PREPARATION OF UNIFORM STEREOREGULAR POLYMER, STEREOBLOCK POLYMER AND COPOLYMER OF METHACRYLATE, AND THEIR STEREOCOMPLEX FORMATION

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Abstract: Isotactic (*it*-) and syndiotactic (*st*-) uniform poly(methyl methacrylate)s (PMMAs) were prepared by stereospecific living polymerizations followed by supercritical fluid chromatographic separation. The *it*- and *st*-uniform PMMAs were used to study the mechanism of stereocomplex formation in solution with the aid of gel permeation chromatography and ^{1}H NMR spectroscopy. The *it*- and *st*-uniform PMMAs with hydroxy end-group were prepared and reacted with sebacoyl dichloride to form uniform stereoblock PMMA. The stereoblock PMMA was found to form intra- and intermolecular stereocomplexes in acetone. A uniform stereoblock copolymer, *it*-PMMA-block-*st*-poly(ethyl methacrylate), was prepared and its stereocomplex formation was also studied.

INTRODUCTION

It has been known that isotactic (*it*-) and syndiotactic (*st*-) poly(methyl methacrylate) (PMMA) chains associate to form a stereocomplex in certain solvents such as acetone, toluene, and tetrahydrofuran (THF). This is one type of stereocomplex which forms between a pair of diastereomeric macromolecules. The phenomenon of stereocomplex formation was first reported in 1961 by Watanabe *et al.* (Ref. 1). In 1965 Liquori *et al.* reported a structure model of PMMA stereocomplex in the solid state (Ref. 2). Later, Challa and coworkers proposed another model known as a double-stranded helix model (Refs 3,4), in which a helix of *it*-PMMA chain with a smaller radius is surrounded by an *st*-PMMA helical chain with a larger radius.

The Challa's helix model requires 1:2 ratio of associated monomeric units in *it*- and *st*-PMMAs. There have been a number of contradictory results about the stoichiometry of the stereocomplex (Ref. 5). Most of the results show the stoichiometry *it*:*st*=1:2 (Refs 2,6), but papers indicating the stoichiometry *it*:*st*=1:1 (Ref. 7) or

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it:*st*=1:1.5 (Refs 8,9) also exist. The stoichiometries reported in the past concern the ratio of associated monomeric units or the weight fractions of *it*- and *st*-PMMAs. To understand the initial stage of the complex formation in solution, however, the stoichiometry of the complex as the ratio of *it*- and *st*-PMMA molecules should be important instead of monomeric unit ratio.

Another important problem in the study of the stereocomplex so far discussed is the minimum degree of polymerization (DP) of PMMA chains required for the complex formation (Ref. 9). When *it*- and *st*-PMMAs with molecular weight distribution (MWD) are used for the experiment of stereocomplex formation, fractions of the polymer molecules having larger molecular weights should form the stereocomplex first, occluding the other fractions with lower molecular weights. This makes the problem ambiguous; the minimum chain-length required for the stereocomplex formation may be underestimated.

When *it*- and *st*-PMMA chains are linked by chemical bonds, the complex formation may take place not only intermolecularly but also intramolecularly . We have reported the synthesis of stereoblock PMMA by stereospecific living polymerization and its peculiar solution viscosity, which was ascribed to the contribution of intramolecular complexation (Ref. 10). However, the direct evidence of the formation of intramolecular stereocomplex was not obtained.

We have been successful in developing stereospecific living polymerizations of methacrylate which afford stereoregular PMMAs, *it*-PMMA(Ref. 11) and *st*-PMMA (Ref. 12), with narrow MWD. Recognizing the limitation of living polymerization that gives polymers with narrow MWD but never the molecularly uniform polymer, we have devoted ourselves in developing the separation of uniform polymers by supercritical fluid chromatography (SFC) (Refs 13-19). A combination of the stereospecific living polymerization and highly efficient separating power of SFC has allowed us to obtain stereoregular uniform PMMAs. Using the polymers without MWD, we could observe the complex formation process precisely by means of conventional gel permeation chromatography (GPC) by appreciating extreme narrowness of the GPC peaks of the uniform PMMAs with unambiguously defined molecular weight (Ref. 14).

