Macromol. Symp. ***129,*** *89–97 (1998)*

UNIFORM POLYOLEFIN AND POLYMETHACRYLATE

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Abstract: Preparations and properties of synthetic uniform polyolefins and polymethacrylates are described with emphasizing the necessity of their utilization for understanding the fundamental problems in polymer chemistry. Uniform polymer is a polymer composed of molecules uniform with respect to molecular weight and constitution. While classical organic chemistry provides means of constructing uniform polymers such as poly(methylene)s in stepwise manners, recent advances in separation technology such as supercritical fluid chromatography (SFC) have made it possible to isolate synthetic uniform polymers from its homologous mixture. Combinations of stereospecific polymerizations and the SFC technique have enabled us to prepare uniform polystyrenes and poly(methyl methacrylate)s with high stereoregularities, which are very useful for systematic studies on the nature of polymers. The thermal properties of these uniform polymers are discussed in some detail.

INTRODUCTION

Most text books of organic chemistry include a figure of the relationship of boiling points and melting points of alkane family with the number of carbons. The figure suggests the existence of high molecular weight alkanes, i.e., polyethylene, or poly(methylene) according to the IUPAC nomenclature. This kind of figure is often used to introduce students the concept of macromolecule in the beginning of polymer chemistry course. The presentation of physical data with increasing molecular weight was one of the important strategies that Hermann Staudinger took during his establishment of the concept of "Hochmoleculare Verbindungen". For example, Staudinger prepared polystyrenes by cationic or radical mechanism, fractionated them by solvents, determined the number-average molecular weight by freezing point depression, and measured viscosities of the fractionated polymers (*Ref.* 1). Another Staudinger's attempt to obtain such a relationship between physical properties and molecular weights was the isolation and characterization of uniform poly(oxymethylene) diacetates with degrees of polymerization (*DP*) ranging from 1 to 22 (*Refs* 2-4). The isolation was made by careful solvent fractionations using ether or ethyl acetate at different temperatures. These are great and challenging works which demonstrate that a polymer comprises a mixture of homologous molecules with high molecular weights. To convince the chemists who were against him, Staudinger probably needed uniform polymer samples which could be used as pure substances on the same scientific basis that the most of chemists at that time had stood in the chemistry of low molecular weight compounds.

CCC 1022-1360/98/$ 10.00

As defined in an IUPAC document (*Ref.* 5), "uniform polymer" herein means "a polymer composed of molecules uniform with respect to relative molecular mass and constitution". The relative molar mass is practically identical with molecular weight, and the constitution means chemical structure such as monomeric units and end groups. Thus, a polyethylene comprising polymer molecules (A) and (B) with the same molecular weight but different end groups is not a uniform polymer.

$CH_3 \left(CH_2-CH_2 \right)_{100} CH_2-CH=CH_2$ (A)

$CH_3 \left(CH_2-CH_2 \right)_{100} CH=CH-CH_3$ (B)

Synthetic polymers usually consist of a mixture of macromolecules of different molecular weights, although polymers with narrow molecular weight distribution (MWD) obtained by living polymerization are often called uniform or monodisperse, inconsistently with the above definition. Thus synthetic polymers are usually nonuniform, and the properties of a polymer sample are always observed as average values. Since synthetic polymers are usually used as raw materials for plastics, elastomers, or synthetic fibers, the existence of the distribution of molecular weight is not critically a deficiency. If uniform polymers were available, however, fundamental understanding of the structures and properties of polymers could be greatly advanced, and thus the preparation of synthetic uniform polymers is an important and challenging subject in the field of polymer science.

Recognizing the limitation of living polymerization that gives polymers with narrow MWD but never the molecularly uniform polymers, we have concerned with the uniformity of synthetic polymers and devoted ourselves in developing the separation of uniform polymers by supercritical fluid chromatography (SFC) (*Refs* 6-11). This paper describes recent advances in the preparation and isolation of synthetic uniform polymers including polyolefins and polymethacrylates, emphasizing their importance toward the deeper understanding of macromolecular systems.

