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NOTE

Facile Synthesis of Highly Syndiotactic and Isotactic Polymethacrylates via Esterification of Stereoregular Poly(methacrylic acid)s

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Introduction

Stereoregular poly(methyl methacrylate)s (PMMAs), isotactic (it-) and syndiotactic (st-) PMMAs, are of great interest due to their unique higher-order structures based on their helical structures, which are rare examples formed by commodity polymers. The it-PMMA helical structure has been reported to be a double-stranded helix consisting of 10 monomer units per turn (10/1) in the solid state.[1−4] The st-PMMA helical structure is a single helix of 74 monomer units per 4 turns (74/4) and with a large cavity of ∼1 nm; this polymer forms a gel in organic solvents such as toluene, and hence, solvent molecules are encapsulated in the inner helix cavity.[5−8] Recently, it has been found that the st-PMMA helix formed in toluene encapsulates fullerenes such as C_{60}, C_{70}, and C_{84} within the helical cavity to form an inclusion complex.[9,10] It has also been found that st-PMMA folds into a preferred-handed helix with the assistance of chiral alcohols and encapsulates fullerenes to form an optically active inclusion complex.[9,11] This induced helicity is retained even after the complete removal of the chiral alcohols by washing with toluene. Interestingly, the st-PMMA helix recognizes the size and chirality of fullerenes through an induced-fit mechanism and can selectively encapsulate higher-fullerene enantiomers.[12]

It has also been known that it- and st-PMMA chains assemble to form a crystalline stereocomplex in specific solvents.[11,13−16] Using atomic force microscopy, Kumaki et al. studied a PMMA stereocomplex prepared by the Langmuir−Blodgett (LB) technique and proposed a triple-stranded helical model for the stereocomplex in which a double-stranded it-PMMA helix is included in a single st-PMMA helix.[17,18] This supramolecular PMMA stereocomplex has been used to create advanced materials such as ultrathin films,[19] microcellular foams,[20] dialyzers,[21] thermoplastic elastomers,[22] and ion gels.[23] It is also a versatile structural motif that is useful for template polymerization[16,24] and for the preparation of self-assembled nanomaterials.[25]

Stereoregular PMMAs form unique higher-order structures with sophisticated functionalities because of their helical structures, which are reminiscent of biomolecules such as DNA. However, apart from PMMA, only a limited number of studies on polymethacrylates have been reported. We expect that highly stereoregular polymetacrylates with various ester groups as pendants can provide new functionalized inclusion complexes and stereocomplexes.

One approach for preparing highly stereoregular polymethacrylates is the stereospecific polymerization of methacrylate monomers. Kitayama et al. have reported the preparation of various syndiotactic polymethacrylates with moderate tacticity (*rr* = 57−93), including primary and secondary esters by anionic living polymerization with *tert*-butyllithium (*t*-BuLi) in the presence of trialkylaluminum in toluene.[26] Another approach is a polymer reaction of stereoregular poly(methacrylic acid)s (PMAAs). Nishikubo et al. reported that esterification of atactic PMAA with alkyl halides proceeds smoothly when 1,8-diazabicyclo[5.4.0]-7-undecene (DBU) is used as a base.[27,28] Herein, we report a facile method for the synthesis of highly syndiotactic and isotactic polymethacrylates; the method involves the use of the esterification method and stereoregular PMAAs prepared through stereospecific anionic living polymerization. The influence of reaction conditions on the degree of esterification was investigated. Highly syndiotactic polymethacrylate random copolymers were also prepared by two-step esterification. Stereocomplex formation between copolymers and it-PMMA was examined by differential scanning calorimetry (DSC) and X-ray measurements.

Experimental Section

Measurements. NMR spectra were recorded on a Varian Mercury 300 spectrometer (300 MHz for ^1H and 75 MHz for ^{13}C) in $CDCl_3$ using tetramethylsilane (TMS) as the internal standard. Size exclusion chromatography (SEC) measurements were performed with a Jasco (Hachioji, Japan) PU-2080 liquid chromatograph equipped with a refractive index detector (Jasco, RI-2031). Two Tosoh (Tokyo, Japan) Multipore H_{XL}-M (30 cm) SEC columns were connected in series, and $CHCl_3$ was used as the eluent at a flow rate of 1.0 mL/min. The molecular weight calibration curve was obtained with poly(methyl methacrylate) standards (Shodex, Tokyo, Japan). DSC measurements were conducted on a Rigaku (Tokyo, Japan) Thermo Plus 2 DSC-8230 under a nitrogen atmosphere. X-ray measurements were performed with a Rigaku R-AXIS VII system (Rigaku, Tokyo, Japan) equipped with a Rigaku FR-E rotating-anode generator with confocal mirror monochromated Cu Kα radiation (0.154 18 nm) focused through a 0.5 mm pinhole collimator, which was supplied at 45 kV and 45 mA current, equipped with a flat imaging plate having a specimen-to-plate distance of 300 mm. The samples were measured in glass capillaries.

