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Preparation and solution properties of uniform three-arm star poly(methyl methacrylate)

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ABSTRACT

Syndiotactic (*st*-) poly(methyl methacrylate) (PMMA) with a hydroxy group at the chain end (*st*-PMMA-OH) was prepared by *st*-living polymerization with $t\text{-}C_4H_9Li/(n\text{-}C_4H_9)_3Al$ in toluene at -78°C. The resulting *st*-PMMA-OH was fractionated into uniform polymers by means of supercritical fluid chromatography. Uniform *st*-PMMA-OH with degree of polymerization of 26 was reacted with 1,3,5-benzenetricarbonyl trichloride as a coupling agent and the three-arm star polymer uniform with respect to branch length was isolated from the reaction mixture by the aid of gel permeation chromatography (GPC). Viscometric property of the uniform star PMMA was studied in some detail by using a GPC-differential viscometer.

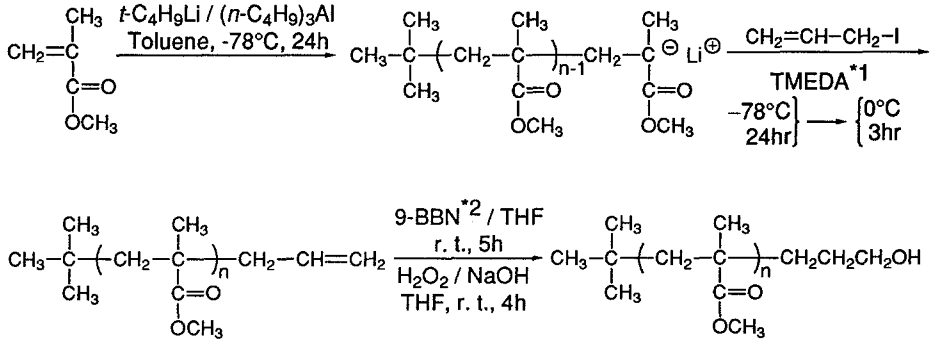
INTRODUCTION

Star polymers attract much attention due to their characteristic topological structure. Many investigations have been made on the preparation and properties of star polymers[1,2]. Recent advances in living polymerization techniques have enabled us to prepare various kinds of star polymers with controlled structure. Reaction of living or end-functionalized polymers with multi-functional coupling agents is one of the plausible ways to prepare star polymers with a well-defined branch number. However, the living or end-functionalized polymers, even if they are prepared by controlled living polymerizations, are not devoid of molecular weight distribution. When a star polymer is prepared from the linear precursors with molecular weight distribution, each star polymer molecule formed may consist of branches of different lengths. As a consequence, the star polymer should involve the complexity due to intramolecular distribution of branch length in addition to the distribution of molecular weight of the whole star polymer molecules. In other words, the molecular weight of the star polymer molecule does not necessarily correspond to the number of branch. Such complexity should hinder the clear understanding of the properties of star polymers in regard of their structural characteristics such as branch number and molecular weight. To overcome this difficulty, one needs star polymers with defined length and number of branch, which may be prepared from uniform precursor polymers, that is, end-reactive polymers without molecular weight distribution.

Recently, we succeeded in separating uniform and highly stereoregular poly(methyl methacrylate) (PMMA) having a hydroxy group at the chain end (PMMA-OH) using supercritical fluid chromatography (SFC)[3-6]. Stereoblock PMMA uniform with respect to both the total molecular weight and the block lengths was prepared by the coupling reaction of the isotactic and syndiotactic uniform PMMA-OHs[3]. In this communication we report the preparation of uniform three-arm star polymer and its viscometric behavior.

EXPERIMENTAL

Materials Two samples of syndiotactic (*st*-) PMMA-OH of different number-average degree of polymerization ($\overline{X}$n) were prepared as shown in Scheme 1 according to the literature[3]; sample#1 ($\overline{X}$n=14.2, $\overline{M}$w/$\overline{M}$n=1.11, *mm*/*mr*/*rr*=1.5/8.5/90.0, end functionality=0.91) and sample#2 ($\overline{X}$n=32.7, $\overline{M}$w/$\overline{M}$n=1.04, *mm*/*mr*/*rr*=1/11/88, end functionality=1.00). The trifunctional coupling agent, 1,3,5-benzenetricarbonyl trichloride (Aldrich), was used as tetrahydrofuran (THF) solution without further purification.



