereoblock polymer is almost the superposition of the spectra of the corresponding homopolymers. Since the signals due to initiator fragment, *t*-C₄H₉-group, attached to the *it*-PMMA block (0.968 ppm) and *st*-PMMA block (0.957 ppm) were observed separately, the ratio of *it*-PMMA and *st*-PMMA blocks could be determined from the peak intensities. The observed ratio was 49.6/50.4, which also indicates that the *it*-st-stereoblock polymer obtained here is truly "uniform".

Stereocomplex Formation of Stereoblock PMMA

Figure 5 shows a DSC thermogram of the uniform stereoblock PMMA annealed at 90°C for 48 hours together with that of a mixture of uniform 18 mer of *it*-PMMA-OH and uniform 30 mer of *st*-PMMA-OH. Both thermograms show endothermic peaks due to the melting of stereocomplex. The heat of fusion (ΔH) for the stereoblock PMMA is 2.4 times larger than that of the corresponding mixture, indicating that stereocomplex formation occurred more effectively in the case of stereoblock PMMA.

A similar observation was reported for a stereoblock



Figure 5. DSC thermograms of a mixture of 18 mer of it-PMMA-OH and 30 mer of *st*-PMMA-OH (a) and of uniform stereoblock PMMA (b) annealed at 90°C for 48 h.

PMMA having molecular weight distribution, whose average DP's and tacticities of it- and st-PMMA blocks were as follows; *it*-PMMA block: DP = 29, mm: mr: rr = 96:3:1, st-PMMA block: DP = 27, mm:mr: $rr = 7:17:76^{19}$ The stereoregularity of the *st*-PMMA block is lower than that of the uniform stereoblock PMMA (mm:mr:rr=1:11:88). Although the lower stereoregularlity causes a smaller extent of the stereocomplex formation,²⁰ the ΔH value for the complex $(4.7 \operatorname{cal} g^{-1})$ is much larger than that of the uniform stereoblock PMMA. The larger DP in average of the it-PMMA block in the non-uniform stereoblock might contribute to some extent to the larger ΔH value. However, the most important factor for the larger ΔH of the non-uniform stereoblock PMMA should be ascribed to the fact that the non-uniform polymer contains higher molecular weight fractions, which undergo the complex formation more easily, even with the lower molecular weight fractions being involved. Moreover, the ratio of it- and st-PMMA blocks in each polymer molecule has a distribution. Thus the average DP values are meaningless for the explicit understanding of the block length required for the complex formation and most effective ratio of the itand st-PMMA blocks. The latter information is particularly important in conjunction with the structure of the stereocomplex. To overwhelm these difficulties, the uniform stereoblock PMMAs with a series of DP should be most useful and the further studies are now underway.

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