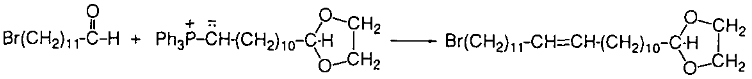
RESULTS AND DISCUSSION

1. Uniform Polyolefin

1.1 Poly(methylene) and cyclopoly(methylene)

Polyethylene, the simplest polyolefin, is the most widely studied chain molecules. Since Keller (*Ref.* 12), Till (*Ref.* 13) and Fischer (*Ref.* 14) independently, in 1957, proposed a chain-folding hypothesis from electron diffraction of polyethylene single crystals, a lot of arguments on chain folding in a single crystal have been made by means of x-ray diffraction, Raman spectroscopy and other spectroscopies.

In order to investigate chain folding of polyethylene chains, uniform poly(methylene)s with carbon numbers up to 390 were prepared by a stepwise reaction starting from ω-bromoalkanal and phosphorus ylide(*Refs* 15,16).



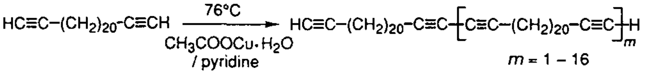
$$Br(CH_2)_{11}-\overset{\overset{O}{\|}}{C}-H + Ph_3\overset{+}{P}-\overset{-}{C}H-(CH_2)_{10}-\overset{O-CH_2}{\underset{O-CH_2}{CH}} \longrightarrow Br(CH_2)_{11}-CH=CH-(CH_2)_{10}-\overset{O-CH_2}{\underset{O-CH_2}{CH}}$$

The acetal group was deprotected to release an aldehyde group, and the bromide group was converted to a phoshorus ylide for further coupling reaction. The synthetic strategy is in principle the same as peptide syntheses. Several uniform polymers have been prepared in a similar manner; poly(oxyethylene) (*Ref.* 17), poly[(R)-3-hydroxybutyrate] (*Ref.* 18), dendrimers by a convergent growth method (*Ref.* 19). In each growth step of the reaction, the coupled products should be isolated from the starting compounds.

Lamellar crystals of a series of uniform poly(methylene)s were obtained under several conditions, and the number of carbon atoms in the straight stems of the crystals (n_{LAM}) was determined from the longitudinal acoustic mode (LAM) band of low-frequency Raman spectra. The ratio of the number of total carbon atoms in the poly(methylene) (n) to n_{LAM} was found to be very close to integers which correspond to the number of chain folding. Chain folding was found in all poly(methylene)s with n of larger than 150. For the case of $n = 150$, a lamellar crystal with one folding was obtained. The number of chain folding increased with an increase in n, and lamellar crystals with a maximum of four folds were obtained in the case of $n = 390$, when crystallized from petroleum ether. The fold length is always an integral reciprocal of the extended chain length, and thus the end groups are located at the lamellar surface and the fold itself must be sharp and adjacently reentrant. It should be noted that this conclusion could not be obtained without the uniform poly(methylene)s.

Polymerization or polycondensation of high molecular weight, bifunctional monomers or uniform oligomers with functional groups is one of the more promising means for preparing uniform polymers in one step reaction, as far as the difference in molecular weight between the components i and $(i + 1)$ in the products is large enough for each product to be isolated as uniform species by chromatography such as gel permeation chromatography(GPC).

Oxidative polymerization of tetracosa-1,23-diyne by Eglinton's method (*Ref.* 20) followed by chromatographic separation and hydrogenation over Pd/C gave a series of uniform linear poly(methylene)s up to $C_{384}H_{770}$ (*Ref.* 21).



$$HC\equiv C-(CH_2)_{20}-C\equiv CH \xrightarrow[\mathrm{CH_3COOCu\cdot H_2O}\ /\ \mathrm{pyridine}]{76°\mathrm{C}} HC\equiv C-(CH_2)_{20}-C\equiv C\left[C\equiv C-(CH_2)_{20}-C\equiv C\right]_m H \qquad m = 1-16$$

When the reaction was conducted at high dilution, a mixture of cyclic oligomers were obtained, from which uniform cyclopoly(methylene)s up to $C_{288}H_{576}$ (MW=4040) was obtained.

