

## SHORT COMMUNICATIONS

## Intra- and Intermolecular Stereocomplex Formation of Uniform Stereoblock Poly(methyl methacrylate)

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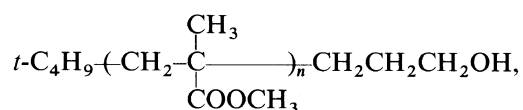
KEY WORDS Uniform Polymer / Poly(methyl methacrylate) (PMMA) / Stereoblock Poly(methyl methacrylate) / Stereocomplex / Supercritical Fluid Chromatography (SFC) / Gel Permeation Chromatography (GPC) /

In 1961, Watanabe and his coworkers reported that isotactic (*it*-) and syndiotactic (*st*-) poly(methyl methacrylate) (PMMA) chains associate to form a crystalline polymer–polymer complex, “stereocomplex”.<sup>1</sup> Since then, many studies have been made on the structure and the properties of stereocomplex.<sup>2–19</sup> The stereocomplexes other than PMMA stereocomplexes were also studied.<sup>20–29</sup>

Recently, we studied the mechanism of stereocomplex formation in tetrahydrofuran (THF) between isotactic (*it*-) and syndiotactic (*st*-) PMMAs using uniform polymers, and concluded that the complexation stoichiometry was *it*-PMMA : *st*-PMMA = 1 : 1 at the initial stage of complex formation and that the minimum degree of polymerization (*DP*) required for the stereocomplex formation was in the range from *DP* of 42 to 46.<sup>30,31</sup>

In the present work, we found that a uniform stereoblock PMMA [*it*-(MMA)<sub>46</sub>-block-*st*-(MMA)<sub>46</sub>] showed three peaks in GPC chromatogram measured in acetone, which were ascribable to intermolecularly stereocomplexed, non-complexed and intramolecularly stereocomplexed polymer molecules with increasing elution volume. The results are briefly reported in this paper.

*it*- and *st*-Poly(methyl methacrylate)s with terminal hydroxy group,



(*it*-PMMA-OH and *st*-PMMA-OH) were prepared by the procedure reported previously.<sup>32–34</sup> From the resulting PMMAs, *it*- and *st*-46 mers of MMA were isolated by supercritical fluid chromatography (SFC) using liquefied CO<sub>2</sub> as an eluent and methanol as an entrainer. The instrumental set-up for SFC was similar to that described elsewhere.<sup>30</sup>

The hydroxy end-functionality of the *it*- and *st*-46 mers were determined as 0.98 and 1.00, respectively, by <sup>1</sup>H NMR spectroscopy. Uniform stereoblock PMMA was prepared by the reaction of the *it*-46 mer (17.45 mg, hydroxy end-group = 3.29 μmol), the *st*-46 mer (15.22 mg, hydroxy end-group = 3.09 μmol) and sebacyl dichloride (4.16 μmol) in toluene (0.14 ml) in the presence of pyridine (16.62 μmol) at 25°C for four days. The reaction mixture contains three coupling products of (*it*-46 mer)–

(*it*-46 mer), (*st*-46 mer)–(*st*-46 mer), and (*it*-46 mer)–(*st*-46 mer). These three block PMMAs have the same molecular weight and GPC is incompetent to isolate each product. However, with the aid of SFC, it was possible to isolate each product as shown in Figure 1. The stereostructures of the isolated products were confirmed by the <sup>1</sup>H NMR spectra and the results are indicated in Figure 1.

Figure 2 shows GPC curves of the isolated stereoblock PMMA, (*it*-46 mer)–(*st*-46 mer), measured in chloroform and in acetone at 0°C. GPC curve in chloroform showed a single peak. On the other hand, three peaks appeared in the chromatogram obtained in acetone.

Figure 3 shows the GPC curves for the stereoblock PMMA measured in acetone at various sample concentrations. With a decrease in sample concentration the relative intensities of the peak with the largest elution volume increased and those with the smallest elution volume decreased. It is well known that *it*- and *st*-PMMAs forms stereocomplex in acetone but not in chloroform.<sup>35</sup> There may be two types of stereocomplexes in the acetone solution of the stereoblock PMMA, intramolecular and intermolecular stereocomplexes. In-

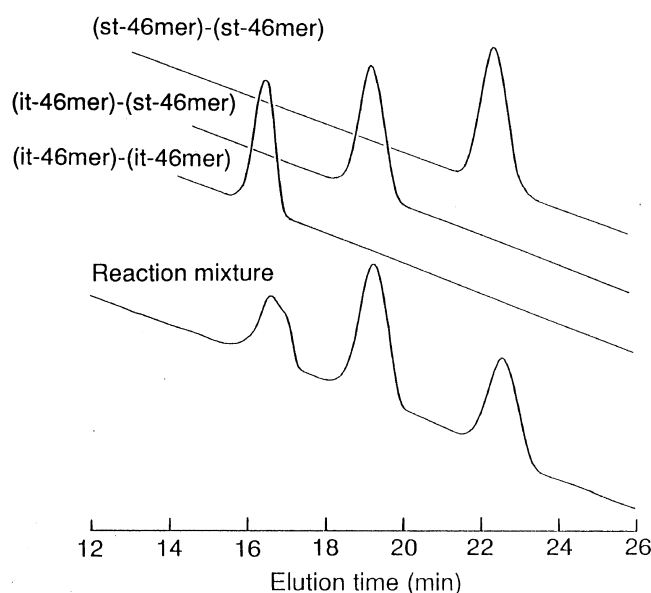
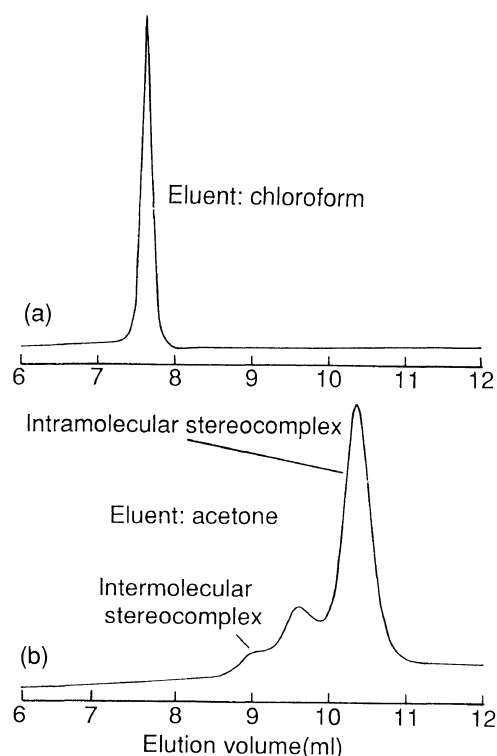