Materials. Trimethylsilyl methacrylate (TMSMA) was prepared from potassium methacrylate and trimethylsilyl chloride according to the previously reported method.[29] *tert*-Butyl methacrylate (*t*-BuMA) was obtained from Tokyo Kasei (TCI, Tokyo, Japan) and repeatedly washed with aqueous NaOH to remove an inhibitor. These monomers were purified by fractional distillation under reduced nitrogen pressure, kept over CaH_2, and finally distilled under high vacuum just prior to polymerization. Anhydrous toluene (water content $< 0.005\%$) obtained from Wako (Osaka, Japan) was mixed with a small amount of *n*-butyllithium (Aldrich) and distilled under high vacuum just before use. *sec*-Butyllithium (*sec*-BuLi, 1.4 M solution in cyclohexane) and *t*-BuLi (1.7 M solution in pentane) were obtained from Aldrich. 1,1-Diphenylethylene

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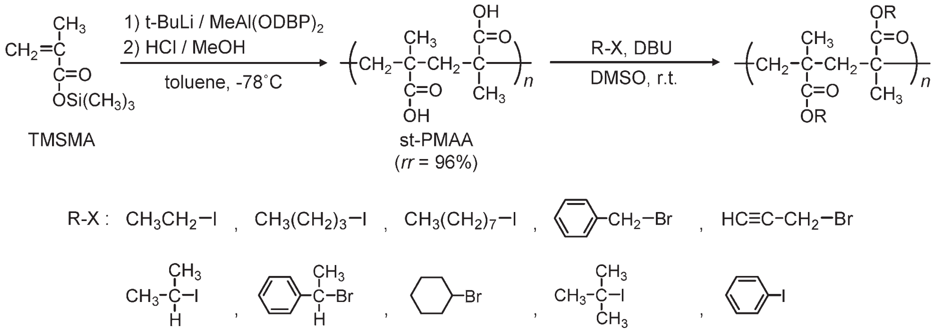
Scheme 1. Synthetic Route of Highly Syndiotactic Polymethacrylates



obtained from Aldrich was purified by distillation over CaH_2. Bis(2,6-di-*tert*-butylphenoxy)methylaluminum [$MeAl(ODBP)_2$] was prepared according to the previous report.[29,30] 1,8-Diazabicyclo[5.4.0]-7-undecene (DBU) was purchased from Wako and used without further purification. Methyl iodide, ethyl iodide, *n*-butyl iodide, *n*-octyl iodide, benzyl bromide, propargyl bromide, isopropyl iodide, 1-phenylethyl bromide, cyclohexyl bromide, benzene iodide, and *tert*-butyl iodide were purchased from Wako or Aldrich and used as received. Diazomethane in diethyl ether was generated from *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (TCI) just before use.

Synthesis of Highly Syndiotactic Poly(methacrylic acid). Syndiotactic-specific anionic polymerization of TMSMA using a combination of *t*-BuLi and $MeAl(ODBP)_2$ as initiator was carried out in a dry glass ampule under a dry nitrogen atmosphere.[29] The initiator solution was prepared by adding *t*-BuLi (0.18 mL, 0.3 mmol) to a $MeAl(ODBP)_2$ (1.5 mmol) solution in toluene (20 mL) at −78 °C and keeping for 10 min at −78 °C. The polymerization reaction was initiated by adding TMSMA (4.0 mL, 22.2 mmol) slowly to the initiator solution at −78 °C. After completion of the polymerization, the reaction was quenched with CH_3OH containing a small amount of aqueous 14 N HCl. By the procedure, the polymer formed was quantitatively converted to PMAA. The mixture was poured into a large amount of acetone, and the precipitate was collected by filtration, washed with acetone several times, and then dried under vacuum at 35 °C to give st-PMAA. A small amount of this polymer was converted to PMMA by the methylation with diazomethane to determine the number-average molecular weights (M_n), the molecular weight distributions (M_w/M_n), and tacticities (*mm*:*mr*:*rr*).[29,31] The M_n and M_w/M_n values were measured by SEC in chloroform using PMMA standards (Shodex, Tokyo, Japan) for the calibration. The tacticities were determined from the ^{1}H NMR signals of the α-methyl protons. The values were as follows: M_n = 9100, M_w/M_n = 1.33, and *mm*:*mr*:*rr* = 0:4:96.