The living nature of the stereospecific polymerizations mentioned above has made it possible to prepare end-functional stereoregular PMMAs, which could also be separated into uniform PMMAs by SFC. They could be used in constructing elaborated uniform polymer architectures such as stereoblock (Refs 20, 21), star (Ref. 22) and comb polymers (Ref. 23). These uniform polymers should be useful in understanding of the relationship between polymer structures and properties. The present pa-

per focuses on the PMMA stereocomplex and describes the use of stereoregular uniform PMMAs, stereoblock PMMA and stereoblock copolymer comprising *it*-PMMA block and *st*-poly(ethyl methacrylate) block in the elucidation of stereocomplex formation in solution at molecular level.

RESULTS AND DISCUSSION

Stereocomplex formation between uniform *it*- and *st*-PMMAs

The stereoregular PMMAs, *it*- and *st*-PMMAs, were prepared by stereospecific living polymerizations with *t*-C_4H_9MgBr (Ref. 11) and *t*-C_4H_9Li/R_3Al (Ref. 12) in toluene at −78°C, respectively. The polymers obtained were separated into uniform components by SFC using liquefied CO_2 as an eluent and methanol as an modifier and the resulting uniform PMMAs were used for the study of stereocomplex formation in THF.

When a solution of a 1:1 mixture of *it*- and *st*-50mers in THF was subjected to GPC measurement certain times after mixing at −15°C, there appeared two peaks at the elution volumes corresponding to the 50mers and 100mers (Ref. 14). The observation of the extra peak indicates the formation of 1:1 aggregates of the two 50mers comprising 100 monomeric units, although the hydrodynamic volume of linear PMMA may not

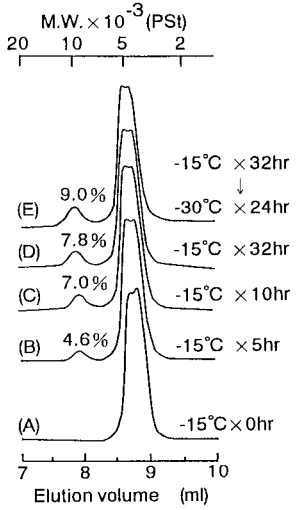


Fig. 1 GPC curves of a 1:1 mixture of *it*- and *st*-50mers of MMA stored at −15°C for 0 (A), 5 (B), 10 (C), and 32hr (D). The mixture (D) was allowed to stand at −30°C for further 24hr (E). Eluent THF, flow rate 0.5 ml/min, column temp. 3°C, concn of sample solution 1.0 mg/ml

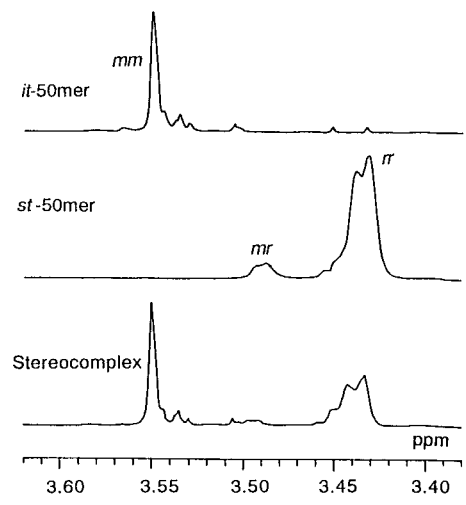


Fig. 2 ^1H NMR signals due to the CH_3O groups in *it*- and *st*-50mers of MMA and their stereocomplex. The complex was separated from the 1:1 mixture of the 50mers by means of GPC. [C_6D_6, 75°C, 500MHz]

be the same as that of the aggregate. The peak corresponding to the 50mers exhibits a small splitting due to the difference in elution volume of *it*- and *st*-50mers.

The intensity of the extra small peak increased with an increase in the time after mixing (Figs 1A-1D) and a decrease in the temperature (Fig. 1E) at which the solution was kept. The polymer fraction was collected from the small peak and subjected to ^{1}H NMR measurement (Fig. 2). The fraction contained both the *it*- and *st*-PMMAs and the ratio of *it*-50mer and *st*-50mer was found to be 1:1.2. When the initial mixing ratio of the *it*-50mer against *st*-50mer was decreased, the ratio of the *it*-50mer to *st*-50mer in the fraction collected from the small peak decreased, while the elution volume of the small peak was almost constant. The results indicate that the predominant process at the initial stage of the stereocomplex formation is the association of one *it*-50mer and one *st*-50mer molecules, though the 1:2 complex also forms to some extent even in the initial stage of aggregation.