*1 *N,N,N',N'*-Tetramethylethylenediamine *2 9-Borabicyclo[3.3.1]nonane

Scheme 1. Preparation of syndiotactic PMMA-OH

SFC The instrumental set-up of SFC is described elsewhere$^{7)}$. SFC fractionation of PMMA-OH#1 was performed under the following conditions; flow rate of liquefied CO_2: 9.0ml/min (initial) to 8.0ml/min (30min), flow rate of methanol as an entrainer: 1.5ml/min (initial) to 2.5ml/min (30min), fluid pressure: 200kgf/cm^2, column temperature: 100°C to 40°C (rate of cooling: 1°C/min). SFC fractionation of PMMA-OH#2 was performed under the following conditions; flow rate of liquefied CO_2: 9.0ml/min, flow rate of methanol as an entrainer: 1.8ml/min, fluid pressure: 200kgf/cm^2, column temperature: 80°C to 40°C (rate of cooling: 1°C/min). SFC chromatograms were recorded using a UV-detector operated at a wavelength of 220nm.

Synthesis of uniform three-arm star polymer Uniform PMMA-OH (26 mer) (23.87mg, 8.78μmol) and 1,3,5-benzenetricarbonyl trichloride (0.80mg, 2.96μmol) was reacted in THF (0.30ml) at 25°C in the presence of pyridine (3.48mg, 44.0μmol) for 6 days. The reaction was carried out in a 5mm (*i. d.*) glass tube under dried nitrogen. After the excess of methanol was added to the reaction mixture, the reaction products were recovered by evaporating volatiles and then dried in vacuo. Uniform three-arm star polymer was separated from the products by means of gel permeation chromatography (GPC).

Measurement GPC measurements were performed on a JASCO 880-PU chromatograph equipped with Shodex GPC columns KF803 (8.0mm *i. d.* x 300mm *length*, maximum porosity=7 x 10^4) and KF802.5 (8.0mm *i. d.* x 300mm *length*, maximum porosity=2 x 10^4) using THF as an eluent. The flow rate was 1.0ml/min and the column temperature was 40°C. GPC chromatograms were recorded using a UV-detector operated at a wavelength of 234nm.

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

GPC-differential viscometric (GPC-DV) analysis was made by using a VISCOTEK model 110 differential viscometer.

RESULTS AND DISCUSSION

Two samples of *st*-PMMA-OH of different $\bar{X}n$ were prepared according to the literature$^{3)}$; sample#1 ($\bar{X}n$=14.2) and sample#2 ($\bar{X}n$=32.7). Figures 1a and 1b show the results of SFC analysis of these PMMA-OHs. The chromatograms consist of well-separated peaks due to homologous *st*-PMMA-OHs. Sample#1 mainly consists of *st*-PMMA-OHs with degree of polymerization (X) from 3 to 23. The X value of the component indicated as A in Figure 1a was determined by FD-mass spectrometric analysis to be 5 from the mass number of the parent ion ($[M+1]^+$) being 617. Accordingly, the peak indicated as B in Figure 1a should correspond the component of X=19 by following the elution order from peak A (X=5) in the SFC chromatogram. The component B (X=19) was fractionated and purified by SFC and was used as an authentic sample for the SFC analysis of sample#2. Figure 1b shows an SFC chromatogram of *st*-PMMA-OH#2 to which a small amount of the purified 19 mer was added. The X value for each component in the chromatogram could be determined similarly to the case of *st*-PMMA-OH#1 as indicated in the figure. The fractionation of the individual

