Synthesis and Chiroptical Properties of Vinyl Polymers Containing Laterally Attached 4,4″-Digalactosyloxy-*p*-terphenyl Side Groups

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ABSTRACT: The synthesis and chiroptical properties of two novel optically active helical glycopolymers, poly{2,5-bis[4′-(2,3,4,6-tetra-*O*-acetyl-beta-D-galactosyloxy)phenyl]styrene} (PTAGPS) and poly{2,5-bis[4′-(β-D-galactosyloxy)phenyl]styrene} (PGPS), were reported. The former was obtained via radical polymerization of 2,5-bis[4′-(2,3,4,6-tetra-*O*-acetyl-β-D-galactosyloxy)phenyl]styrene (TAGPS), while the later by either direct radical polymerization of deacetylized monomer, 2,5-bis[4′-(β-D-galactosyloxy)phenyl]styrene (GPS), or deacetylation of PTAGPS. PTAGPS had a thermodynamically controlled conformation (TCC) regardless of the nature of the solvent where it was polymerized. However, PGPS prepared via radical polymerization of GPS in dimethyl sulfoxide (DMSO) had TCC, and that in *N*,*N*-dimethylformamide (DMF) had a kinetically controlled conformation (KCC), which could undergo an irreversible evolution to TCC by annealing in DMSO. PGPS derived from PTAGPS showed the essential chiroptical characteristics of both its precursor and PGPS with KCC obtained in DMF. These results demonstrated that achiral acetyl groups in the monomer molecule had a remarkable effect on the formation of chiral secondary structure of the polymer.

Introduction

Synthetic helical polymers have been the topic of intense study in recent years due to the challenge they offer in polymer chemistry as well as their wide practical and potential applications, such as chiral recognition, asymmetric catalysis, molecular scaffolding, optical switch, and polarization-sensitive materials.[1] A variety of optically active polymers with helical main chains have been available. Examples include polyolefins,[2,3] polymethacrylates,[4–11] polychlorals,[12,13] polyisocyanides,[14–16] polyisocyanates,[17–19] polysilanes,[20,21] N-alkylated aromatic polyamides,[22] and some conjugated polymers/oligomers.[23–28] In order to control macromolecular stereostructure efficiently, ionic and coordination polymerization are frequently selected to prepare such polymers. A main disadvantage of this approach is the rigorous requirement for the purities of monomer and solvent and the high sensitivity of propagation center to moisture, oxygen, and polar functional group, which limit significantly the type of viable monomer and therefore polymer. On the other hand, although radical polymerization is a convenient process with advantages of relatively low synthetic demand, good reproducibility of the polymerization result, a high tolerance to a polar functional group, and easy control over macromolecular parameters by means of recently well-developed living radical polymerization techniques,[29] it is seldom employed to obtain a helical polymer because of the planar nature of the growing radical, which disfavors control over the stereostructure of the polymer backbone.

Okamoto et al. first reported the synthesis of optically active helical poly(triphenylmethyl methacrylate) and its analogues via radical polymerization.[30–35] The helix-sense-selection was achieved by the chirality of a monomer itself or by a chiral additive acting as a guide to the polymerization process. The helical conformation was generated and stabilized by the sterically congested side groups.[36] All these polymers showed quite high isotacticity although they were prepared through radical polymerization. It has long been thought that an exclusive conformational chirality in vinyl polymer can only be obtained when atropisomerism and stereoregularity are simultaneously present in the structure.[36] However, it was reported recently that the helical polymer main chain could also be formed in vinyl polymers with atactic configuration.[37,38] For example, in a class of acrylic polymers bearing flat-tapered monodendrons,[37] the backbone takes helical conformation due to the self-assembly of the dendritic side groups once the degree of polymerization is high enough. The formation of helices in such polymers is independent of the configuration of main chain.