To examine the critical DP for the stereocomplex formation, GPC investigations were also carried out for mixtures of uniform PMMAs with lower DPs than 50. When a mixture of the *it*-42mer and *st*-42mer in THF was kept at −15°C for 32hr and subsequently at −30°C for 24hr, a small shoulder was observed, showing the formation of a stereocomplex (Fig. 3C). A mixture of the *it*-46mer and *st*-46mer or *it*-50mer and *st*-50mer shows clear indication of stereocomplex formation as shown in Figs. 3B and 3A, but no sign of the complexation was observed in the case of 40mers (Fig. 3D). The results clearly indicate that the minimum DP for the stereocomplex formation between *it*- and *st*-PMMAs under these conditions lies between 40 and 42 (Ref. 24). The reported values of the critical DP for the PMMAs with MWD in benzene (Ref. 9) are much less than 40; the reason should be ascribed to the existence of higher DP components in the polymers with MWD, as already mentioned in the INTRODUCTION.

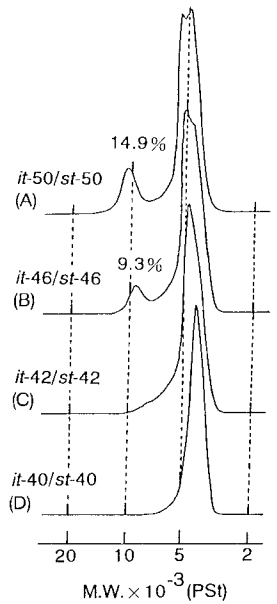


Fig. 3 GPC curves of 1:1 mixtures of uniform *it*-PMMA and *st*-PMMA of different DPs. Eluent THF, flow rate 0.5 ml/min, column temp. 3°C, concn of sample solution 1.0 mg/ml

An equimolar mixture of *it*-24mer and *st*-48mer in THF after being kept at −15°C for 32hr did not show any sign of complex formation, but after being kept subsequently at −30°C for 24hr, it showed a small peak due to the stereocomplex (Fig. 4A).

On the contrary, the mixture of *it*-48mer and *st*-24mer showed no detectable sign of complex formation under the same conditions (Fig. 4B) (Ref. 24). The results suggest that the minimum DP for the complex formation is larger for *st*-PMMA than for *it*-PMMA, apparently consistent with the structure model given by Challa, in which a helix of *it*-PMMA chain with a smaller radius is surrounded by an *st*-PMMA chain with a larger radius (Refs 3,4).

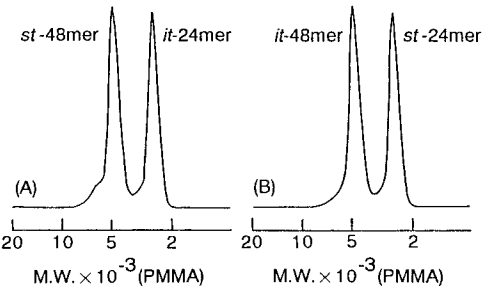
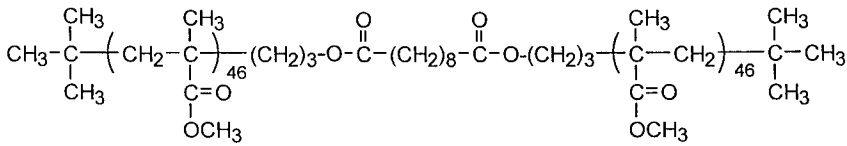


Fig. 4 GPC curves of 1:1 mixtures of *it*-24mer and *st*-48mer (A) and of *it*-48mer and *st*-24mer (B), kept at −15°C for 32hr and then at −30°C for 24hr
Eluent THF, flow rate 0.5 ml/min, column temp. 3°C, concn of sample solution 1.0 mg/ml

Stereocomplex formation of uniform stereoblock PMMA

One of the synthetic merits of living polymerization is to afford end-functionalized polymers. Using the stereospecific living polymerizations, stereoregular PMMAs with terminal hydroxyl group, *it*- and *st*-α-3-hydroxypropyl-ω-*t*-butyl-PMMAs (PMMA-OH) were prepared (Ref. 25). The *it*- and *st*-PMMA-OHs were fractionated into uniform polymers by SFC technique (Refs 20-22). The uniform *it*- and *st*-PMMA-OHs with DP of 46 were reacted with sebacoyl dichloride in toluene in the presence of pyridine to form three types of block PMMAs, *it*-PMMA-block-*it*-PMMA, *st*-PMMA-block-*st*-PMMA, and the objective *it*-PMMA-block-*st*-PMMA with 46 monomeric uinits in both *it*- and *st*-