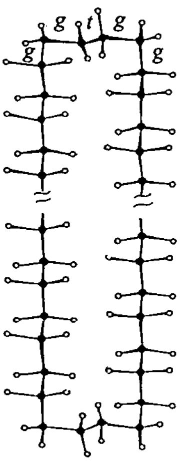


Figure 1 Schematic drawing of the conformation of cyclopoly(methylene)

Uniform cyclopoly(methylene)s with molecular weights up to 2805 were also prepared by metathesis polymerization of cyclooctene with $WCl_6/EtAlCl_2$ followed by GPC fractionation and subsequent hydrogenation (*Refs* 22-25).

Cyclopoly(methylene)s assume a compact conformation in the solid state with the shape of two parallel straight chains bridged at both ends and thus inevitably contain folding segments (Figure 1), which should be closely related to the chain-folded structure of poly(methylene) lamellar crystals. As the number of carbon atoms increases from 80 and 160, the crystallographic form of the cyclopoly(methylene)s changes from triclinic to orthorhombic. It is interesting to note that the crystallographic form of poly(methylene) single crystals is orthorhombic and that chain folding in the uniform linear n-alkane crystal begins to occur when the number of carbon atoms reaches 150 as described above.

The ^{13}C CP/MAS NMR chemical shifts of polyolefins are known to sensitive to the chain conformation and crystalline form (*Ref.* 25). The average chemical shift of the methylene carbons in the *trans* zigzag conformation of orthorhombic cyclopoly(methylene)s is 32.8

ppm, which is close to that for the poly(methylene) crystal. Characteristic peaks ascribable to the methylene carbons in the fold part having *ggtgg* conformation was found to appear between 22 and 27 ppm, whose relative peak intensity decreased with an increase in the number of carbon atoms. The high-field shift from that for the *trans* conformation was explained by the γ-*gauche* effect. From the comparison with the spectra of the cyclopoly(methylene)s, a peak at 30.7 ppm observed in the spectra of poly(methylene) was ascribed to the fold portion of the poly(methylene). The stem length in the crystal could be estimated from the peak intensities in the spectrum, and was consistent with the crystal thickness measured independently by electron microscopy (*Ref.* 23).

1.2 Uniform polystyrene

In the case of vinyl-type polymers such as polystyrene and polymethacrylate, a mixture of homologous series of polymer molecules of different *DP*s is formed, even in the well controlled living polymerizations, where a limit of $\overline{M}_w/\overline{M}_n$ value is give by a Poisson distribution as $\overline{M}_w/\overline{M}_n = (1 + DP) / DP$ (*Ref.* 26). SFC has proved highly effective for isolating uniform polymers from such a homologous polymer mixture (*Refs* 6-11). Narrow MWD should help effective isolation of uniform polymers, and, naturally, a narrow MWD polystyrene obtained by anionic living polymerization was the first target to be separated by SFC. In 1969, Jentoft and Gouw (*Ref.* 27) reported the first SFC separation of a standard polystyrene sample with an average molecular weight of 578. Preparative-scale SFC fractionation of a polystyrene was demonstrated later by Klesper and Hartmann (*Ref.* 28). The 15 fractions from unimer to 15mer were isolated from a polystyrene of nominal molecular weight of 2200. Using a 2 mm *i.d.* × 2 m column packed with porous silica gel with particle size of 37~75 μm and pentane/methanol (9:1) as a supercritical mobile phase, more than 16 hr was required for each chromatographic run as shown in Figure 2.

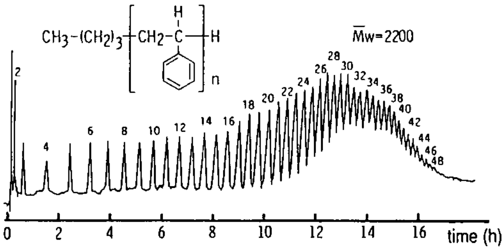


Figure 2 SFC trace of a standard polystyrene prepared with *n*-C_4H_9Li (*Ref.*28). Mobile phase: *n*-pentane/metanol = 9/1, stationary phase: Porasil A, column: 2mm i.d. × 2m, 230℃.

