

## ORIGINAL ARTICLE

# Uniform poly(methyl methacrylate) stereostars: synthesis, separation and stereocomplex formation

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Isotactic (*it*-) and syndiotactic (*st*-) uniform poly(methyl methacrylate)s (PMMA) with hydroxyl end groups were isolated by supercritical fluid chromatography (SFC) and reacted with benzene-1, 3, 5-tricarbonyl trichloride. Two types of uniform three-arm *star*-PMMA with different stereoregular arms, [*it/it/st*]- and [*it/st/st*]-3-*star*-PMMA, that is, 'stereostar PMMA', were isolated by SFC from the product mixture (According to IUPAC nomenclature for nonlinear polymers, star PMMA with three arms is named 3-*star*-PMMA. In this paper, the stereoregularity of the three arms is designated as [*it/it/st*], for example, and thus, the polymer is named [*it/it/st*]-3-*star*-PMMA. By analogy to 'stereoblock' PMMA, these star PMMA are termed 'stereostar PMMA'). The formation of stereocomplexes by these stereostar PMMA was examined in acetone. Although both stereostar PMMA formed intramolecular stereocomplexes, the [*it/st/st*]-3-*star*-PMMA formed two types of intramolecular stereocomplexes with different hydrodynamic volumes because of the different compositions of the *it*- and *st*-PMMA arms involved in the stereocomplexes.

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**Keywords:** PMMA; star polymer; stereocomplex; stereoregular polymer; supercritical fluid chromatography; uniform polymer

## INTRODUCTION

Isotactic (*it*-) and syndiotactic (*st*-) poly(methyl methacrylate) (PMMA) chains are known to associate to form a stereocomplex in certain solvents, such as acetone, toluene and tetrahydrofuran. The phenomenon of stereocomplex formation was first reported in 1961 by Watanabe *et al.*<sup>1</sup> In 1965, Liquori *et al.*<sup>2</sup> reported a structural model of the stereocomplex in the solid state. Later, Challa and co-workers<sup>3,4</sup> proposed another model known as a double-stranded helix model, in which a helix of the *it*-PMMA chain with a smaller radius is surrounded by an *st*-PMMA helical chain with a larger radius.

Recently, Kumaki *et al.*<sup>5</sup> demonstrated multistranded models based on atomic force microscopic observation of PMMA stereocomplexes formed at the air–water interface through two-dimensional crystallization, in which the double-stranded *it*-PMMA helix was surrounded by the *st*-PMMA helix. Both helix models developed in that work indicated that a 1:2 ratio of associated monomeric units in *it*- and *st*-PMMA is required for complex formation. Although most experimental results indicate that the stoichiometry of the stereocomplex is *st*-/*it*- = 2/1,<sup>2,6</sup> a number of contradictory results have been reported about the stoichiometry,<sup>7</sup> with some results suggesting *st*-/*it*- = 1/1<sup>8</sup> or *st*-/*it*- = 1.5/1.<sup>9,10</sup> Previous stoichiometry results were related to the ratio of associated monomeric units or the mass fractions of *it*- and *st*-PMMA. To obtain a molecular-level understanding of the mechanism and stoichiometry of stereocomplex formation, however, the critical factor should be the stoichiometry of the complex, that is, the ratio of *it*- and *st*-PMMA molecules, rather than the monomeric unit ratio.

With non-uniform polymer samples, however, numerous combinations of polymer molecules with different molar masses are possible, even for one-to-one associated species, and a clear-cut identification of the associated species is almost impossible. With uniform polymers, associated and non-associated species can clearly be differentiated by size exclusion chromatography (SEC). A typical example is the study of the formation of stereocomplexes between *it*-PMMA and *st*-PMMA in solution.

Ute *et al.* reported that uniform 50 mers of *it*- and *st*-PMMA in tetrahydrofuran showed SEC elution peaks corresponding to 50 mers and 100 mers, with the latter peak attributed to a one-to-one association between *it*- and *st*-50 mers.<sup>11</sup>

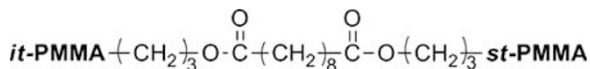
Later, they analyzed the uniform PMMA stereocomplex formed in acetone using an online SEC-NMR method to identify the stoichiometry of the complexed component. The *st*-/*it*- compositions of the stereocomplex in the mixtures were determined to be 1.61–1.94, indicating the coexistence of at least two types of stereocomplexes with different compositions (for example, *st*-/*it*- = 1/1 and 2/1).<sup>12</sup>

The uniform PMMA was also used to perform atomic force microscopic observations of stereocomplex formation at the water–air interface by Kumaki *et al.*,<sup>13</sup> who demonstrated the occurrence of molar-mass recognition in PMMA complex formation.