Glycopolymer is another kind interesting material with unique molecular recognition arising from the pendant saccharide groups.[39] The saccharide side chains can also induce excess screw sense of polymer helix through nonconvalent[40–42] or covalent interaction.[38,43–46] Polypeptides bearing sugar residues reported by Takasu et al. show chiral chain conformation where the saccharide side groups are helically arranged along the main chain.[45] A maltopentaose-carrying polystyrene prepared by Kobayashi et al. takes a large helix of backbone regardless of its atactic nature in 0.1 M urea aqueous solution as demonstrated by small-angle scattering results.[38] In glycosylated poly(phenyl isocyanide), the rigid helical main chain generates three-dimensionally regulated array of side sugar groups.[43] Moreover, the chiroptical property of the acetylated polymer is affected mainly by the chirality of the stereoceter, which is the most close to isocyano group, while that of the polymer with free saccharide group is determined by hydrogen-bond networks. Although these glycopolymers with ordered saccharide packing reveal weak specific interaction with bioactive matters like lectin, more polymers are need to fully understand the structure−property relationship.[43]

In a previous communication, we described the synthesis of a radically initiated optically active vinyl polymer, poly{2,5-bis[4′-(*S*-(+)-methylbutoxy)pheny]styrene} (**1a**).[47] The polymer consists of a flexible polyethylene backbone substituted on every repeating units by chiral 4,4″-dialkoxyterphenyl group through

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waist position. The steric repulsion of bulky and crowded side groups gives rise to stereoisomerism by restricting the rotation around single bonds linking main chain carbons. The asymmetry coupling between the main chain helix and the remote stereocenters in the side groups induces a prevailing screw sense of polymer backbone. Herein, we will report synthesis and chiroptical properties of two novel glycopolymers, poly{2,5-bis[4′-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyloxy)phenyl]-styrene} (PTAGPS) and poly{2,5-bis[4′-(β-D-galactopyranosyloxy)phenyl]styrene} (PGPS). They have architectures similar to that of **1a** and are therefore expected to generate helical conformations through radical polymerization. One aim of this work is to test the viability of inducing an excess helical sense of vinyl polymer chain with saccharides, which are robust in nature. Another is to provide a facile way to obtain glycopolymer with a definite geometrical pattern of saccharide groups. In addition, the helical sense transition tuned by external stimulation, such as solvent,[48,49] light,[50,51] temperature,[48,52–54] annealing, and additive,[41,55–57] is of great interest in chiral materials. In particular, Novak et al.[46,58,59] systematically studied the thermodynamically controlled conformation (TCC) and kinetically controlled conformation (KCC) and their transition of a series of polyguanidines with bulky side groups. The main chain and the appended terphenyl groups of PGPS studied here are hydrophobic, while the sugar extremities of side groups are hydrophilic. Such types of amphiphilic architectures may impart remarkable effects on the formation and transition of helical conformations of the polymer main chain, which is distinguished from other systems in structural origin.

Experimental Section

Material. 2,5-Dibromotoluene (99%, Acros), *N*-bromosuccinimide (NBS, 99%, Aldrich), dihydro-4*H*-pyran (DHP, 99%, Acros), 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl bromide (95%, Sigma), trimethylborate (99%, Acros), triphenylphosphine (PPh_3, 99%, Acros), silver oxide (AR, Beijing Chemical Co.), tetrachloromethane (CCl_4, AR, Beijing Chemical Co.), and aqueous formaldehyde (40%, AR, Beijing Chemical Co.) were used as purchased. Azobisisobutyronitrile (AIBN, AR, Wuhan Chemical Co.) was recrystallized from ethanol and dried under vacuum at room temperature. Tetrahydrofuran (THF, AR, Beijing Chemical Co.) was refluxed with sodium and distilled out just before use. Anisole (AR, Beijing Chemical Co.), dimethyl sulfoxide (DMSO, AR, Beijing Chemical Co.), and *N*,*N*-dimethylformamide (DMF, AR, Beijing Chemical Co.) were distilled out from calcium hydride. Quinoline (AR, Beijing Chemical Co.) and methanol were purified by distillation. Tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$) was prepared according to the literature procedure and kept in refrigerator under argon.[60] β-Galactosidase (β-Galactoside galactohydrolase from *Aspergillus oryzae*, ≥8 units/mg solid) was purchased from Sigma and kept at −20 °C before use.