Recent advances in SFC apparatus and column packings have made it possible to carry out the fractionation in a much shorter time with improved separation efficiency. Figure 3A shows an SFC trace of a standard polystyrene with $\overline{M}_n$=2800 prepared

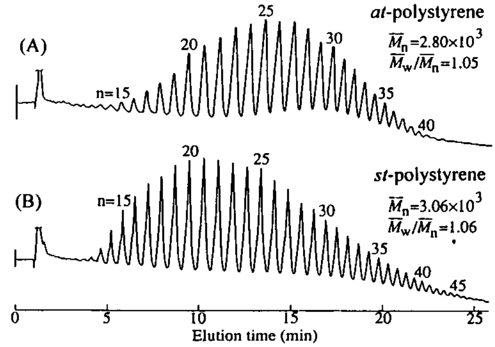


Figure 3 SFC traces of *at*- (A) and *st*- (B) polystyrenes. The latter contains polymers with saturated and unsaturated end groups (see text). Mobile phase: CO_2/CH_2Cl_2 =6/4 (initail) to 4/6 (30min), stationary phase: Develosil 100-5, column: 10mm *i.d.* × 25cm, 200℃, 23.3 MPa.

by anionic living polymerization (*Ref.* 29). The homologues from 10mer to 40mer are clearly resolved within a total run time of 25min under the conditions specified in the figure.

The standard polystyrene sample is low in stereoregularity. Transition-metal catalyzed polymerizations of styrene produce two distinctive stereoregular polymers. Isotactic (*it*-) polystyrene was prepared by Natta in 1955 with titanium-based Ziegler-Natta catalyst (*Ref.* 30). Later, metallocene-based catalysts were found to give syndiotactic (*st*-) polystyrene (*Ref.* 31), which has higher melting temperature (T_m=270℃) than *it*-polystyrene and has been commercialized as a new engineering plastic. The physical properties of *st*-polystyrene have been of great interest.

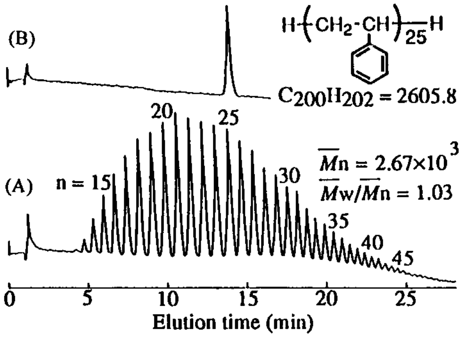


Figure 4 SFC traces of nonuniform *st*-polystyrene with saturated end (A) and uniform 25mer isolated therefrom (B). Mobile phase: CO_2/CH_2Cl_2=6/4 (initail) to 4/6 (30min), stationary phase: Develosil 100-5, column: 10mm i.d.×25cm, 200℃, 23.3 MPa.

An *st*-polystyrene of relatively low molecular weight was prepared with (η-C_5H_5)$TiCl_3$ /methylalumoxane/(i-C_4H_9)$_3$Al in toluene at 80℃. Figure 3B illustrates an SFC trace of the *st*-polystyrene. The peak widths of the *st*-polystyrene sample are narrower than those of *at*-polystyrene (Figure 3A), owing to high stereoregularity of the former sample, resulting in base-line separation even at higher *DP* region of the chromatogram. The result suggests that SFC is also sensitive to stereoregularity of polymers (*Ref.* 32).

The *st*-polystyrene was found by ^{1}H NMR spectroscopy to contain molecules having saturated and unsaturated ends. Splittings observed in the SFC peaks of low *DP* species (Figure 3B) are due to the presence of two types of end groups. As mentioned in the introductory section, SFC fractionation of this sample in regard to *DP* should not give uniform polymers as defined by the IUPAC rule (*Ref.* 5). Therefore, the unsaturated end group of the *st*-polystyrene was hydrogenated with Pd/C in tetrahydrofuran (THF) for 24 h, before the polymer was subjected to SFC fractionation. ^{1}H NMR spectrum of the product did not show any signals at 5.94 - 5.96 ppm where a β-proton of the unsaturated end (-C*H*=CH-Ph) showed a multiplet signal. Figure 4 shows an SFC trace of an isolated uniform 25mer with saturated end, together with that of the nonuniform *st*-polystyrene from which the uniform 25mer was fractionated. The molecular weight of the 25mer was verified by field-desorption mass spectrometry.

