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Tacticity Effect on Size Exclusion Chromatography Retention of Stereoregular Poly(ethyl methacrylate)

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Introduction

Synthetic polymers may have various heterogeneities in molecular weight, chemical composition, chain architecture, microstructures, etc., which affect their physical properties significantly. In the characterization of such polymers, measurements of individual distributions of all existing molecular heterogeneity would be the ultimate goal even though it would be extremely complicated and difficult. Since heterogeneities occur simultaneously, it is necessary to measure each molecular characteristic without the influence of the others.

Tacticity is one of the molecular characteristics, which strongly influences the crystallization behavior of polymers. For a simple situation, let us consider a polymer that has only two independent distributions: molecular weight and tacticity. Is it possible to characterize the distribution of the two molecular characteristics independently? A recent two-dimensional chromatography analysis of stereoregular poly(ethyl methacrylate) (PEMA) appears to provide a promising solution for the problem.[1] This method was based on the assumption that tacticity has negligible effect on the hydrodynamic volume of polymer chains and size exclusion chromatography (SEC) can separate the polymer according to the molecular weight only.[1,2] Then the SEC fractions of homogeneous molecular weight can be further analyzed by other chromatographic techniques sensitive to the tacticity.[3−5] However, the insensitivity of SEC retention to tacticity has not been examined rigorously mainly due to the limited availability of well-characterized polymer samples. One of the rare works on this issue is of Ute et al., in which they fractionated individual “mers” of stereoregular poly(methyl methacrylate) (PMMA) by supercritical fluid chromatography and compared the SEC retention of 25mer and 50mer of isotactic and syndiotactic PMMA. They found that isotactic 50mer eluted a little faster than syndiotactic 50mer, but the difference was negligible for 25mer.[6] This result clearly showed that the tacticity affects the SEC retention to some extent. However, there have been no more experimental efforts on this issue. The molecular weight of the PMMA 50mer is about 5000, and it is impractically laborious to obtain uniform PMMAs with higher molecular weight by individual fractionation with supercritical fluid chromatography. Meanwhile, there has been a significant progress in polymer characterization methods, in particular HPLC fractionation and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI−TOF MS) analysis.

Table 1. Molecular Characteristics of Stereoregular Poly(ethyl methacrylate)s and Their Fractions

sample code[a]	M_w (kg/mol) (M_w/M_n)[b]	M_w (kg/mol) (M_w/M_n)[c]	triad (%)		
			mm	mr	rr
s1	6.3 (1.05)	6.4 (1.07)	0	9	91
s1f1, s1f2		5.0 (1.03), 5.9 (1.009)			
s1f3, s1f4		6.7 (1.007), 7.7 (1.01)			
s2	13.3 (1.05)	13.3 (1.05)	0	9	91
s2f1, s2f2		10.9 (1.05), 12.7 (1.02)			
s2f3, s2f4		14.0 (1.01), 16.0 (1.02)			
m	13.8 (1.09)	13.4 (1.11)	2	45	53
mf1, mf2		10.0 (1.25), 12.7 (1.02)			
mf3, mf4		14.8 (1.02), 16.3 (1.02)			
i1	9.8 (1.10)	10.6 (1.08)	96	4	0
i1f1, i1f2		8.7 (1.02), 10.2 (1.004)			
i1f3		11.9 (1.007)			
i2	16.0 (1.07)	16.5 (1.05)	91	5	4
i2f1, i2f2		13.0 (1.02), 14.9 (1.005)			
i2f3, i2f4		16.0 (1.005), 17.5 (1.006)			

[a] s = syndiotactic, m = moderately syndiotactic, i = isotactic. [b] Mother PEMA, determined by SEC-MALLS. [c] Mother PEMA and fractions, determined by MALDI−TOF MS.

In this work, we combined HPLC fractionation and MALDI−TOF MS analysis for different stereoregular PEMA samples with the molecular weight ranging from 5000 to 17 500. Using the PEMA samples with very narrow molecular weight distribution, we rigorously examined the tacticity effect on SEC retention by constructing SEC calibration curves.

Experimental Section

Materials. The PEMAs with different tacticity and narrow molecular weight distribution were prepared by stereospecific living anionic polymerizations at low temperatures. The detailed synthetic procedures were reported previously.[4,7−9] The tacticity was determined from carbonyl signals in 125 MHz ^{13}C NMR spectra measured in $CDCl_3$ at 55 °C. The molecular weight of the PEMAs was characterized by SEC with two mixed bed columns (Polymer Lab., Mixed C) coupled with a multiangle laser light scattering (MALLS, Wyatt, miniDAWN) as well as MALDI−TOF MS. The characteristics of the two highly syndiotactic (s-), one moderately syndiotactic (m-), and two highly isotactic (i-) PEMA samples are summarized in Table 1.