Measurements. ^{1}H NMR and ^{13}C NMR spectra were recorded on Brucker ARX400 or Brucker ARX300 spectrometers. The chemical shifts were reported in ppm (δ) relative to tetramethylsilane. Elementary analysis was run on a GmbH Vario EL instrument. Mass spectrum was recorded on a Bruker Inc. BIFLEX III spectrometer. Infra-Red (IR) spectra were obtained on a Nicolet Magna-IR 750 Fourier transform infrared spectrometer. The number-average molecular weight (M_n), weight-average molecular weight (M_w), and the polydispersity (M_w/M_n) of polymers was estimated by gel permeation chromatography (GPC, Varian) apparatus with a Waters 2410 refractive-index detector and a Waters 515 pump. Three Waters Styragel columns with a 10-mm bead size were connected in series. Their effective molecular weight ranges were 100−10000 for Styragel HT2, 500−30000 for Styragel HT3, and 5000−600000 for Styragel HT4. The pore sizes were 50, 100, and 1000 nm for Styragel HT2, HT3, and HT4, respectively. THF was used as the eluent at a flow rate of 1.0 mL/min at 35 °C. All GPC curves were calibrated against a series of monodispersed polystyrene standards. Optical rotations were determined with a JASCO Model P-1030 digital polarimeter using a water-jacketed 100 mm cell. The temperature of water bath was mediated with a PolyScience programmable temperature controller. UV−vis absorption spectra were recorded on a Varian Cary 1E UV−vis spectrometer. Circular dichroism (CD) spectra were recorded on a JASCO J-810. The sample solution was thermostatted at the desired temperature with a Julabo F25-Me controller. The light path length of the quartz cell used was 10 mm. The concentration was 2×10^{-5} mol/L.

Monomer Synthesis. *2,5-Dibromostyrene.* A solution of 2,5-dibromotoluene (10.0 g, 0.04 mol), NBS (7.12 g, 0.04 mol), and BPO (0.20 g, 0.8 mmol) in CCl_4 (250 mL) was refluxed for 3 h. When cooled to room temperature, the solids suspended on the surface of the reaction mixture were separated by filtration. After evaporation of solvent under reduced pressure, yellow solids were obtained and were mixed with PPh_3 (10.5 g, 0.04 moL) and acetone (250 mL). The mixture was heated to reflux and a lot of precipitates appeared immediately. The reaction was allowed to continue for 4 h. The solids were collected by filtration and washed with chilly acetone and then dissolved in aqueous formaldehyde (40%, 250 mL). With a rapid stirring, 10 wt % NaOH aqueous solution was dropped slowly at room temperature. The mixture was stirred for 24 h.

When the reaction was completed, 3 × 150 mL potions of CH_2Cl_2 were used to extract the mixture. The organic layers were combined and dried over anhydrous Na_2SO_4. The solvent was taken away under reduced pressure and the residue was purified by column chromatography on silica gel (dichloromethane/petroleum ether: 1/3 (v/v) as eluent) to give 6.4 g of product as a yellow liquid. Yield: 61%. ^{1}H NMR (300 MHz, CDC1$_3$, δ, ppm): 5.40−5.43 (d, 1H; vinyl), 5.68−5.74 (d, 2H; vinyl); 6.92−7.02 (q, 1H; vinyl); 7.22−7.67 (m, 3H; Ar).