Another approach to understanding PMMA stereocomplexes is a synthetic one, that is, a stereoblock PMMA in which the *it*- and *st*-PMMA chains are linked together to restrict possible combinations

of the stereoisomeric chains. Thus, syntheses of non-uniform stereoblock PMMAs have been reported.<sup>14–17</sup>

The authors succeeded in preparing uniform stereoblock PMMAs consisting of *it*-PMMA and *st*-PMMA blocks with exactly the same degree of polymerization (DP) using a supercritical fluid chromatographic (SFC) separation technique.<sup>18</sup>



Stereocomplex formation of the stereoblock PMMA in acetone was investigated using SEC and was found to take place intramolecularly, as well as intermolecularly. The intramolecular complex of stereoblock PMMA had a larger elution volume in the SEC chromatogram (smaller hydrodynamic volume) than the non-complexed PMMA, whereas the intermolecular complexes were observed at smaller elution volumes (larger hydrodynamic volumes). This phenomenon implicitly demonstrates the usefulness of uniform polymers as tools to gain a molecular-level understanding of aggregation.<sup>18</sup>

In this work, the authors attempted to extend the above uniform polymer approach to uniform 3-*star*-PMMA<sup>19</sup> with different stereoregular arms, which may be termed 'stereostar' PMMA by analogy to stereoblock PMMA. Because the 3-*star*-PMMA has three arms, the possible combinations of the arm stereoregularity are [*it*/*it*/*st*] and [*it*/*st*/*st*]. In these stereostar PMMAs, the ratio of stereoregular PMMA arms within a molecule is inherently regulated as *st*-/*it*-=1/2 and *st*-/*it*-=2/1. Thus, the intramolecular stereocomplexes may include different forms of aggregates depending on the *st*-/*it*- arm ratio within the stereostar PMMAs. In fact, SEC analyses of these two types of stereostar PMMAs in acetone revealed the existence of at least two types of intramolecular complexes with different hydrodynamic volumes.

## EXPERIMENTAL PROCEDURE

### Materials

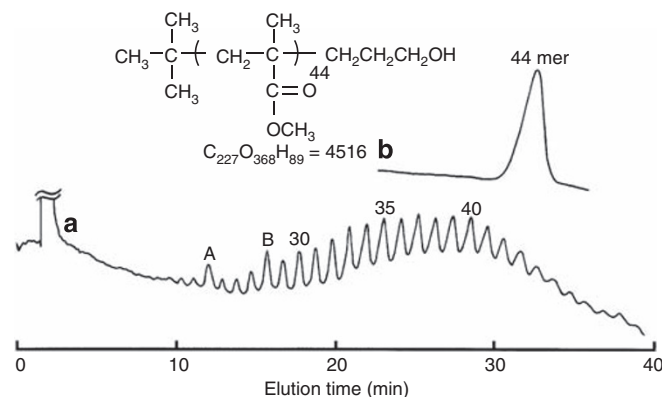
Isotactic (*it*-) and syndiotactic (*st*-) PMMA-OHs were prepared according to previously reported procedures.<sup>20,21</sup> The characteristics of the samples were as follows: *it*-PMMA-OH ( $M_n=3190$ ,  $M_w/M_n=1.23$ ,  $mm/mr/rr=96/3/1$ , end functionality=0.86) and *st*-PMMA ( $M_n=4490$ ,  $M_w/M_n=1.10$ ,  $mm/mr/rr=1/10/89$ , end functionality=0.86). The trifunctional coupling agent, benzene-1,3,5-tricarbonyl trichloride (Aldrich, St. Louis, MO, USA), was obtained in a tetrahydrofuran solution and was used without further purification.

### Measurements

<sup>1</sup>H NMR spectra were measured on a JEOL JNM-AL400 spectrometer (JEOL, Tokyo, Japan) or on a Varian UNITY INOVA500 spectrometer (Varian, Santa Clara, CA, USA). Solvents and temperatures used for conventional measurements were nitrobenzene-*d*<sub>5</sub> at 110 °C and benzene-*d*<sub>6</sub> at 75 °C. Stereocomplex formation was investigated using acetone-*d*<sub>6</sub> as a solvent in the temperature range of 0–40 °C.

Mass spectra were recorded on a JEOL JMS-DX303HF spectrometer operated in the field-desorption mode.

Conventional SEC measurements were performed on a JASCO 880-PU chromatograph (JASCO, Tokyo, Japan) equipped with two Shodex SEC columns KF806 L (Shodex, Tokyo, Japan) (8.0 mm *i.d.* × 300 mm, maximum porosity = 2 × 10<sup>7</sup>) using tetrahydrofuran as an eluent at a flow rate of 1.0 ml min<sup>-1</sup> and a column temperature of 40 °C. SEC measurements for the stereocomplex studies were determined using a JASCO 980-PU chromatograph equipped with Shodex SEC columns K803 (8.0 mm *i.d.* × 300 mm, maximum porosity = 7 × 10<sup>4</sup>) using acetone as an eluent. The temperature of the column was controlled by placing it in a cooling jacket connected to an SCINICS thermostat (SCINICS, Tokyo, Japan). The chromatograms obtained at different temperatures are presented using the molar mass axis, which was calibrated at each temperature against standard PMMA samples, instead of the elution volume. In both cases, the SEC curves were recorded using a JASCO RI detector SE-61.



**Figure 1** Supercritical fluid chromatography traces of *st*-PMMA-OH (degree of polymerization=44.2,  $M_w/M_n=1.10$ ) containing authentic samples of 24 mer (A) and 28 mer (B) (a), and the 44 mer isolated from (b).

### Supercritical fluid chromatography

The SFC was set up as described elsewhere.<sup>11</sup> SFC fractionation of *it*- and *st*-PMMA-OHs was performed under the following conditions: flow rate of liquefied CO<sub>2</sub>: 9.0 ml min<sup>-1</sup>; flow rate of methanol entrainer: 1.80 ml min<sup>-1</sup> (for *it*-PMMA-OH) or 1.88 ml min<sup>-1</sup> (for *st*-PMMA-OH); fluid pressure: 200 kgf cm<sup>-2</sup>; initial column temperature: 80 °C (for *it*-PMMA-OH) or 70 °C (for *st*-PMMA-OH); and rate of cooling: 1 °C min<sup>-1</sup>. SFC chromatograms were recorded using a ultraviolet detector operated at a wavelength of 220 nm.