Chromatography. The reversed-phase HPLC (RPLC) experiments were carried out with a C18 bonded silica column (LUNA, 100 Å pore, 250 × 4.6 mm, 5 μm particle size). The mobile phase was a mixture of CH_2Cl_2 and CH_3CN (Duksan, HPLC grade, 30/70, v/v), and the flow rate was 0.5 mL/min. Each PEMA sample was dissolved in the mobile phase (2.0 mg/mL), and a 100 μL was injected. The column temperature was controlled by circulating a fluid through a column jacket from a bath/circulator (Neslab, RTE-111). The RPLC chromatograms were recorded with a UV absorption detector (TSP, UV 100) at a wavelength of 235 nm. For the SEC experiments of the PEMA fractions, two mixed C columns (Polymer Lab.)

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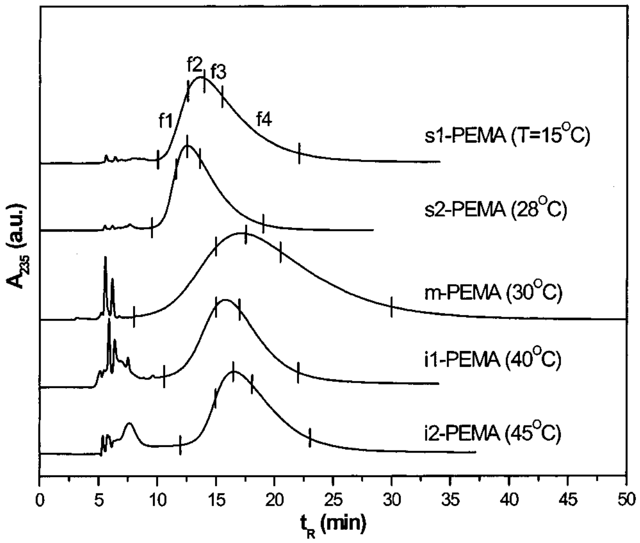

Figure 1. RPLC chromatograms of five different stereoregular PEMAs in Table 1. The elution peak of each sample was fractionated into 3−4 parts as marked with vertical bars. Each chromatogram was taken at different temperatures in order to make the retention time of different samples similar. Column: LUNA C18, 100 Å, 250 × 4.6 mm. Eluent: CH_2Cl_2/CH_3CN (30/70, v/v) at a flow rate of 0.5 mL/min.

were used. Eluent was THF at a flow rate of 0.8 mL/min. The column temperature was kept at 40 °C.

MALDI−TOF MS. A MALDI−TOF mass spectrometer (Bruker, REFLEX III) was used at an accelerating potential of 20 kV in the reflection mode. The spectrometer was equipped with a nitrogen laser (λ = 337 nm), a pulsed ion extraction, and a reflector.[10] A 5 μL aliquot of dilute polymer solution (ca. 2 mg/mL in THF) was mixed with 50 μL of the matrix (*trans*-3-indoleacrylic acid, Aldrich) solution (10 mg/mL in THF) and 1.5 μL of sodium iodide solution (1 mg/mL in THF). A 0.5 μL aliquot of the final mixture was deposited onto a sample target plate.

Results and Discussion

Figure 1 shows RPLC chromatograms of the five different tactic PEMA samples. The column temperature was adjusted so that the PEMA samples of different tacticity and different molecular weight elute in a reasonable elution time. The small peaks appearing at low t_R (5−10 min) are due to the impurity in the polymers, which is present in the largest amount in the i-PEMAs.[5]

The resolution of the interaction chromatography (IC) is much higher than SEC, and it can fractionate the polymers prepared by anionic polymerization further into the fractions having a narrower molecular weight distribution.[11−13] To obtain different molecular weight samples with even narrower distributions, the five PEMA samples were fractionated as shown in Figure 1, where small vertical bars indicate the boundary of each fractions: four fractions were collected from s1 (f1: 10.0−12.5 min, f2: 12.5−14.0 min, f3: 14.0−15.5 min, f4: 15.5−22.0 min), four from s2 (f1: 9.5−11.5 min, f2: 11.5−12.5 min, f3: 12.5−13.5 min, f4: 13.5−19.0 min), four from m (f1: 8.0−15.0 min, f2: 15.0−17.5 min, f3: 17.5−20.5 min, f4: 20.5−30.0 min), three from i1 (f1: 10.5−15.0 min, f2: 15.0−17.0 min, f3: 17.0−22.0 min), and four fractions from i2 (f1: 12.0−15.0 min, f2: 15.0−16.5 min, f3: 16.5−18.0 min, f4: 18.0−23.0 min). The collected fractions were dried and redissolved in THF for MALDI−TOF MS analysis to determine the accurate molecular weight.