4-(Tetrahydro-2H-pyran-2-yloxy)phenylboronic Acid. To a stirred solution of 4-bromophenol (100 g, 58 mmol) and *p*-toluenesulfonic acid monohydrate (1.78 g, 8.6 mmol) in dioxane kept at 0 °C was introduced dropwise DHP (65 mL, 71 mmol). After 30 min the solution was diluted with ether (200 mL) and then washed with $NaHCO_3$ solution and water. The organic layer was separated and dried over anhydrous Na_2SO_4 and evaporated to remove solvent under reduced pressure. The residue was kept at 0 °C and white crystals, 4-(tetrahydro-2*H*-pyran-2-yloxy)phenyl bromide, formed gradually. After washing with ethanol, 128 g of product was obtained. Yield: 86%. ^{1}H NMR (300 MHz, CDC1$_3$, δ, ppm): 1.55−1.99 (m, 6H; CH_2), 3.57−3.63 (m, 1H; CH_2), 3.81−3.88 (m, 1H; CH_2), 5.36−5.39 (t, 1H; CH), 6.92−6.98 (d, 2H; Ar); 7.36−7.40 (d, 2H; Ar).

Magnesium metal turnings (9.7 g, 0.36 mol) and THF (300 mL, distilled prior to use) were add into a flask under a continuous stream of argon. To the mixture was introduced 4-(tetrahydro-2*H*-pyran-2-yloxy)phenyl bromide (80 g, 0.31 mol) in THF (100 mL) dropwise, and the solution was stirred for an additional 1 h. The solution was introduced slowly to a trimethylborate (56 g, 0.54 mol) solution in 150 mL of THF, which was previously cooled to −78 °C. The solution was then stirred overnight. After addition of 10 wt % NH_4Cl aqueous solution, the mixture was stirred for 2 h and was extracted with ethyl acetate. After evaporation of solvent under reduced pressure, the residue was washed with petroleum ether and dried under vacuum to give 63 g of a white product. Yield: 92%. ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 1.54−2.00 (m, 6H; CH_2), 3.58−3.63 (m, 1H; CH_2), 3.83−3.89 (m, 1H; CH_2), 5.40−5.46 (t, 1H; CH), 7.01−7.08 (d,2H; Ar), 7.69−7.74 (d, 2H; Ar), 8.2 (s, 2H; borate).

2,5-Bis[4′-(tetrahydro-2H-pyran-2-yloxy)phenyl]styrene. To a degassed mixture of 2,5-dibromostyrene (6.40 g, 24.4 mmol), 4-(tetrahydro-2*H*-pyran-2-yloxy)phenylboronic acid (13.0 g, 58.5 mmol), and $Pd(PPh_3)_4$ (1.68 g, 1.44 mmol) were added benzene (74 mL), ethanol (54 mL), and aqueous Na_2CO_3 solution (2 mol/mL, 108 mL) under a continuous stream of argon. The solution was vigorously stirred at reflux for 36 h under argon. Afterward, the organic layer was separated and dried over anhydrous Na_2SO_4.

The solvent was removed under reduced pressure and 9.60 g of product was obtained, which was used directly in the following reaction without further purification. Yield: 86.2%. ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 1.65−1.93 (m, 12H; CH_2), 3.61−3.68 (m, 2H; CH_2), 3.85−3.93 (m, 2H; CH_2), 5.21−5.25 (d, 1H; vinyl), 5.49−5.50 (d, 2H; CH), 5.73−5.79 (d, 1H; vinyl), 6.73−6.91 (m, 1H; vinyl), 7.10−7.17 (t, 4H; Ar), 7.27−7.33 (d, 2H; Ar), 7.50−7.60 (m, 3H; Ar), 7.8 (s, 1H; Ar).

2,5-Bis(4′-hydroxyphenyl)styrene. To a solution of 2,5-bis[4′-(tetrahydro-2*H*-pyran-2-yloxy)phenyl]styrene (7.0 g, 15 mmol) in THF (250 mL) and MeOH (60 mL) was added hydrochloric acid (37 wt %, 10 mL). The mixture was then stirred at room temperature for 4 h. The solution was diluted with ethyl acetate (200 mL) and washed with aqueous $NaHCO_3$ and water. The organic layer was dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to provide 3.6 g of product. Yield: 83%. ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 5.21−5.25 (d, 1H; vinyl), 5.71−5.77 (d, 1H; vinyl), 6.64−6.78 (m, 1H; vinyl), 6.83−6.88 (t, 4H; Ar), 7.13−7.16 (d, 2H; Ar), 7.22−7.28 (d, 2H; Ar), 7.51−7.57 (t, 3H; Ar), 7.8 (s, 1H; Ar); 9.57 (s, 2H; OH).