### SFC fractionation of uniform *it*- and *st*-PMMA-OHs

Figure 1 shows the SFC analysis of *st*-PMMA-OH. The chromatogram consists of well-separated peaks due to homologous *st*-PMMA-OHs. The DP values of components A and B in Figure 1a were determined in advance by field-desorption-mass spectrometric analysis and <sup>1</sup>H NMR analysis to be 24 and 28, and then the components were used as authentic samples. The fractionation of the individual components from 24 mers to 45 mers was carried out about 100 times. The amount of sample injected for each run was 25 mg (50 μl of 50% acetone solution). Because each collected fraction was found to contain a small amount of one-unit-smaller DP component (~3%) at a smaller elution volume as a shoulder peak, the obtained fractions were purified by SFC to remove those contaminants and finally subjected to SFC analyses that showed no shoulder peak.

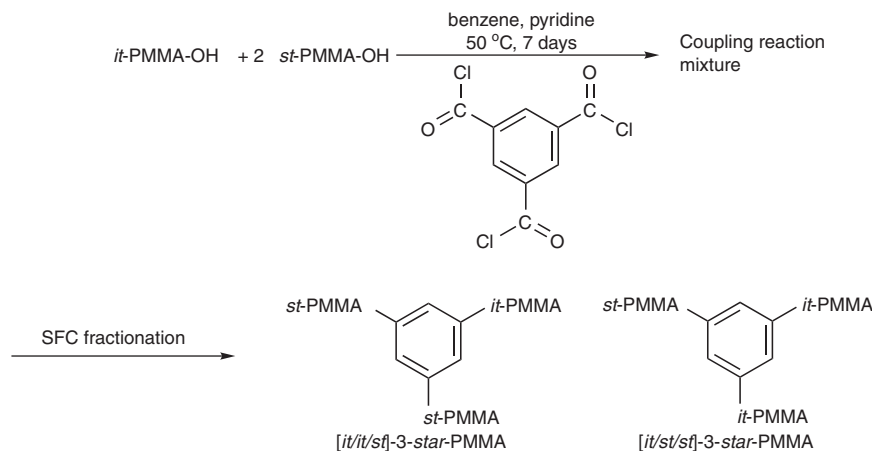
### Synthesis of uniform stereostar PMMA

A typical experimental procedure for the preparation of uniform stereostar PMMA is as follows. A 1:2 mixture of uniform *it*-PMMA-OH (37 mer) (5.01 mg, 1.35 μmol) and *st*-PMMA-OH (37 mer) (13.89 mg, 2.66 μmol) was reacted with benzene-1,3,5-tricarbonyl trichloride (2.03 μmol) in benzene (0.24 ml) at 50 °C in the presence of pyridine (20.3 μmol) for 7 days. The reaction was carried out in a 5 mm (*i.d.*) glass tube under dried nitrogen. After an excess of methanol was added to the reaction mixture, the reaction products were recovered by evaporating volatiles and then dried *in vacuo*. Uniform stereostar PMMAs were isolated from the products by SFC (Scheme 1).

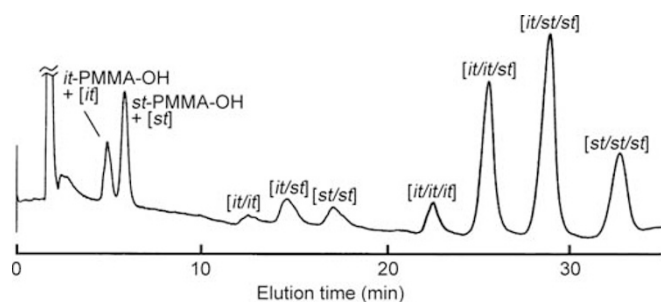
## RESULTS AND DISCUSSION

### Synthesis and isolation of stereostar PMMAs

The 1:2 mixture of uniform *it*-PMMA-OH and *st*-PMMA-OH with a discrete DP of 32 was reacted with benzene-1,3,5-tricarbonyl trichloride in benzene at 50 °C in the presence of pyridine for 7 days, affording a mixture of four types of 3-*star*-PMMAs with different stereoregularities in their arms, as well as three types of dimeric products, two types of monomeric products and unreacted PMMA-OHs. Figure 2 shows an SFC chromatogram of the reaction mixture that demonstrates that the product was separated not only by molar mass (number of PMMA arms) but also by the stereoregularity of the



**Scheme 1** Preparation of uniform three-arm stereostar poly(methyl methacrylate)s (PMMA).



**Figure 2** Supercritical fluid chromatography (SFC) curve of the reaction mixture of uniform *it*- and *st*-PMMA-OHs (degree of polymerization=32) with benzene-1,3,5-tricarbonyl trichloride. SFC conditions: 7.0 ml min<sup>-1</sup> CO<sub>2</sub>, 3.0 ml min<sup>-1</sup> CH<sub>3</sub>OH, 90 °C initial temperature, 1.0 °C min<sup>-1</sup> cooling.