Figure 5 shows differential scanning calorimetric (DSC) curves of uniform and nonuniform *st*-polystyrenes. Glass transition temperature (*Tg*) of the uniform *st*-polymers (*DP* = 12, 16, 20, and 24) increases with increasing *DP*; the data obeyed the Fox-Flory's equation; $Tg = Tg_\infty - K/M$, where *M* and Tg_∞ denote molecular weight and *Tg* at infinite M, respectively (*Ref.* 33). Tg_∞ and K values were estimated to be 85.2℃ and 5.5×10^4℃. The *Tg* of nonuniform *st*-polystyrene with average *DP* of 25.7 is lower than that of the 24mer by 4℃, probably due to a plastisizing effect by the presence of lower *DP* fractions.

The 20mer and 24mer exhibited crystallizing exotherms and melting endotherms in the course of DSC runs, while the 12mer and 16mer did not. The exothermic and endothermic peaks of the 20mer and 24mer are narrower than those of the nonuniform polymer, suggesting higher crystallinity of the uniform polymers than the nonuniform one. T_m value for the 24mer was 187℃ at a heating rate of 10℃, while the value of the nonuniform polymer ($\overline{DP}$=25.7) was 179℃. These results suggest the higher crystallinity of the uniform *st*-polystyrenes than the nonuniform one.

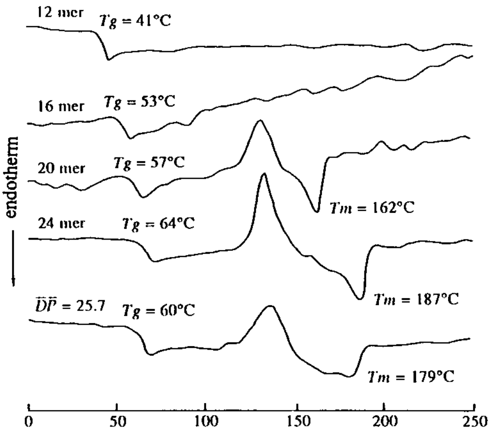
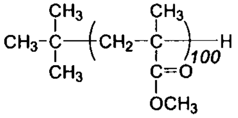


Figure 5 DSC curves of uniform and nonuniform *st*-polystyrene samples (heating rate : 10℃/min)

2. Uniform Poly(methyl methacrylate)

Combined with recently developed stereospecific living polymerizations of methyl methacrylate (MMA) (*Refs* 34,35), SFC technique has enabled us to prepare uniform poly(MMA)s (PMMAs) with high stereoregularities (*Refs* 36-40). By this technique stereoregular uniform PMMAs have been isolated up to the 100mer ($C_{504}H_{810}O_{200}$= 10070) and characterized by NMR spectroscopy and matrix-assisted Laser-desorption ionization time-of-flight (MALDI-TOF) mass spectrometry (*Ref.* 7). Since uniform PMMAs of a continuous series of *DP* are obtainable through SFC fractionation, *DP* dependences of physical properties could be minutely studied. In the following are mainly described thermal properties of stereoregular uniform PMMAs.



$CH_3-C(CH_3)_2-[CH_2-C(CH_3)(COOCH_3)]_{100}-H$

$C_{504}H_{810}O_{200}$=10070

2.1 Glass transition and melting temperatures

Tg of *it*-41mer was 38.1℃ which was higher than that of nonuniform *it*-PMMA with a similar *DP* by 6.6℃, as observed for *st*-polystyrene. A similar phenomenon was also observed for *st*-PMMA (*st*-41mer; *Tg*=100.9℃, *st*-PMMA ($\overline{DP}$=41.4); *Tg*=94.4℃). Use of uniform polymers affords precise *DP* dependence of *Tg* values. It was found that the *Tg* values of the uniform *it*- and *st*-PMMA series with *DP*=19~50 obeyed the Fox-Flory's equation. The values of Tg_{∞} for *it*-PMMA (*mm*=96.1%) and *st*-PMMA (*rr*=92.0%) were determined to be 51.9 and 125.7℃, respectively. The K-value was larger for *st*-PMMA (1.02×10^5 ℃) than that for *it*-PMMA (0.52×10^5 ℃).