Figure 1. SFC curves of the reaction mixture *it*-46 mer, *st*-46 mer, and sebacyl dichloride and block PMMAs isolated therefrom. (MeOH, 3.0 ml min<sup>-1</sup>; CO<sub>2</sub>, 7.0 ml min<sup>-1</sup>; initial temp, 85°C; rate of cooling, 2°C min<sup>-1</sup>.)

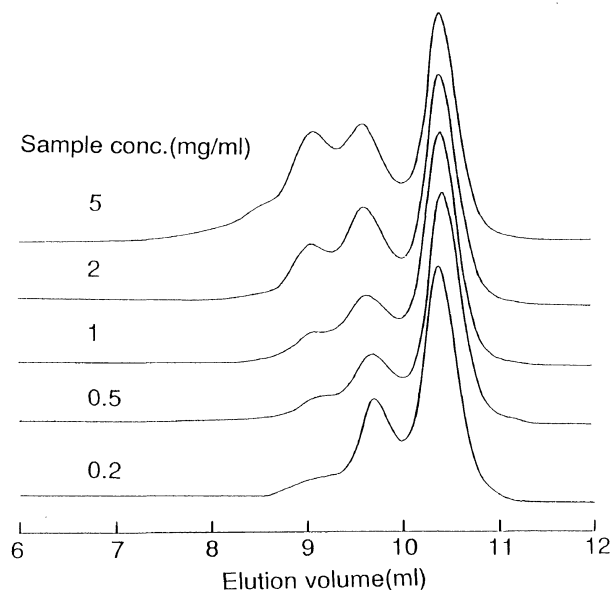


**Figure 2.** GPC curves of uniform stereoblock PMMA in chloroform (a) and in acetone (b). (Flow rate,  $0.5 \text{ ml min}^{-1}$ ; sample concentration,  $1.0 \text{ mg ml}^{-1}$ ; temperature,  $0^\circ\text{C}$ .)

tramolecular association causes the decrease in the hydrodynamic volume of the PMMA molecules leading to the increase in the elution volume. On the contrary, intermolecular association leads to the decrease in the elution volume. Thus, the three peaks in Figure 2 are ascribable to intermolecularly stereocomplexed, non-complexed and intramolecularly stereocomplexed PMMA molecules with an increase in the elution volume. The results in Figure 3 indicate that the amount of intermolecular stereocomplex increases with an increase in the sample concentration. The peak at the elution volume of 9.1 ml may be due to the dimer, and the shouldered peak at 8.5 ml for the sample concentration of  $5 \text{ mg ml}^{-1}$  to the trimer. Equimolar mixture of the *it*-46 mer and the *st*-46 mer showed two peaks in GPC curve in acetone, the elution volumes of which were close to those of the peaks for the intramolecularly complexed and non-complexed PMMAs in the GPC curve of the stereoblock PMMA.\* This is the additional evidence for the peak assignment indicated in Figure 2.

In the previous paper<sup>36</sup> we reported that stereoblock PMMA shows larger Huggins' coefficient  $k_H$ , that is, stronger concentration dependence of reduced viscosity in acetone than the corresponding mixture of *it*- and *st*-PMMA. This peculiar behavior of solution viscosity was not observed in chloroform. From the results ob-

\* There is another possibility that the peak assigned to the non-complexed polymer is due to an aggregated dimer of the intramolecularly complexed polymer with a doubled hydrodynamic volume, though the temperature dependence of the GPC curve showed that the peak increased in its intensity with increasing temperature, probably due to the dissociation of the intramolecular complex to the non-complexed polymer. The details are now under investigation and the results will be reported in the near future.



**Figure 3.** GPC curves of uniform stereoblock PMMA at various sample concentrations. (Eluent acetone; flow rate,  $0.5 \text{ ml min}^{-1}$ ; temperature,  $0^\circ\text{C}$ .)

tained in the present work it now becomes clear that there exist intramolecularly and intermolecularly associated stereocomplexes in acetone solution of stereoblock PMMA and with increasing polymer concentration the fraction of the former decreases in association with an increase of the fraction of the latter. This causes the strong concentration dependence of the solution viscosity of stereoblock PMMA as compared with that in chloroform. The strong concentration dependence observed for the graft PMMA with *it*-main chain and *st*-side<sup>37</sup> chains can be explained in the same way. It should be noted that the results obtained in the present work can not be obtained without uniform polymer, that is, uniform polymer makes ambiguous problem in polymer chemistry very clear.

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