arm PMMAs. Peak assignments were tentatively made by elution order and peak intensities expected on the basis of the feed ratios of *it*- and *st*-PMMA-OHs ( $st/it=2/1$ ), and each fraction was isolated from the mixture and confirmed by <sup>1</sup>H NMR spectrometric analysis. <sup>1</sup>H NMR spectra of the uniform 3-*star*-PMMAs isolated in this way are presented in Figure 3. The spectra at the top and bottom clearly indicate that these 3-*star* PMMAs consist of *it*- and *st*-PMMA arms, respectively (see, for example, AB-type quartet CH<sub>2</sub> signals for *it*-*star* PMMA and a singlet signal for *st*-*star*-PMMA). The second and third spectra suggest that these 3-*star*-PMMAs contain both *it*- and *st*-PMMA arms, that is, these are stereostar PMMAs. Moreover, the signal intensity ratios of the -CH<sub>2</sub>-, α-CH<sub>3</sub> and -OCH<sub>3</sub> regions were used to determine the compositions of these stereostar PMMAs as reported in the figure. The 3-*star*-PMMAs have *t*-C<sub>4</sub>H<sub>9</sub> groups at their arm ends that are derived from the initiator (*t*-butyllithium) used for the preparation of the PMMA-OHs. Note that the *t*-C<sub>4</sub>H<sub>9</sub> signals shown in Figure 3 (right) are sensitive to the stereoregularity of the adjacent PMMA chain, and split into two parts. The intensity ratios of the split signals change from top to bottom, reflecting the number of *it*- and *st*-PMMA arms, further confirming the assignments. The *m* diad and *r* diad contents of the star polymers are indicated in the figure, together with the calculated values in parentheses. (This calculation was based on the composition and diad tacticity values of the *it*- and *st*-PMMA-OHs (*it*:-  $m=0.975$ ,  $r=0.025$ ; *st*:-  $m=0.060$ ,  $r=0.940$ ). For example, in the case of [it/it/st]-3-*star* PMMA:

$$m = (0.975 \times 2 + 0.060) / 3 = 0.67, r = (0.025 \times 2 + 0.940) / 3 = 0.33$$

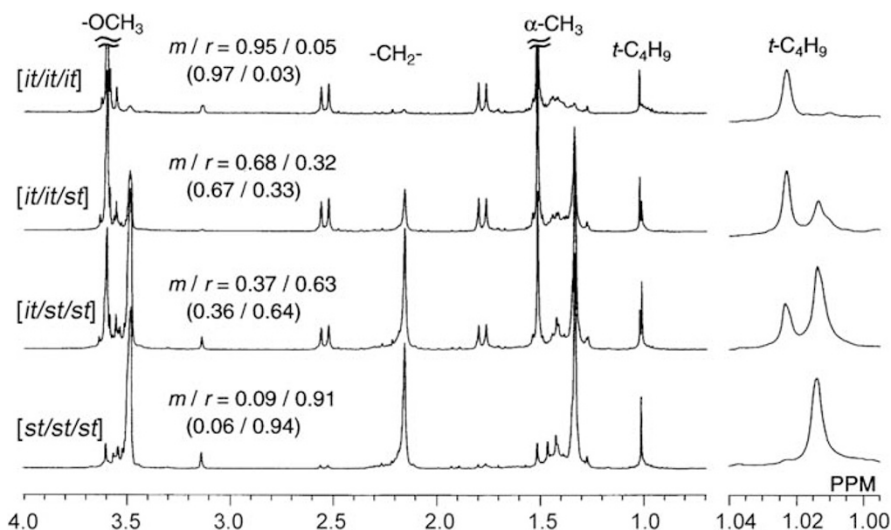
The observed values were slightly different from the calculated ones, indicating that each fraction contains a small amount of preeluted fraction. The deviations are so small that the purity is sufficiently high for the further experiments conducted in this study.

The effect of DP and the stereoregularity of PMMA-OHs on the coupling reaction were examined using uniform PMMA-OHs of different DPs. The effect of DP on the observed product ratios of four types of 3-*star*-PMMAs, [it/it/it], [it/it/st], [it/st/st], and [st/st/st], are summarized in Table 1, together with calculated values. At a DP of 42, the difference between the observed and calculated values is negligible, indicating that the *it*- and *st*-PMMA-OHs have almost identical reactivities. At a DP of 32, however, the [st/st/st] and [it/st/st] fractions are significantly smaller than the expected values, suggesting that *it*-PMMA-OH has a higher reactivity than *st*-PMMA-OH. This phenomenon could result from the difference in chain flexibility between the *it*- and *st*-PMMA chains. At lower DPs, the difference in flexibility between *it*- and *st*-PMMA chains is significant, and more flexible *it*-PMMA chains react more easily than the *st*-PMMA chains. As the DP increases, the difference in flexibility becomes negligible.

### Stereocomplex formation

Stereocomplex formation of the two types of uniform stereostar PMMAs, [it/it/st]-3-*star*-PMMA and [it/st/st]-3-*star*-PMMA, was examined by SEC in the complex-forming solvent acetone. Figure 4 presents SEC curves of the uniform stereostar PMMAs with arm DPs of 32 measured in acetone at various temperatures. [it/it/st]-3-*star*-PMMA showed two major peaks (B and C) at 0 °C accompanying a small minor peak (A) in the higher molar mass region. With increasing temperature, peak C became weaker and almost disappeared or coalesced to the major peak C at 20 and 30 °C. Because the maximum of peak B is about 10<sup>4</sup>, close to the nominal molar mass of the star polymer (10 117 g mol<sup>-1</sup>), peak B can be ascribed to non-complexed stereostar PMMA. Thus, peak C with a smaller hydrodynamic volume can be ascribed to the intramolecular complex stereostar PMMA, in which *it*- and *st*-PMMA arms in the star macromolecule associate to form a smaller species. The small peak A at larger molar mass is thus due to intermolecular dimer complexation.