Synthesis of Highly Isotactic Poly(methacrylic acid). (1,1-Diphenyl-3-methylpentyl)lithium (*sec*-BuDPE-Li) used as an initiator was the reaction products of *sec*-BuLi (2.97 mL, 3 mmol) with DPE (0.53 mL, 3 mmol) in tetrahydrofuran (3 mL) at room temperature. Anionic polymerization of *t*-BuMA was carried out in a dry glass ampule under a dry nitrogen atmosphere.[32−34] The initiator solution (25 μmol in 40 mL of toluene) was prepared in the ampule, and the polymerization reaction was initiated by adding *t*-BuMA (3.28 mL, 20 mmol) to the initiator solution at −78 °C. After 24 h, the reaction was quenched with CH_3OH containing a small amount of aqueous 14 N HCl. The mixture was then poured into a large amount of CH_3OH, and the precipitate was collected by filtration, washed with CH_3OH, and then dried under vacuum to give it-poly(*t*-BuMA).

The it-poly(*t*-BuMA) was hydrolyzed by refluxing in CH_3OH/THF (1/1, v/v) containing a small amount of aqueous 14 N HCl. After 12 h, the reaction mixture was poured into a large amount of acetone to precipitate the polymeric product, which was then collected by filtration, washed with acetone, and then dried under vacuum, yielding it-PMAA. A small amount of this polymer was converted to PMMA by the methylation with diazomethane to determine M_n, M_w/M_n, and tacticities. The values were as follows: M_n = 131 000, M_w/M_n = 1.17, and *mm*:*mr*:*rr* = 98:2:0.

Esterification of Highly Stereoregular PMAA. A typical experimental procedure is described below. To a solution of st-PMAA (103 mg, 1.2 unit mmol) in DMSO (2.4 mL) were added CH_3CH_2I (0.25 mL, 2.4 mmol) and DBU (0.36 mL, 2.4 mmol), and the mixture was stirred at room temperature. After 180 min, the reaction mixture was neutralized with 1 N HCl. The resulting polymer was precipitated into a large amount of water, collected by filtration, and washed with water. The crude product was purified by dissolving into THF, precipitating into water, washing with water, and then drying under vacuum.

To determine the degree of ethyl esterification, the residual carboxylic acid group in the polymer was converted to methyl ester group, in chloroform, by adding an excess amount of diazomethane in diethyl ether. After 24 h at room temperature, the reaction mixture was concentrated under reduced pressure at room temperature and was then poured into a large amount of hexane. The precipitates were collected by filtration, washed with hexane, dried under vacuum, and then subjected to NMR analysis.

Results and Discussion

i. Synthesis of Highly Syndiotactic Polymethacrylates. Syndiotactic-specific anionic living polymerization of TMSMA with *t*-BuLi in the presence of $MeAl(ODBP)_2$ was carried out in toluene at −78 °C.[29] The polymerization was quenched with CH_3OH containing a small amount of aqueous HCl. Through quenching, poly(TMSMA) was quantitatively converted to st-PMAA via side-chain hydrolysis (Scheme 1). The values of M_n, M_w/M_n, and *rr* content were estimated to be 9,100, 1.33, and 96%, respectively, for st-PMMA derived from st-PMAA by methylation using diazomethane.[35]

We investigated esterification of st-PMAA using ethyl iodide (CH_3CH_2I). Esterification of st-PMAA with CH_3CH_2I in the presence of DBU (st-PMAA 0.6 unit mmol, CH_3CH_2I 1.2 mmol, DBU 1.2 mmol, polymer concentration 0.5 unit mol/mL) was carried out in DMSO at room temperature. After 60 min, the reaction mixture was neutralized with 1 N HCl and poured into a large amount of water to precipitate the polymeric product, which was collected by filtration followed by washing with water. The product was purified by dissolving in THF, precipitating in water, washing with water, and drying in a vacuum, which yielded st-poly(ethyl methacrylate) (st-PEMA) as white powder. To determine the degree of ethyl esterification, st-PEMA was reacted with diazomethane to convert the residual carboxylic acid group to a methyl ester group and subjected to ^{1}H NMR measurement. Figure 1 shows the ^{1}H NMR spectrum of st-PEMA. Signals at 1.26 and 4.04 ppm were assigned to ethoxyl protons in the PEMA unit, confirming that ethyl esterification of st-PMAA