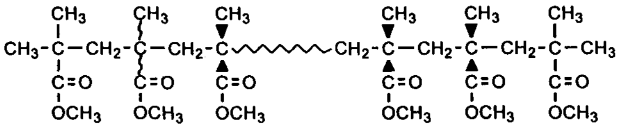
The reciprocal melting points ($1/T_m$) of uniform *it*-PMMAs with *DP*=28~44, recovered from methanol solutions, increased linearly with increasing 1/*DP*, consistent with the following equation given by Flory (*Ref.* 41) ;

$$\frac{1}{T_m} = \frac{R(1+b)}{\Delta Hu}\cdot\frac{1}{DP} + \frac{1}{T_{m\infty}} \qquad b = \left(1 - \frac{\zeta_e}{DP} + \frac{1}{DP}\right)^{-1}$$

where $T_{m\infty}$ is an equilibrium melting temperature of the polymer with infinite *DP*, ΔHu a heat of fusion, ζ_e an equilibrium length of crystallite in number of repeat unit, R the gas constant. Extrapolation of the linear relation to 1/*DP*=0 gives the $T_{m\infty}$ of *it*-PMMA to be 171.1℃. The values of ζ_e for uniform 28, 31, 36, 41, and 44mers are 87~88% of the *DP* values, indicating that the degrees of crystallinity are almost constant for these uniform *it*-

PMMAs. The results demonstrate that melting behavior of the crystalline uniform *it*-PMMAs with *DP*=28~44 could be explained by the statistical thermodynamic theory (*Ref.* 41) for extended chain crystals.

The uniform *it*-PMMAs used in the above studies have stereochemical defects in the chain as expected from its *mm* triad value (96.1%). Completely isotactic PMMA was derived from poly(1-phenyldibenzosuberyl methacrylate) prepared in THF at −78°C with methyl α-lithioisobutyrate as an initiator and methyl iodide as a terminator. The main-chain tacticity of the PMMA was 100% isotactic. The meso/racemo ratio only at the initiating diad was less than 100% (89/11). The structure of the *it*-PMMA is depicted as follows:



$$CH_3-\overset{CH_3}{\underset{\underset{OCH_3}{C=O}}{C}}-CH_2-\overset{CH_3}{\underset{\underset{OCH_3}{C=O}}{C}}-CH_2-\overset{CH_3}{\underset{\underset{OCH_3}{C=O}}{C}}\sim\sim\sim CH_2-\overset{CH_3}{\underset{\underset{OCH_3}{C=O}}{C}}-CH_2-\overset{CH_3}{\underset{\underset{OCH_3}{C=O}}{C}}-CH_2-\overset{CH_3}{\underset{\underset{OCH_3}{C=O}}{C}}-CH_3$$

Uniform PMMAs were obtained by SFC fractionation of the completely isotactic PMMA and their crystallization behaviors were compared with those of uniform *it*-PMMAs with the corresponding *DP*s but with a small stereochemical in-chain defects (*Ref.* 40). Figure 6 shows melting endotherms of 41mers and 44mers of the two kinds of uniform *it*-PMMAs crystallized from methanol by solvent evaporation. In each *DP*, the uniform *it*-PMMA with 100% isotacticity had higher T_m and larger ΔH, clearly indicating that the crystallinity and T_m of uniform *it*-PMMA increase significantly by the improvement in tacticity from 96.1 to 100%.

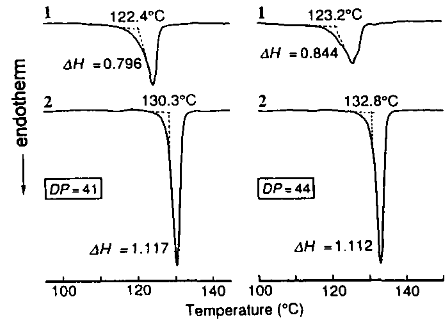


Figure 6 Melting endotherms of uniform 41mers and 44mers of highly isotactic PMMA 1 (*mm*=96.1%) and 100% isotactic PMMA 2 (heating rate; 5°C/min). ΔH values are given in kcal/mol.