The SEC curve of [it/st/st]-3-*star*-PMMA at 0 °C consists of two major peaks B and D, together with two smaller shoulder peaks A and C. Peak B remained and became a single major peak at higher



**Figure 3** 400 MHz  $^1\text{H}$  NMR spectra of uniform stereostar poly(methyl methacrylate)s (PMMA) with an arm degree of polymerization of 32 measured in benzene- $d_6$  at 75 °C. The expanded spectra of terminal  $t\text{-C}_4\text{H}_9$  group signals are shown on the right side.

**Table 1** DP dependence of the product distribution in the preparation of stereoregular uniform 3-*star*-PMMA

DP	<i>st</i> / <i>it</i> <sup>a</sup>	Relative product ratio <sup>b</sup>				
		[ <i>it/it/it</i> ]	[ <i>it/it/st</i> ]	[ <i>it/st/st</i> ]	[ <i>st/st/st</i> ]	
32	1.74	Obsd (Calcd)	1.0 (1.0)	5.0 (5.2)	7.5 (9.1)	3.4 (5.3)
37	1.97	Obsd (Calcd)	1.0 (1.0)	5.6 (5.9)	10.4 (11.6)	6.5 (7.6)
42	2.01	Obsd (Calcd)	1.0 (1.0)	6.0 (6.0)	12.1 (12.2)	8.9 (8.2)

Abbreviations: DP, degree of polymerization; PMMA, poly(methyl methacrylate).

<sup>a</sup>Feed ratio of *it*-PMMA-OH (end functionality=0.86) and *st*-PMMA-OH (end functionality=0.86).

<sup>b</sup>Estimated from peak areas in supercritical fluid chromatography chromatograms.

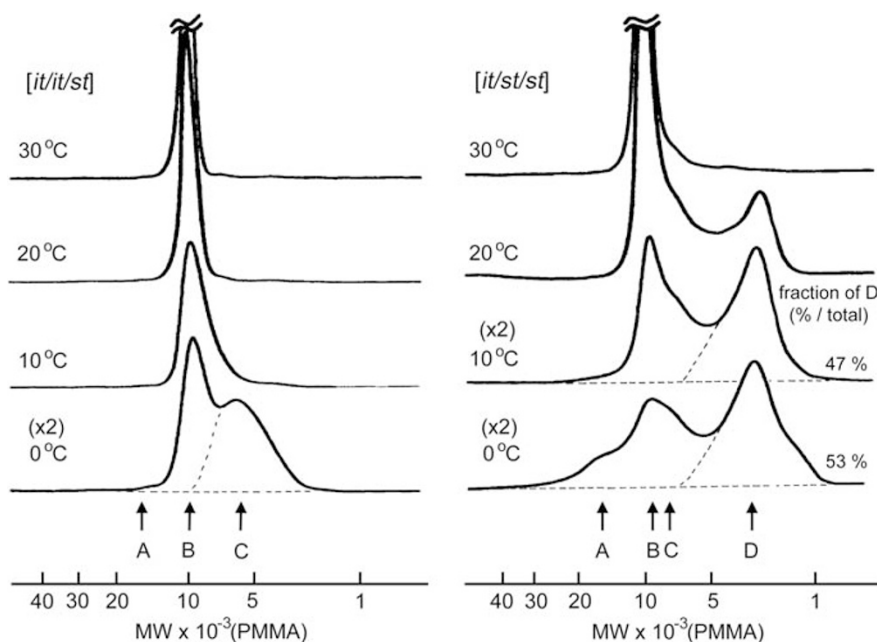
temperature; thus, peak B can be ascribed to the non-complexed species. Peak D observed at a lower molar mass than peak A should result from the intramolecular complex. In contrast, peak D for [*it/st/st*]-3-*star*-PMMA could still be observed even at 20 °C, indicating that this complex is more stable than [*it/it/st*]-3-*star*-PMMA, which did not show a peak corresponding to the intramolecular complex even at 10 °C. Moreover, the apparent molar mass of the complexed species represented by peak D at its elution maximum is evidently smaller than that for [*it/it/st*]-3-*star*-PMMA, suggesting a more compact or compressed molecular size due to the stereospecific entanglement between the *it*- and *st*-PMMA arm chains in this stereostar PMMA with two *st*-PMMA arms. The higher molar mass shoulder peak A almost disappeared at 10 °C because of the dissociation of the complex; thus, peak A can be ascribed to the intermolecular complex. The peak intensity of the intramolecular complex was greater than that for [*it/it/st*]-3-*star*-PMMA. Another shoulder peak C remained observable even at 20 °C, similarly to peak D, and could also be ascribed to intramolecular complexes with a different hydrodynamic volume than species D. Thus, intramolecular complexes of [*it/st/st*]-3-*star*-PMMA contained at least two species with different sizes.

To elucidate the change in size arising from the intramolecular complexation between *it*- and *st*-PMMA arm chains, a uniform stereoblock PMMA with *it*- and *st*-PMMA arms with a DP of 35 attached to a phenylene linker at the *meta* position was prepared and isolated in a manner similar to that of the uniform star PMMA.