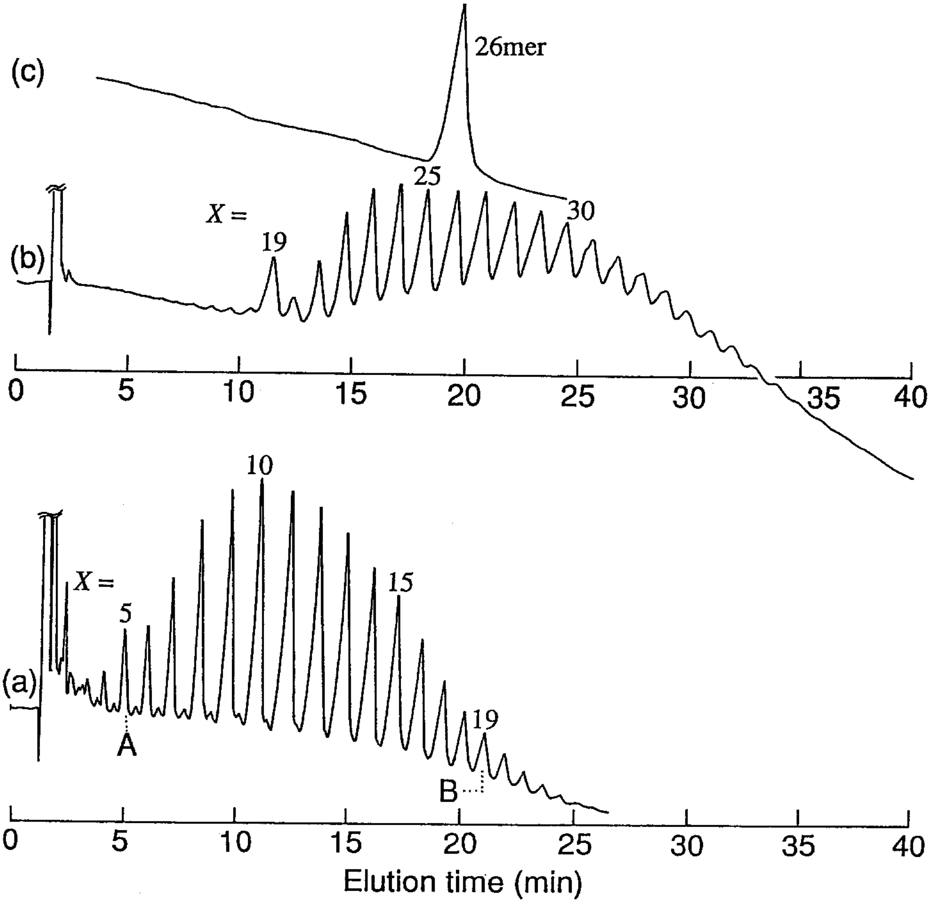
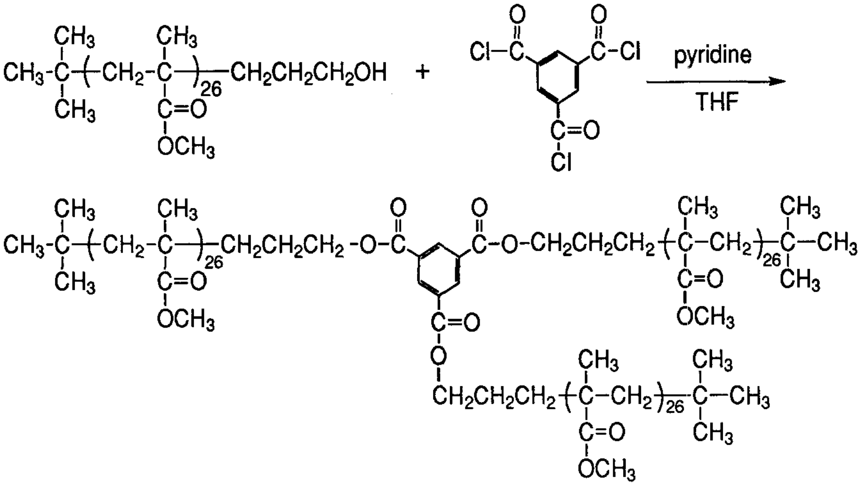


Figure 1. SFC chromatograms of (a) *st*-PMMA-OH (#1) ($\bar{X}n$=14.2, $\bar{M}w/\bar{M}n$=1.11, end functionality=0.91), (b) *st*-PMMA-OH (#2) ($\bar{X}n$=32.7, $\bar{M}w/\bar{M}n$=1.04, end functionality=1.00) containing an authentic sample of 19 mer, and (c) the 26 mer isolated from sample #2.
Chromatographic conditions for (a) are different from those for (b) and (c).
See the experimental section for the detail.



Scheme 2. Preparation of uniform three-arm star PMMA

components from 21 mer to 33 mer was carried out about 100 times. The amount of the sample injected for each run was 25mg (50μl of 50w/v% acetone solution). Each fraction was subjected to further purification by SFC to remove a small amount of lower *X* components. An SFC trace of the purified 26 mer obtained from *st*-PMMA-OH#2 is shown in Figure 1c as an example.

The coupling reaction between uniform *st*-PMMA-OH with *X* of 26 and 1,3,5-benzenetricarbonyl trichloride was carried out in THF at 25°C in the presence of pyridine to obtain the uniform three-arm star PMMA (Scheme 2). Figure 2a shows a GPC chromatogram of the reaction mixture, which mainly consists of well-separated three peaks due to three-arm star polymer, two-arm product and one-arm product, in the elution order. The peak due to the one-arm product has a shoulder at larger elution-volume side due to the starting *st*-PMMA-OH. The three-arm star polymer could be separated from the mixture by GPC fractionation and the chromatogram of the star polymer is shown in Figure 2b. The reaction mixture of non-uniform *st*-PMMA-OH (#2) with $\bar{X}n$ of 32.7 and 1,3,5-benzenetricarbonyl trichloride showed severe overlap of the peaks of three-arm and two-arm products in its GPC chromatogram, and thus the fractionation of the non-uniform three-arm star polymer was difficult.