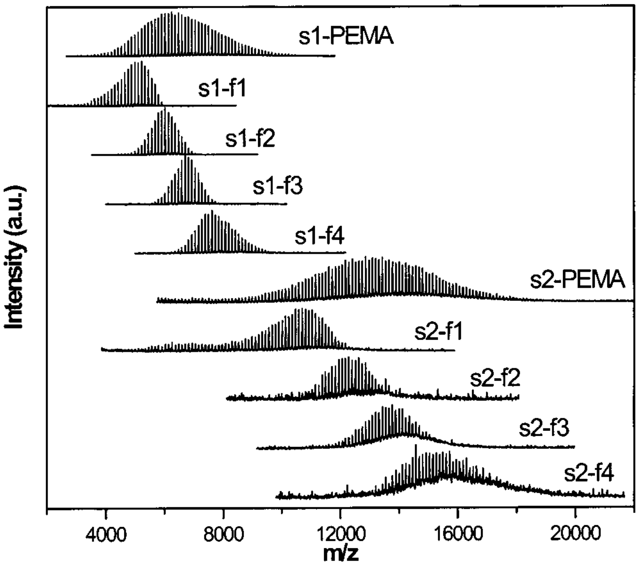

Figure 2. MALDI−TOF MS spectra of s1 and s2 and their fractions.

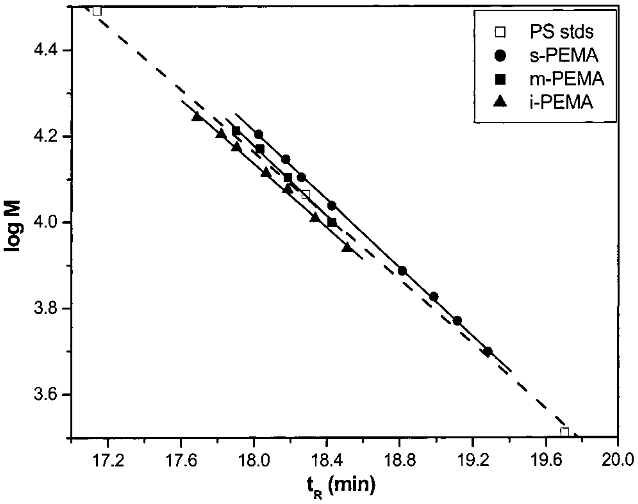

Figure 3. SEC calibration curves of different stereoregular PEMA samples (●, s-PEMA; ■, m-PEMA; ▲, i-PEMA). Dashed line is a calibration curve obtained from three PS standards: 3.3, 11.6, and 30.9 kg/mol. Column: two mixed bed columns (Polymer Lab., Mixed C). Eluent: THF at a flow rate of 0.8 mL/min. Column temperature: 40 °C.

Figure 2 displays MALDI−TOF MS spectra of s1 and s2 and their fractions. The mass spectra show that the fractions are not sharply resolved, and their molecular weight ranges overlap each other significantly. It is in part due to the chromatographic band broadening,[13] but the main cause is that the IC retention is affected by both molecular weight and tacticity.[5] Nonetheless, the mass spectra in Figure 2 show that IC can separate the anionically polymerized PEMAs into the fractions with much narrower molecular weight distribution. The molecular characteristics of the fractions are summarized in Table 1.

The SEC retention time of each fraction was measured, and Figure 3 displays the SEC calibration curves of the different stereoregular PEMA fractions. The weight-average molecular weights determined from the MALDI−TOF MS spectra and the peak positions of the SEC retention time were used to make the plot. We can see that there are small but clear differences among the PEMAs of different tacticity. Since the s1/s2 pair and i1/i2 pair have similar triad distributions, each pair constitutes a single line. The hydrodynamic volume of the same molecular weight PEMA decreases with the rr triad content. The calibration curve of the m-PEMA having 53% rr triad content is almost the same as that of polystyrene (PS). The difference in the SEC calibration curves would give rise to about 20% error in the molecular weight determination between the highly isotactic and syndiotactic PEMAs near $M_w = 10$ kg/mol. The difference appears to decrease as the molecular weight decreases. This trend is consistent with the finding of Ute et al. for PMMA.[6]

For stereoregular PMMA samples, it has been known that i-PMMA is more expanded than s-PMMA in the unperturbed state as well as in several good solvents.[14] Also, at the Θ condition the hydrodynamic volume of i-PMMA was found larger than that of atactic PMMA, and it has been considered to arise from the difference in chain stiffness and local chain conformation.[15] These results are consistent with the trend in SEC retention of PEMA found in this study.

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