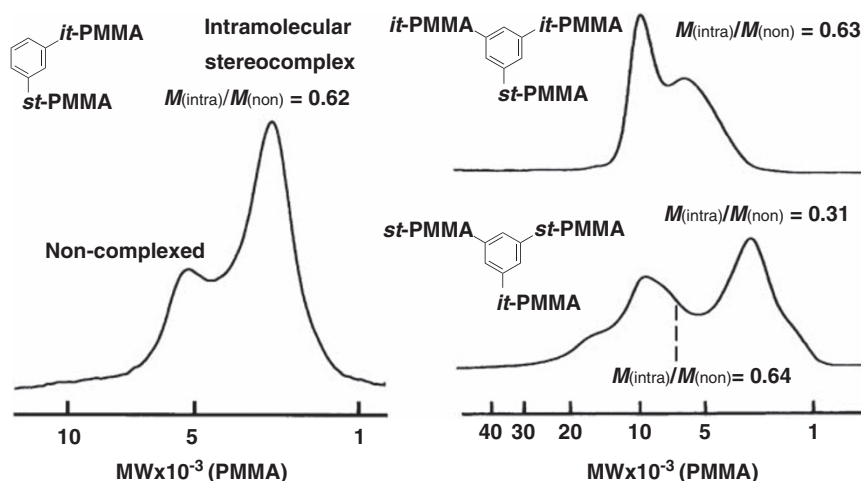
Figure 5 shows an SEC curve of the stereoblock PMMA obtained at 0 °C, together with curves of the two types of stereostar PMMA. The chromatogram of the stereoblock PMMA consists of non-complexed species as the minor component and intramolecular complexes as the major component. The intermolecular complex was scarcely observed, in contrast to the previously reported case of stereoblock PMMA with hexamethylene linker.<sup>18</sup> The rigid and directional *meta*-phenylene linker might favor intramolecular complexation. This effect of the structure of the linker is also observed in the case of stereostar PMMA. A detailed investigation of this issue is now under way, and the results will be published in a separate article.

As the stereoblock PMMA has one *it*-PMMA arm and one *st*-PMMA arm, the intramolecular complex should be a 1:1 complex based on the *it*- and *st*-PMMA chain composition, but not on the monomer unit base. The extent of contraction of the stereostar PMMA resulting from complex formation can be estimated by the ratio of the apparent molar mass of the intramolecular complex to that of the non-complexed species,  $M(\text{intra})/M(\text{non})$ , which is 0.62 for this stereoblock PMMA. This value is close to that for [*it/it/st*]-3-*star*-PMMA, which also showed two peaks with an  $M(\text{intra})/M(\text{non})$  value of 0.63. Thus, the complex of this stereostar PMMA is likely a 1:1 stereocomplex, comprising of one *it*-PMMA arm and one *st*-PMMA arm, leaving one *it*-PMMA arm free from complexation. In contrast, the major intramolecular complex (peak D) of [*it/st/st*]-3-*star*-PMMA has an  $M(\text{intra})/M(\text{non})$  value of 0.31, evidently smaller than the above cases, whereas another intramolecular complex (peak C) has a value of  $\sim 0.6$ , although the position of peak C is somewhat ambiguous. These results suggest that the [*it/st/st*]-3-*star*-PMMA forms two types of stereocomplexes corresponding to peaks C and D, with peak C representing a complex similar to the 1:1 complex observed for [*it/it/st*]-3-*star*-PMMA and stereoblock PMMA (type-I), and peak D representing a more contracted complex (type-II) (Figure 6).

Given that the monomer unit ratio of *it*- and *st*-PMMA stereocomplexes is 1:2, one *it*-PMMA arm in [*it/st/st*]-3-*star*-PMMA can associate with two *st*-PMMA arms in the same star macromolecule. One possible form of such a complex is a braid-type complex in which the three chains are twisted around one another (type-II(a)). Another possibility is that a 1:1 complex forms through association of an



**Figure 4** Supercritical fluid chromatography curves of uniform stereostar poly(methyl methacrylate)s (PMMA) with an arm degree of polymerization of 32 measured in acetone at various temperatures. Left:  $[it/it/st]$ -3-*star*-PMMA; right:  $[it/st/st]$ -3-*star*-PMMA. Sample concentration:  $1.0 \text{ mg ml}^{-1}$ .



**Figure 5** Supercritical fluid chromatography curves of uniform stereoblock poly(methyl methacrylate) (PMMA) with a block degree of polymerization (DP) of 35 (left) and uniform stereostar PMMA with an arm DP of 32 (right) measured in acetone at  $0^\circ\text{C}$ . Sample concentration:  $1.0 \text{ mg ml}^{-1}$ .