Intrinsic viscosities [η] of the three-arm star PMMA, and the one- and two-arm coupling products were determined by GPC-DV method in THF at 40°C. Plots of log [η] against logarithmic molecular weight (log M) are shown in Figure 3. It is worth noting that the molecular weights of the three-arm and two-arm products are precisely determined based on the defined molecular weight of the

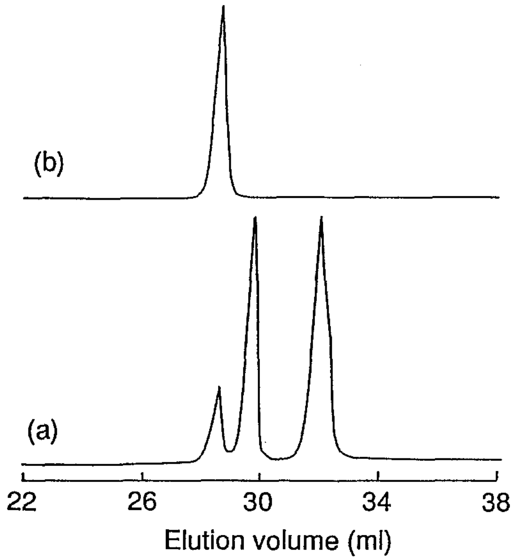


Figure 2. GPC chromatograms of (a) the reaction mixture of *st*-PMMA-OH (26 mer) and 1,3,5-benzenetricarbonyl trichroride and (b) the uniform three-arm star PMMA isolated from the mixture.

branches. The value of [η] of the three-arm star polymer deviates clearly from the broken line which indicates the expected value of [η] for linear PMMA based on Mark-Houwink-Sakurada equation ($[\eta]=9.49\mathrm{x}10^{-4}M^{0.488}$) (in THF at 40°C). The parameters of the equation were determined from the [η] values of one- and two-arm products, which are linear polymers.

The ratio of [η] of a branched molecule to that of a linear molecule with the same molecular weight ($g_\eta=[\eta]_{\mathrm{branched}}/[\eta]_{\mathrm{linear}}$) for the uniform three-arm PMMA was determined as 0.90 from the results shown in Figure 3.

Zimm and Kilb calculated the g_η for a branched polymer with long, flexible uniform branches in the unperturbed state as shown in equation (1),

$$g_\eta= (2/f)^{3/2}[0.390(f - 1)+0.196]/0.586 \qquad (1)$$

where f represents the number of branches[8)]. The value of g_η (0.90) obtained from our experiment agrees well with the g_η(=0.91) obtained from equation (1) with f=3, though the applicability of eqation (1) to the star polymer with short branches obtained in this work is in question.

The present results demonstrate, in addition to the previous report[2)], that end-functional uniform linear polymer is successfully used for constructing uniform polymer architecture with more elaborated structural feature, which

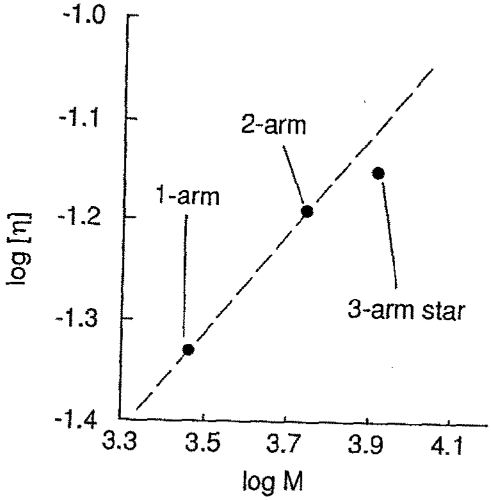


Figure 3. log[η]-logM plot for the three-arm star PMMA and other coupling products having one- and two-PMMA arms. The broken line shows the value of [η] for linear PMMA calculated from Mark-Houwink-Sakurada equation ($[\eta]=9.49\times10^{-4}M^{0.488}$).

are useful as a primary model for the fundamental studies of polymer properties. Studies on uniform star polymer, in particular, is now being extended to prepare a series of uniform star PMMA having different branch lengths and uniform isotactic star PMMA.

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