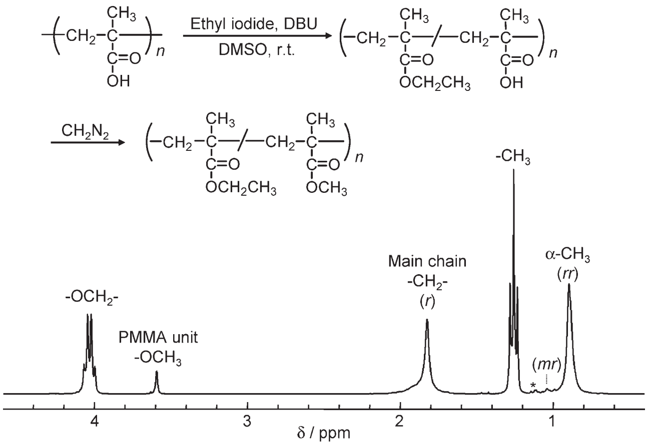


Figure 1. ^{1}H NMR spectrum of st-PEMA derived from st-PMAA by esterification with CH_3CH_2I followed by methylation with diazomethane. The asterisk denotes impurity. The measurement was performed in $CDCl_3$ at 25 °C.

was successful. However, the methoxyl proton signal corresponding to the PMMA unit is observed at 3.57 ppm, indicating that the carboxylic acid group partially remained after the ethyl esterification reaction. The degree of ethyl esterification was estimated to be 94% based on the integration ratio of ethoxyl and the methoxyl signals. In addition, the *rr* content of st-PEMA is estimated to be 96% from the α-CH_3 signals in Figure 1, showing that the stereoregularity of the polymer chain is maintained after the reaction.

The influence of reaction conditions, reaction time, and polymer concentration on the degree of ethyl esterification was examined. The relationship between reaction time and degree of ethyl esterification at various polymer concentrations is shown in Figure 2a. At a polymer concentration of 0.5 unit mol/mL (● in Figure 2a), the degree of ethyl esterification was 93% after 10 min, but this value did not increase with time. However, the degree of esterification reached as high as 99% at a polymer concentration of 2.0 unit mol/L (□ in Figure 2a) for 30 min. In contrast, the value at a polymer concentration of 0.125 unit mol/L was saturated ca. 92%. The degree of ethyl esterification strongly depends on polymer concentration.

Influence of polymer concentration on the degree of esterification was also examined for the reaction of st-PMAA with 1-phenylethyl bromide, which has a lower reactivity than CH_3CH_2I (Figure 2b). The degree of esterification at a polymer concentration of 2.0 unit mol/L reached as high as 95% after 30 min and 97% after 120 min, though the value reached only 90% after 120 min at 0.5 unit mol/L. Therefore, further PMAA esterification reactions with various halogenated compounds were carried out at a polymer concentration of 2.0 unit mol/L for 180 min.

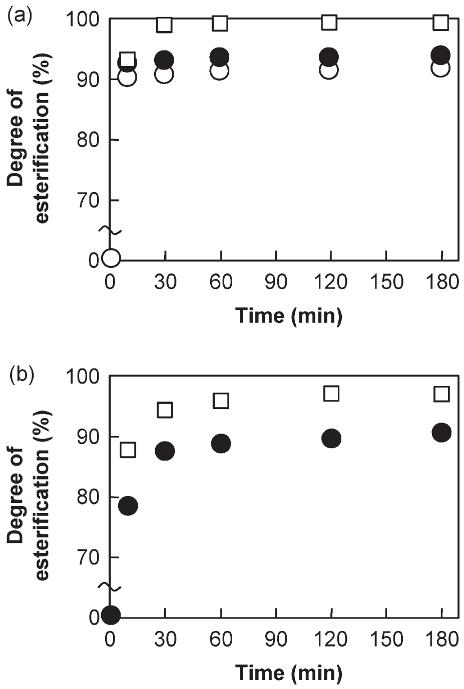


Figure 2. Plots of degree of esterification for the reactions of st-PMAA (0.6 mmol) with CH_3CH_2I (a) and with 1-phenylethyl bromide (b) (1.2 mmol) in the presence of DBU (1.2 mmol) versus reaction time. $[PMAA]_0$ = 0.125 (○), 0.5 (●), and 2.0 (□) unit mol/L.