it-PMMA block
(*mm* : *mr* : *rr* = 97 : 2 : 1)

st-PMMA block
(*mm* : *mr* : *rr* = 1 : 10 : 89)

blocks, (*it*-46mer)-(*st*-46mer). The mixture was separated into each uniform PMMA block polymers by SFC (Ref. 21). GPC experiment was conducted on the uniform stereoblock PMMA. A particular interest in this experiment is to observe two types of stereocomplexes of the stereoblock PMMA, intramolecular and intermolecular stereocomplexes. The solvents used were acetone and chloroform, which are known as complex-forming and non-complexing solvents, respectively (Ref. 6).

Figure 5 shows GPC curves measured in chloroform and in acetone at 0°C.

GPC curve obtained with chloroform as an eluent (Fig. 5A) showed a single peak, confirming the uniformity of the sample. On the other hand, three peaks appeared in the chromatogram obtained with acetone (Fig. 5B), in contrast to the case of the GPC experiments on *it*- and *st*-PMMAs where two peaks due to noncomplexed and complexed polymers, respectively, were observed(*cf.* Fig. 1).

Intramolecular association of the stereoblock PMMA may cause the decrease in the hydrodynamic volume of the PMMA molecules leading to the increase in the elution volume. On the other hand, intermolecular association leads to the decrease in the elution volume. Thus, the three peaks in Fig. 5B are ascribable to intermolecularly stereocomplexed, noncomplexed and intramolecularly stereocomplexed PMMA molecules in the increasing order of the elution volume.

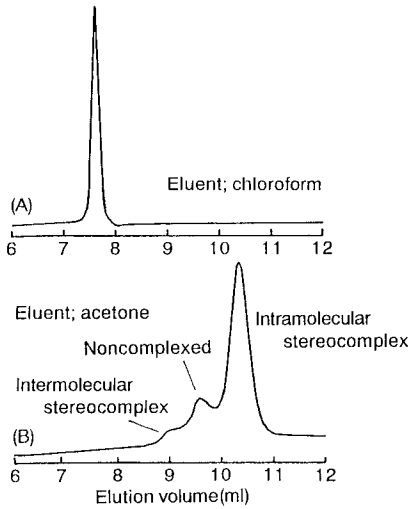


Fig. 5 GPC curves of uniform stereoblock PMMA in chloroform (A) and in acetone (B). Flow rate 0.5 ml/min, column temp. 0°C, concn of sample solution 1.0 mg/ml

Concentration dependence of GPC curves for the stereoblock PMMA was studied using acetone as an eluent (Fig. 6). With increasing sample concentration the relative intensity of the peak with the largest elution volume decreased and that with the smallest elution volume increased. At the sample concentration of 5 mg/ml the fourth peak appeared at the elution volume of 8.5 ml as a shoulder. The results in Fig. 6 indicate that the amount of intermolecular stereocomplex increases with an increase in the sample concentration. The peaks 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 mg/ml to the trimer.

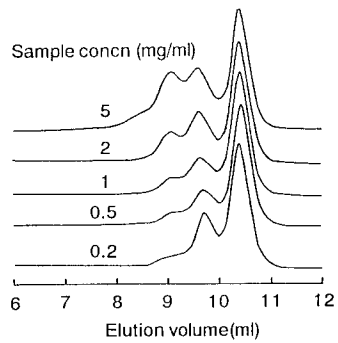


Fig. 6 GPC curves of uniform stereoblock PMMA at various sample concentrations. Flow rate 0.5 ml/min, eluent acetone, column temp. 0°C

The elution volume of the intramolecular stereocomplex is close to those of the starting uniform PMMA-OHs, *it*-46mer and *st*-46mer, This suggests that the intramolecular complex

of the stereoblock PMMA containing 92 MMA units takes a compactly folded conformation so that its hydrodynamic volume becomes close to that of the PMMA chains containing 46 MMA units.