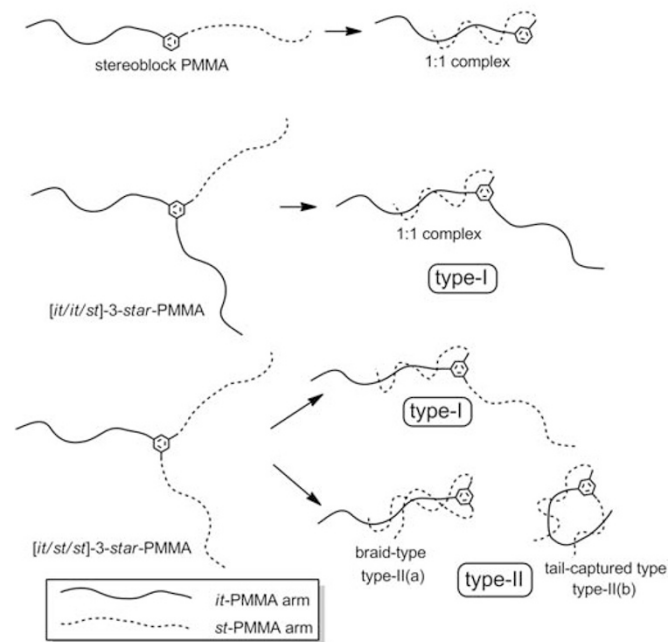
*it*-PMMA chain with one *st*-PMMA chain at a monomer unit ratio of 1:2 (*it*-*st*-), leaving half of the *it*-PMMA segment free from association, which is then captured by the remaining *st*-PMMA arm to form a compact cyclic associated species (typeII(b)). Because the type-I 1:1 complex of  $[it/st/st]$ -3-*star*-PMMA has half of the *it*-PMMA segment and one *st*-PMMA arm free from complexation, two such species may collapse to form an intermolecular complex as observed in the SEC curve. In the case of  $[it/it/st]$ -3-*star*-PMMA, once the 1:1 complex forms, no *st*-PMMA remains to interact with the remaining *it*-PMMA arm or segment. Thus, there is a negligible amount of intermolecular complex in this case (see Figure 4, left). Figure 6 presents a schematic representation of type-I and type-II intramolecular stereocomplexes.

Figure 7 presents  $^1\text{H}$  NMR spectra of the  $[it/it/st]$ - and  $[it/st/st]$ -3-*star*-PMMA in acetone- $d_6$  at 0, 15 and  $40^\circ\text{C}$ . The spectra obtained at

$40^\circ\text{C}$  are simple superpositions of *it*- and *st*-PMMA and almost all the PMMA segments in the stereostar PMMA dissociated in accordance with the single SEC peaks at  $30^\circ\text{C}$  as shown in Figure 4. Although all the signals became broader with decreasing temperature, the broadening is more evident for  $[it/st/st]$ -3-*star*-PMMA than for  $[it/it/st]$ -3-*star*-PMMA. Moreover, the former polymer showed an additional broad peak (indicated with an asterisk in the figure) at around 3.95 p.p.m. in the  $\text{OCH}_3$  region, which can be attributed to  $\text{OCH}_3$  groups in the complexed molecule, whereas no corresponding signal was observed for  $[it/it/st]$ -3-*star*-PMMA. These results are consistent with the structural differences between the major stereocomplex species formed from  $[it/it/st]$ - and  $[it/st/st]$ -3-*star*-PMMA, as discussed above.

$[it/st/st]$ -3-*star*-PMMA with a larger arm DP (42) was successfully isolated and subjected to temperature-dependent SEC measurement as

shown in Figure 8. The overall results are similar to those observed for  $[it/st/st]-3\text{-star-PMMA}$  with an arm DP of 32 (see Figure 4). However, the stability of the complexed species is significantly enhanced so that the complex peaks can even be observed at 45 °C. At 0 °C, the type-II intramolecular complex designated as peak D in Figure 8 became the predominant species, reaching 73%, whereas the 32 mer stereostar PMMA only reached 53%. Peak C, representing the type-I intramolecular complex, is more evident for the 42 mer stereostar PMMA, in which case the intensity of this peak remains constant even at 40 °C,



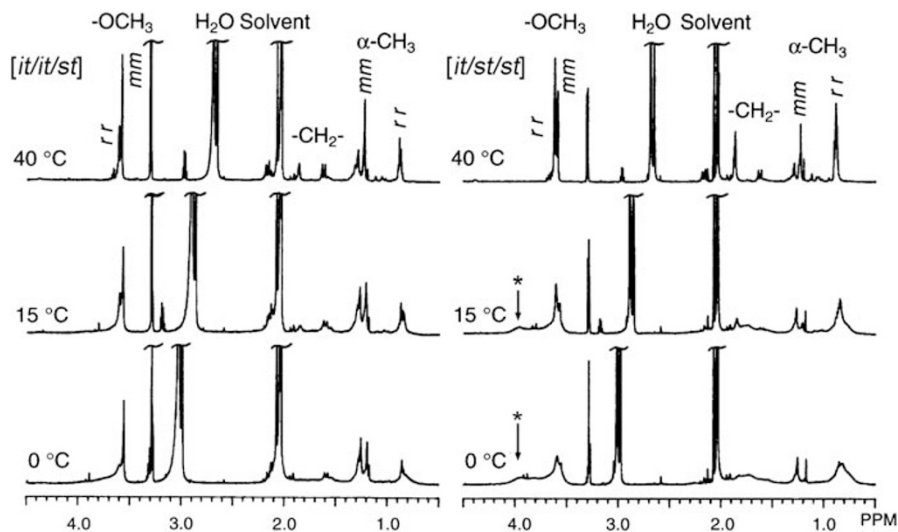
**Figure 6** Schematic representation of intramolecular stereocomplexes of stereoblock and stereostar poly(methyl methacrylate)s (PMMA).

whereas the intensity of the type-II complex decreased monotonically with increasing temperature. These results suggest the possibility that the dissociation of the type-II complex takes place in a stepwise manner, that is, one *st*-PMMA arm dissociates from the complex to yield a type-I complex, keeping the fraction of the intramolecular complex relatively high.