Table 1. Esterification of Stereoregular PMAA with Various Halogenated Compounds in the Presence of DBU at Room Temperature for 180 min[a]

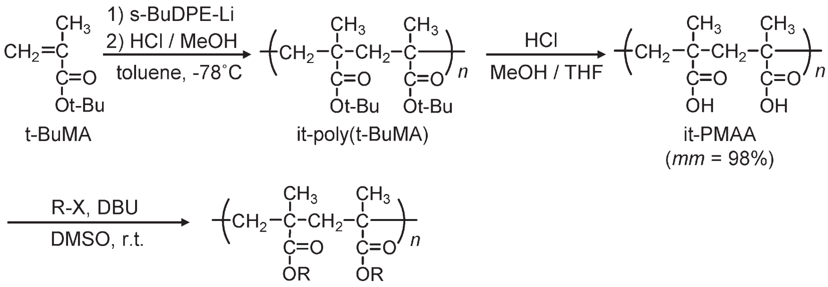
run	stereoregular PMAA	halogenated compounds[b]	degree of esterification/%[c]
1	st-PMAA	ethyl iodide	99
2		*n*-butyl iodide	97
3		*n*-octyl iodide	97
4		benzyl bromide	100
5		propargyl bromide	100[d]
6		isopropyl iodide	95
7		1-phenylethyl bromide	97
8		cyclohexyl bromide	13
9		*tert*-butyl iodide	~0
10		phenyl iodide	~0
11	it-PMAA	ethyl iodide	99
12		*n*-butyl iodide	99
13		*n*-octyl iodide	99
14		benzyl bromide	100
15		propargyl bromide	100[d]
16		isopropyl iodide	98
17		1-phenylethyl bromide	98
18		cyclohexyl bromide	11
19		*tert*-butyl iodide	~0
20		phenyl iodide	~0

[a] PMAA 0.6 mmol, halogenated compounds 1.2 mmol, DBU 1.2 mmol, DMSO 0.3 mL. [b] The chemical structures are shown in Scheme 1. [c] Determined by ^{1}H NMR of the polymethacrylates after reaction with diazomethane. [d] Determined by ^{1}H NMR of the polymethacrylates without the methylation by diazomethane.

Synthesis of various st-polymethacrylates was attempted using the various halogenated compounds (runs 1−10 in Table 1). Esterification reactions using primary halogenated compounds such as *n*-butyl iodide, *n*-octyl iodide, benzyl bromide, and propargyl bromide proceeded smoothly to give the corresponding st-polymethacrylates (runs 1−5 in Table 1). Notably, the propargyl group can be used as a functional group in a click reaction[36,37] with an azide compound, which can easily be introduced in stereoregular polymethacrylates. For secondary halogenated compounds (runs 6−8), the reactions of isopropyl iodide and 1-phenylethyl bromide gave the corresponding st-polymethacrylates quantitatively (runs 6 and 7), whereas the reaction of cyclohexyl bromide did not proceed smoothly and the degree of esterification drastically decreased (run 8). The esterification reaction of *tert*-butyl iodide, which is tertiary halogenated compounds, did not proceed, demonstrating that bulkiness around the halogen atom affects the ability of the reaction to proceed (run 9). The reaction of phenyl iodide also did not occur probably due to its low reactivity caused by the conjugated ring system (run 10).

ii. Synthesis of Highly Isotactic Polymethacrylates. The it-PMAA (M_n = 131 000, M_w/M_n = 1.17, and *mm* = 98% for

Scheme 2. Synthesis of Various Highly Isotactic Polymethacrylates

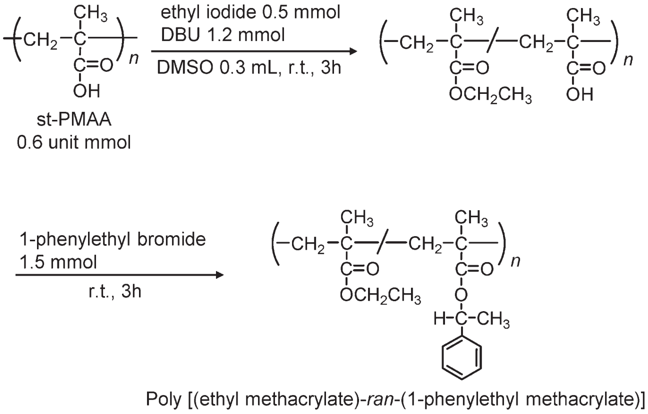


it-PMMA derived from it-PMAA by methylation using diazomethane) was prepared by isotactic-specific anionic polymerization of *t*-BuMA in toluene at −78 °C with *sec*-BuDPE-Li followed by hydrolysis of the pendant esters (Scheme 2).[34] Esterification reactions of it-PMAA using various halogenated compounds in the presence of DBU in DMSO were performed (runs 11−20 in Table 1). Esterification reactions of primary and secondary halogenated compounds, except for cyclohexyl bromide, proceeded to give the corresponding it-polymethacrylates, indicating similar tendencies to the reaction of st-PMAA described above. No significant influence of the stereoregularity on the esterification was observed.