An equimolar mixture of the *it*-46mer and the *st*-46mer was subjected to GPC analysis in acetone at 0℃. The mixture showed a small peak due to the intermolecularly formed stereocomplex, in addition to the peaks for the component polymers, at smaller elution volume. The elution volume of the small peak is close to that of the peak for the noncomplexed stereoblock PMMA with 92 MMA units, suggesting the hydrodynamic volume of the intermolecular stereocomplex between *it*-46mer and *st*-46mer is close to that of the noncomplexed PMMA. This means that the intermolecular stereocomplex is not a compactly associated one as the intramolecular complex of the stereoblock PMMA, but a rather loosely linked aggregate so that the hydrodynamic volume becomes close to that of the PMMA with doubled DP. The result is an additional evidence for the GPC peak assignments indicated in Fig. 5.

Temperature dependence of the complex formation of the stereoblock PMMA was also studied by GPC and ^{1}H NMR spectroscopy at the sample concentration of 1.0 mg/ml. GPC curves of the stereoblock PMMA in acetone were measured in the temperature range from 0 to 30℃. The results of analysis are summarized in Fig. 7. GPC peaks due to inter- and intramolecular complexes became smaller as the temperature of measurement increased. However, the peak due to the intramolecular complex remained observable even at 30℃ while that of the intermolecular complex disappeared at 25 and 30℃. The results suggest the higher stability of the intramolecular complex than the intermolecular one.

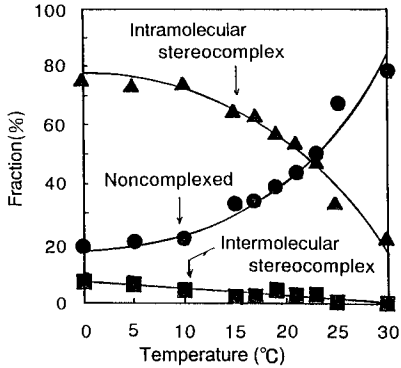


Fig. 7 Fractions of non-complexed, intramolecularly complexed and intermolecularly complexed uniform stereoblock PMMA in acetone as determined by GPC at various temperatures.
Concentration of sample solution 1.0mg/ml

750MHz ^{1}H NMR spectra of the stereoblock PMMA were measured in acetone-d_6 at 0, 30 and 50℃ (Figs 8A-8C). The spectrum measured at 50℃ did not show any characteristic signal due to the stereocomplex but was simply a superpose of those of *it*- and *st*-PMMAs, except for the signals due to the linking unit;

$$[\text{-}(CH_2)_3OCO(CH_2)_8COO(CH_2)_3\text{-}]$$

At 30℃, an extra broad peak was observed at 3.96 ppm, and at 0℃ an additional

signal at 3.75 ppm was observed. With decreasing temperature, the intensity of CH_3 signal of *it*-PMMA block at 3.52 ppm decreased without loosing the sharpness of the peak, while the OCH_3 signal due to *st*-PMMA block at 3.56 ppm became broader with constant intensity. The intensity of the newly observed broad signals corresponds to the decrement of the OCH_3 peak due to *it*-PMMA block. This indicates that the new peak should be ascribed to *it*-PMMA block in the complexed state.

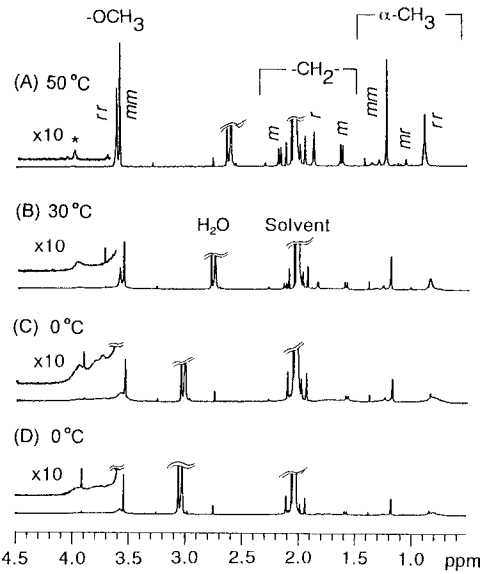


Fig. 8 750MHz ^{1}H NMR spectra of uniform stereoblock PMMA (A), (B) and (C), and of 1:1 mixture of *it*- and *st*-PMMAOHs of DP=46 (D) in acetone-d_6 at sample concentration of 1.0mg/ml
*** The signal due to the linking unit**

In the case of the 1:1 mixture, the characteristic peak at 3.96 ppm was not observed at 30℃ but at 0℃ (Fig. 8D). The peak intensity observed at 0℃ was about a half of that observed for the stereoblock PMMA at 0℃. These results are consistent with the observation in GPC experiment, both indicating the higher stability of the intramolecular complex.