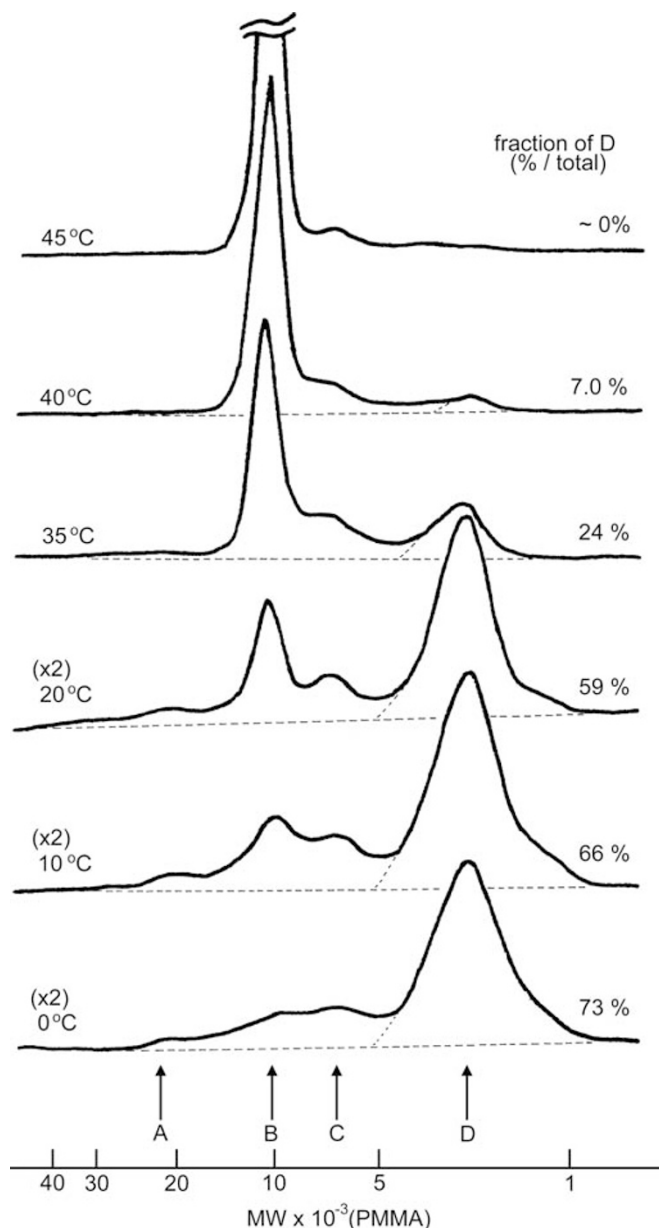
## CONCLUSION

The stereocomplex formation of two kinds of uniform stereostar PMMAs with different combinations of *it*-PMMA and *st*-PMMA arms containing discrete numbers of monomer units,  $[it/it/st]-3\text{-star-PMMA}$  and  $[it/st/st]-3\text{-star-PMMA}$ , was investigated using SEC in acetone, revealing the coexistence of two different types of intramolecular complexes, type-I and type-II.  $[it/it/st]-3\text{-star-PMMA}$  only forms a type-I complex in which one *it*-PMMA arm and one *st*-PMMA arm associate to form a stereocomplex that has a smaller hydrodynamic volume than the non-complexed species. In sharp contrast,  $[it/st/st]-3\text{-star-PMMA}$  was found to form both type-I and type-II complexes, with the latter representing the major component of the mixture and likely involving one *it*-PMMA and two *st*-PMMA arms. The type-II complex had a more compact or compressed shape than the type-I complex, as demonstrated by the smaller hydrodynamic volume indicated by the SEC elution profile. These results are consistent with the reported structure of PMMA stereocomplexes with a unit ratio of  $st/it=2/1$ , the value of which implies that the two *st*-PMMA arms in  $[it/st/st]-3\text{-star-PMMA}$  can associate with one *it*-PMMA arm.

The discrete molar mass of the uniform star PMMAs allows for such distinct observations of the change in molecular size in solution on stereocomplex formation. Moreover, complex formation occurs within a single molecule of the stereostar PMMA in which the number and DP of stereoregular PMMA arms are regulated. In addition, the rigid benzene core that links the PMMA arms through ester groups results in predominant formation of intramolecular complexes as compared with the previously reported hexamethylene linker for the stereoblock PMMA.<sup>18</sup> Although the structure of this unique intramolecular stereocomplex is still speculative and the exact structure remains an open



**Figure 7** 500 MHz  $^1\text{H}$  NMR spectra of stereostar poly(methyl methacrylate)s (PMMA) with an arm degree of polymerization of 32 measured in acetone- $d_6$  at various temperatures. Left:  $[it/it/st]-3\text{-star-PMMA}$ ; right:  $[it/st/st]-3\text{-star-PMMA}$ . Sample concentration:  $1.0\text{ mg ml}^{-1}$ . \*The broader peaks at around 3.95 p.p.m. can be attributed to  $\text{OCH}_3$  groups in the complexed molecule.



**Figure 8** Supercritical fluid chromatography curves of uniform *[it/st]*-3-star-poly(methyl methacrylate) (PMMA) with an arm degree of polymerization of 42 measured in acetone at various temperatures. Sample concentration: 1.0 mg ml<sup>-1</sup>.

question, the present report reveals a unique aspect of PMMA stereocomplex formation in solution at the unimolecular level, providing a molecular-level understanding of stereocomplex formation.

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