iii. Synthesis of Highly Stereoregular Polymethacrylate Random Copolymers. Next, we attempted to synthesize highly stereoregular polymethacrylate random copolymers using a two-step esterification reaction (Scheme 3). In the first step, ethyl esterification of st-PMAA with CH_3CH_2I and DBU was carried out at a $[CH_3CH_2I]_0/[MAA]_0$ ratio of 0.5 in DMSO. After stirring at room temperature for 180 min, 1-phenylethyl bromide ($[\text{1-phenylethyl bromide}]_0/[MAA]_0 = 1.5$) was added to the reaction mixture (step 2). After 180 min, the reaction mixture was neutralized with 1 N HCl and poured into a large quantity of water to precipitate the copolymer, which was collected by filtration. ^{1}H and ^{13}C NMR spectra of the copolymer and each homopolymer were measured (Figure 3). The ^{1}H NMR spectrum of the copolymer (Figure 3c) shows broad signals assigned to both methacrylate units. Copolymer composition was determined to be [EMA]:[1-phenylethyl methacrylate] = 45:55 from the relative signal intensities due to the OCH_2 protons (3.9 ppm) of ethyl methacrylate units and the OCH proton (5.7 ppm) of 1-phenylethyl methacrylate units. The ^{13}C NMR spectrum of st-PEMA homopolymer (Figure 3d) prepared by esterification of st-PMAA with CH_3CH_2I (run 1 in Table 1) shows a sharp carbonyl signal at 177.5 ppm, reflecting high stereoregularity. However, the carbonyl signal of ethyl methacrylate units in the copolymer (Figure 3f) is broader than that of st-PEMA homopolymer, indicating random comonomer sequences.[38] These results indicate that the syndiotactic random copolymer st-poly[EMA-*ran*-(1-phenylethyl methacrylate)] was obtained.

Similarly, a random st-copolymer consisting of propargyl methacrylate and methyl methacrylate units, st-poly[(propargyl methacrylate)-*ran*-MMA], was successfully prepared by a two-step esterification of st-PMAA using propargyl bromide and methyl iodide (Figure 4A). Copolymer composition was determined to be [propargyl methacrylate]:[MMA] = 69:31 by ^{1}H NMR analysis of the copolymer as shown in Figure 4B. The ^{13}C NMR spectrum of the copolymer reveals broad carbonyl resonances corresponding to each component, indicating random comonomer sequences with high stereoregularity (Figure 4C). The st-poly[(propargyl methacrylate)-*ran*-MMA] can be considered a st-PMMA bearing propargyl group. Since the propargyl group is a functional group for click reaction, the st-copolymer may be used to develop novel functionalized stereocomplexes and inclusion complexes.

Scheme 3. Synthesis of Highly Syndiotactic Copolymer by a Two-Step Esterification Method



iv. Stereocomplex Formation between it-PMMA and Novel st-Copolymer. Finally, we examined stereocomplex formation between it-PMMA and the obtained st-copolymers.[39] Solutions of it-PMMA and st-copolymer in acetone, which is the strongly complexing solvent,[40] were separately prepared at a polymer concentration of 4 mg/mL. Since it is generally accepted that stereocomplex of it- and st-PMMAs quantitatively forms at a stoichiometric ratio of it/st = 1/2,[11−26,39,40] the solutions were mixed at a ratio of it-PMMA/st-copolymer = 1/2 in unit molar base. After incubating at room temperature for 24 h, the solvent was removed with a nitrogen purge to give solid followed by drying under vacuum at room temperature for 24 h. Figure 5A shows DSC thermograms of it-PMMA and st-copolymer mixtures, together with that of a stereocomplex between it- and st-PMMAs formed in acetone.[23] The stereocomplex of it- and st-PMMAs revealed a broad endothermic peak at 195 °C with an endothermic amount (ΔH) of 33.0 J/g due to crystalline stereocomplex melting (a in Figure 5A). The mixture of st-poly[EMA-*ran*-(1-phenylethyl methacrylate)] and it-PMMA showed a weak but apparent endothermic peak at 138 °C with a ΔH of 7.2 J/g, confirming stereocomplex formation (Figure 5Ab). The lower melting temperature and decreased ΔH value indicate that the amount of st-copolymer stereocomplex is smaller than that of st-PMMA, potentially due to ester group bulkiness. The mixture of st-poly(propargyl methacrylate)-*ran*-MMA and it-PMMA also showed an endothermic peak at 150 °C with a ΔH of 27.7 J/g, corresponding to the melting of the stereocomplex (Figure 5Ac). Further evidence of st-copolymer stereocomplex formation is the characteristic X-ray diffraction (XRD) patterns (Figure 5B). XRD profile of stereocomplex between it- and st-PMMAs shows reflections at *d* of 2.12, 0.79,