In the early studies on PMMA stereocomplex by NMR, the decrease of signal intensities was used as a measure of degree of association (Ref. 9). It should be pointed out that the total intensity of OCH_3 signal region (3.3~4.2 ppm) was almost constant in the temperature range examined, and thus, all the species existing in the system give the information for the analysis.

Combining the results obtained by GPC and by NMR, we could assume that the peak responsible for the stereocomplex observed at 30℃ is mainly due to the intramolecular complex. The additional signal at 3.75 ppm observed at 0℃ might be ascribed to the newly formed intermolecular complex. However, the relative intensities of the peaks at 3.96 and3.75 ppm does not correspond to the ratio of the GPC peak areas of the intra- and intermolecular complexes and thus further study should be needed to clarify this discrepancy.

^{1}H NOESY of the stereoblock PMMA was measured at 0℃ to extract information on the interacting groups in the complex. The 2D spectrum showed cross peaks

between OCH_3 signals (3.65~4.05 ppm) of *it*-PMMA block and α-CH_3 (0.80 ppm) and CH_2 signals (1.72 ppm) of *st*-PMMA block. On the other hand, the opposite combination, *i.e.* OCH_3 signals (3.58 ppm) of *st*-PMMA block and α-CH_3 (1.18 ppm) of *it*-PMMA block, did not exhibit cross peaks. The results are consistent with the Challa's double-stranded helix model (Refs 3,4), in which OCH_3 groups of *st*-PMMA chain point outward from the double helix and thus do not have direct contact with *it*-PMMA units.

Stereocomplex formation of uniform stereoblock copolymer

We have reported that many *st*-polymethacrylates other than *st*-PMMA form stereocomplexes with *it*-PMMA (Refs 27-29). If a stereoblock uniform copolymer comprising *it*-PMMA block and *st*-poly(alkyl methacrylate) block is used for NMR study of the stereocomplex, the signals from the different ester groups should be diagnostic for differentiating the blocks involved in the complexes.

Thus a uniform stereoblock copolymer with *it*-30mer of MMA and *st*-45mer of ethyl methacrylate (EMA) was prepared accordingly. When ^1H NMR spectrum of the stereoblock copolymer was measured in acetone-d_6 at –15℃, the signal intensity of OCH_3 groups in *it*-PMMA block at 3.53 ppm decreased and a new broad signal appeared at 3.80 ppm whose intensity corresponded to the decrement of the former peak. The OCH_2 signal in *st*-poly(EMA) block at 4.02 ppm did not show such a spectral change (Fig. 9). The results clearly indicate that the newly observed peak at 3.80 ppm is ascribable to the OCH_3 groups of *it*-PMMA block involved in the stereocomplex (Ref. 30). As we reported previously (Ref. 28), the ester groups of *st*-poly(EMA) point outward from the double-stranded helix of the stereocomplex if we adopt the Challa's helix model. Thus an environment of the OCH_2 group of the outer *st*-poly(EMA) block does not change appreciably upon the complexation so that their NMR signal scarcely changed. In contrast, the OCH_3 groups of *it*-PMMA block, which are embedded in the interior of the complex, exhibit the drastic change in chemical shift and peak shape from that for the noncomplexed units. The present results also suggest the validity of the double-stranded helix model. Further NMR and GPC studies are now under way.

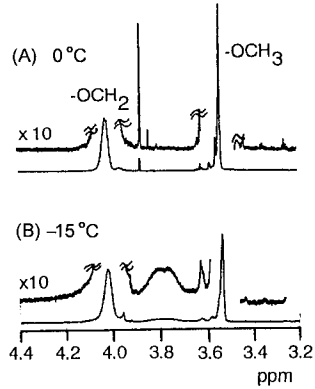


Fig. 9 A Partial 750MHz ^1H NMR spectra of uniform stereoblock copolymer comprising *it*-PMMA block (DP=30) and *st*-PEMA block (DP= 45) at 0℃ (A) and -15℃ (B) in acetone-d_6 at sample concentration of 1.0mg/ml

The phenomena of intramolecular complex formation of the uniform stereoblock polymer and copolymer are interesting examples of self-organization of stereoregular synthetic polymers. Though the corresponding non-uniform polymers may undergo the self-organization, the sure experimental evidences shown above could hardly be obtained without uniform polymers. Thus the present results demonstrate excellent examples of the utilization of uniform polymers for understanding the fundamental problems in polymer science.

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