2.2 Thermal degradation

Thermal degradation of PMMA undergoes through unzipping to form MMA monomer (*Ref.* 42). The degradation behavior is often characterized by a parameter termed "zip length", that is, the average number of monomer units successively released by one event of depolymerization along the chain. We have reported the tacticity dependence of thermal degradation behavior of PMMA having the same chemical structure, t-C_4H_9-$(MMA)_n$-H (*Ref.* 43). From thermogravimetric analysis, the PMMA of this type was found to degrade in a single reaction step through main-chain scission degradation. Thermal degradation behavior of the uniform PMMAs was studied by thermogravimetry and by SFC analysis of the degradation products, leading to the estimation of zip length (*Ref.* 7). Figures 7 and 8 show the SFC traces of *it*-27mer and *st*-27mer and their isothermal degradation products at 300°C for 30min under vacuum, respectively. The chromatograms of the degradation products consisted of peaks due to the original 27mers and those for a series of the degradation products of lower *DP*. The difference between the largest *DP* in the series of the oligomeric products and that of the original 27mer should give the minimum of zip length.

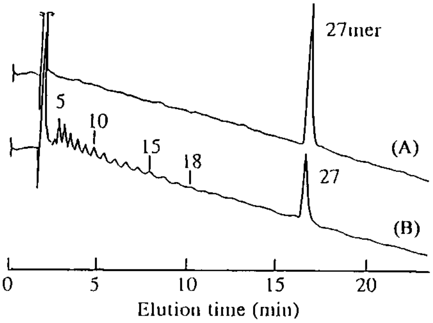


Figure 7 SFC traces of uniform *it*-27mer of MMA (A) and the polymeric residue after isothermal degradation at 300℃ for 30min under high vacuum (B)

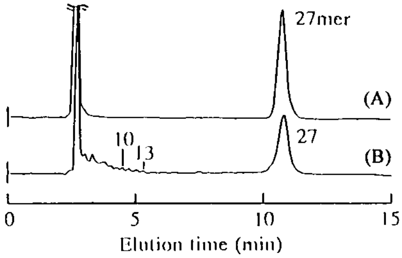


Figure 8 SFC traces of uniform *st*-27mer of MMA (A) and the polymeric residue after isothermal degradation at 300℃ for 30min under high vacuum (B)

The values for the *it*-PMMA and *st*-PMMA under the conditions examined are about 10 and 14, respectively, indicating that the zip length for *it*-PMMA is smaller than that for *st*-PMMA (*Ref.* 44).

Conclusion

Uniform polymers with definite molecular weights are of great significance not only as model compounds of polymers but also as reference materials in analytical science. Uniform *it*-PMMA and *st*-PMMA were used for the direct evaluation of instrumental spreading factors in GPC measurement. The spreading factors were found to be independent of the molecular weight and tacticity (*Ref.* 37). Using uniform *it*- and *st*-PMMAs, we could observe stereocomplex formation process precisely by means of conventional GPC by appreciating extreme narrowness of the GPC peaks of the uniform PMMAs with unambiguously defined molecular weight (*Ref.* 37). GPC measurements of a solution of a 1:1 mixture of the *it*-50mer and *st*-50mer in THF showed a small peak due to the stereocomplex besides the large peaks due to the original PMMAs; the elution volume of the small peak was close to that of the 100mer. By similar experiments the minimum length of the isotactic and syndiotactic sequences for the complex formation was determined as 40mer~42mer (*Refs* 7, 45).

A synthetic merit of living polymerization is to afford end-functionalized polymers, which are useful for the construction of a variety of macromolecular architectures. Isotactic and syndiotactic PMMAs having hydroxy group at the chain ends were fractionated into uniform components by SFC. The resulting uniform PMMA-OHs were used for constructing uniform polymer architecture such as stereoblock (*Refs* 46,47) and star (*Ref.* 48) polymers. A stereoblock PMMA comprising *it*-PMMA (*DP* = 46) and *st*-PMMA (*DP* = 46) blocks was found by GPC to form intra- and intermolecularly associated stereocomplexes in acetone (*Ref.* 47). Uniform macromonomers could also be prepared and polymerized to afford uniform comb polymers (*Ref.* 49).

The method can also be extended to a wider range of uniform polymer architectures to cover multiblock, hyperbranched, and network polymers with uniform structural constituents. The synthetic uniform polymers thus obtained are unique and will be useful in the systematic studies for the fundamental understanding of chain molecules in experimental and theoretical aspects, giving us greater insight into ambiguous problems in polymer chemistry.

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