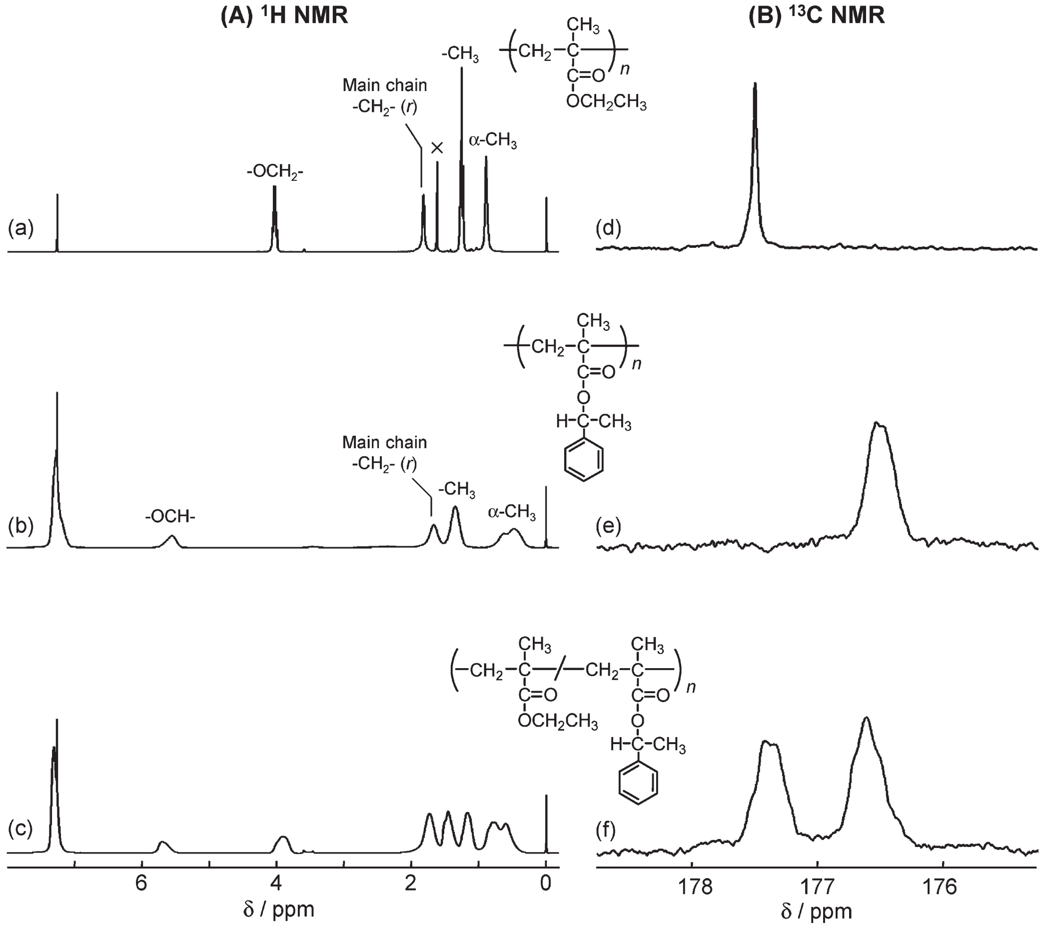


Figure 3. (A) ^{1}H and (B) ^{13}C NMR spectra of st-PEMA prepared with ethyl iodide (a, d), st-poly(1-phenylethyl methacrylate) prepared with 1-phenylethyl bromide (b, e) and st-poly[EMA-*ran*-(1-phenylethyl methacrylate)] prepared with ethyl iodide and 1-phenylethyl bromide (c, f).