2,5-Bis[4′-(2,3,4,6-tetra-O-acetyl-β-D-galactosyloxy)phenyl]styrene (TAGPS). A mixture of 2,5-bis(4′-hydroxyphenyl)styrene (3.54 g, 12.3 mmol), 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl bromide (12.15 g, 29.5 mmol), Ag_2O (6.86 g, 29.5 mmol), and $CaSO_4$ (9.87 g) in ethyl acetate (120 mL) containing anhydrous quinoline (60 mL) was stirred at room temperature for 24 h in a flask protected from light. Afterward, the solution was diluted with ethyl acetate (100 mL). After filteration, the solution was washed with 10 wt % hydrochloric acid, aqueous $NaHCO_3$, and brine, followed by drying over anhydrous Na_2SO_4 and evaporation to dryness. The crude product was purified further by column chromatography on silica gel (dichloromethane/ethyl acetate: 6/1 (v/v) as eluent) to give 5.42 g of yellow solids. Yield: 46%. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 2.03−2.10 (m, 18H; acetyl), 2.2 (s, 6H; acetyl), 4.10−4.25 (m, 6H; H-5 and H-6), 5.1−5.16 (m, 4H; H-1 and H-3), 5.23−5.26 (d, 1H; vinyl), 5.48−5.53 (m, 4H; H-2 and H-4), 5.74−5.78 (d, 1H; vinyl), 6.71−6.78 (m, 1H; vinyl), 7.05−7.26 (m, 4H; Ar), 7.30−7.34 (m, 3H; Ar), 7.48−7.50 (m, 1H; Ar), 7.57−7.59 (d, 2H; Ar), 7.77−7.78 (d, 1H; Ar). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 170.28, 170.17, 170.06, and 169.32 (C═O, acetyl), 156.50, 156.05, 139.58, 138.79, 136.19, 135.99, 135.89, 130.90, 130.48, 128.22, 127.00, 124.37, 117.22, and 116.46 (*p*-terphenyl), 135.41, 115.12 (CH═CH_2), 99.64, 99.52, 71.03, 70.82, 70.80, 68.63, 66.84, 61.32, 61.31 (sugar). Anal. Calcd for $C_{48}H_{52}O_{20}$: C, 60.76; H, 5.52. Found: C, 60.49; H, 5.58. MS (MALDI−TOF, *m*/*z*): 972 (MNa^+). Specific optical rotation $[\alpha]_{365}^{20} = +105°$ (*c* 0.03, THF).

2,5-Bis[4′-(β-D-galactosyloxy)phenyl]styrene (GPS). A mixture of TAGPS (0.949 g, 0.1 mmol) and freshly prepared CH_3ONa in methanol (0.1 mmol/L, 100 mL) was stirred at room temperature for 2 h. The precipitates were filtered and washed with methanol. After drying under vacuum, 0.52 g of GPS was obtained as a white powder. Yield: 85%. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 3.431−3.435 (m, 2H; sugar), 3.55−3.61 (m, 8H; OH), 3.71−3.73 (t,2H; sugar), 4.51−4.52 (d, 2H; sugar), 4.66−4.69 (t, 2H; sugar), 4.87−4.89 (t, 4H; sugar), 5.18−5.19 (d, 2H; sugar), 5.26−5.29 (d, 1H; vinyl), 5.91−5.96 (d, 1H; vinyl), 6.65−6.72 (m, 1H; vinyl), 7.11−7.15 (m, 4H; Ar), 7.26−7.34 (m, 3H; Ar), 7.60−7.62 (d, 1H; Ar), 7.69−7.71 (d, 2H; Ar), 7.9 (s, 1H; Ar). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 157.42, 157.00, 138.92, 138.58, 135.00, 133.35, 133.32, 130.69, 130.56, 127.86, 126.00, 123.58, 116.87, and 116.15 (*p*-terphenyl), 135.44, 115.56 (CH═CH_2), 101.23, 75.70, 73.43, 70.42, 68.29, 60.57, 60.54 (sugar). Anal. Calcd for $C_{32}H_{36}O_{12}$: C, 62.74; H, 5.92. Found: C, 62.37; H, 5.98. MS (MALDI−TOF, *m*/*z*): 635 (MNa^+). Specific optical rotation $[\alpha]_{365}^{20} = -61°$ (*c* 0.03, DMSO).