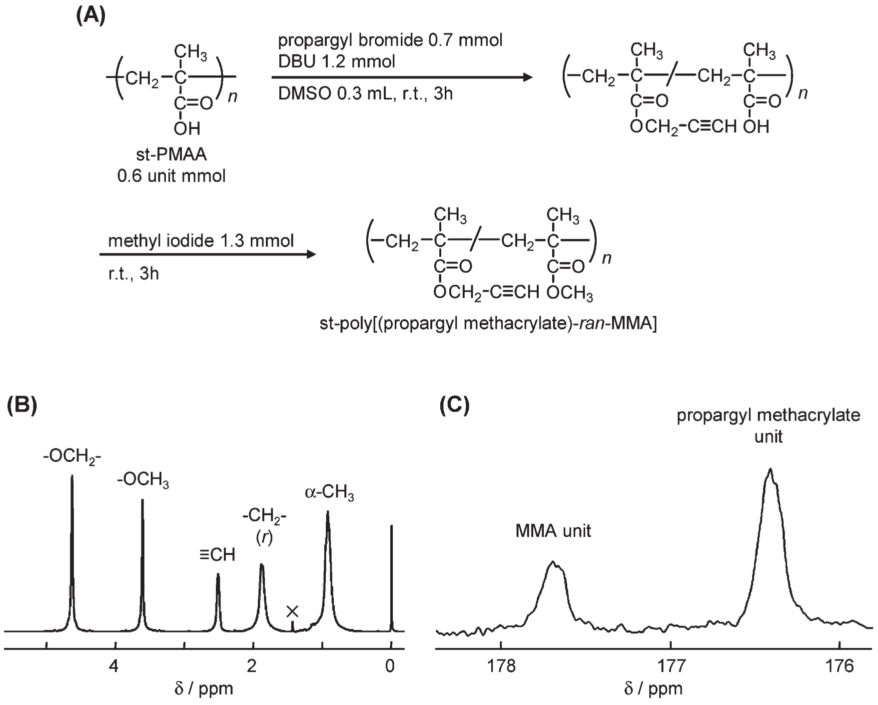


Figure 4. (A) Synthesis of st-poly[(propargyl methacrylate)-*ran*-MMA] by the two-step esterification method. (B) ^{1}H and (C) ^{13}C NMR spectra of st-poly[(propargyl methacrylate)-*ran*-MMA].

0.57, 0.45, and 0.29 nm based on stereocomplex crystalline structure (d in Figure 5B). Similar XRD patterns were observed in XRD profiles of it-PMMA and st-copolymer mixtures (e and f in Figure 5B), confirming stereocomplex formation.

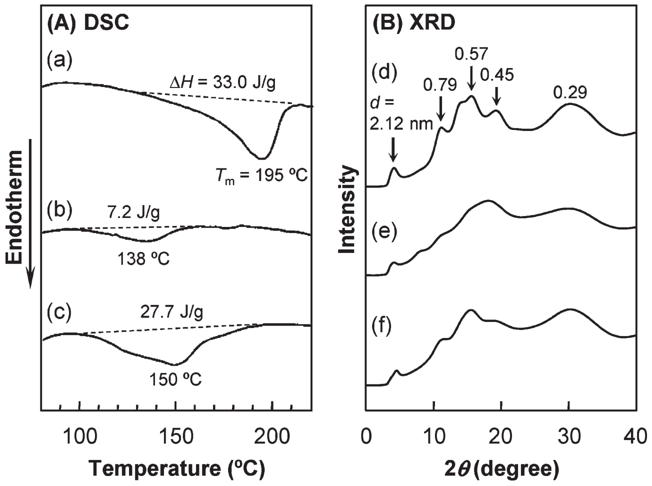


Figure 5. (A) DSC thermograms and (B) XRD profiles of stereocomplexes between it- and st-PMMAs (a, d), it-PMMA and st-poly[(ethyl methacrylate)-*ran*-(1-phenylethyl methacrylate)] (b, e), and it-PMMA and st-poly[(propargyl methacrylate)-*ran*-MMA] (c, f). DSC measurements were conducted from 25 to 280 °C at a heating rate of 10 °C/min.

Conclusion

We synthesized various highly stereoregular polymethacrylates by esterification of st- and it-PMAAs prepared by stereospecific anionic living polymerization. The esterification reaction of PMAAs with various halogenated compounds in the presence of DBU in DMSO at room temperature with a polymer concentration of 2.0 unit mol/L gave primary and secondary polymethacrylates with high stereoregularity (st-polymer $rr = 96\%$, it-polymer $mm = 98\%$). By performing the esterification reaction in a stepwise manner, we succeeded in preparing highly stereoregular copolymers such as st-poly[(ethyl methacrylate)-*ran*-(1-phenylethyl methacrylate)] and st-poly[(propargyl methacrylate)-*ran*-methyl methacrylate]. By performing DSC and XRD analyses, we confirmed that st-copolymers form stereocomplexes with it-PMMA. The proposed method provides highly stereoregular polymethacrylate homopolymers and copolymers bearing rationally designed pendants, which can be used to create advanced polymeric materials with unique characteristics, e.g., materials with a specific optical activity and inclusion ability, because of their helical structures.

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