2,5-Bis[4′-(2,3,4,6-tetra-O-acetyl-β-D-galactosyloxy)phenyl]toluene (TAGPT) and 2,5-Bis[4′-(β-D-galactosyloxy)phenyl]toluene (GPT). The two compounds were prepared in a procedure similar to that of TAGPS and GPS. TAGPT. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 2.03−2.10 (m, 18H), 2.2 (s, 6H), 2.33 (s, 3H), 4.10−4.27 (three m, 6H), 5.1−5.16 (m, 4H), 5.48−5.53 (m, 4H), 7.05−7.09 (t, 4H), 7.25−7.30 (m, 3H), 7.40−7.44 (t, 2H), 7.54−7.56 (d, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 170.37, 170.26, 170.15, and 169.41 (C═O, acetyl), 156.44, 1565.91, 140.01, 139.41, 136.62, 136.14, 135.86, 130.38, 130.34, 128.91, 128.22, 124.34, 117.22, and 116.59 (p-terphenyl), 99.70, 99.65, 71.09, 71.07, 70.90, 70.88, 68.70, 66.90, 61.39 (sugar). Anal. Calcd for $C_{47}H_{52}O_{20}$: C, 60.25; H, 5.59. Found: C, 59.80; H, 5.62. MS (MALDI−TOF, *m*/*z*): 960 (MNa^+). Specific optical rotation $[\alpha]_{365}^{20} = +106°$ (*c* 0.3, THF). GPT. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 2.3 (s, 3H), 3.43−3.45 (m,2H), 3.52−3.60 (m, 8H), 3.71−3.73 (t,2H), 4.51−4.52 (d, 2H), 4.66−4.68 (t, 2H), 4.86−4.88 (t, 4H), 5.17−5.19 (d, 2H), 7.09−7.13 (m, 4H), 7.23−7.25 (d, 1H), 7.30−7.31 (d, 2H), 7.47−7.50 (m, 1H), 7.54−7.55 (d,1H), 7.62−7.64 (d, 2H). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 157.26, 156.73, 139.62, 138.54, 135.42, 133.53, 130.24, 130.07, 128.36, 127.65, 123.92, 116.83, and 116.09 (*p*-terphenyl), 101.21, 75.68, 73.43, 70.42, 68.29, 60.56, 60.53 (sugar). Anal. Calcd for $C_{31}H_{36}O_{12}$: C, 61.99; H, 6.04. Found: C, 61.73; H, 6.21. MS (MALDI−TOF, *m*/*z*): 623 (MNa^+). Specific optical rotation $[\alpha]_{365}^{20} = -69°$ (*c* 0.03, DMSO).

Radical Polymerization of TAGPS. The radical polymerizations of TAGPS were carried out in solution. As a typical example, the detailed procedure for TAGPS in anisole was described as follows. TAGPS (0.189 g, 0.2 mmol), AIBN (0.16 mg, 0.001 mmol), and anisole (2 mL) were added into a reaction tube. After three freeze−pump−thaw cycles, the tube was sealed under vacuum and put into an oil-bath thermostatted at desired temperature for 20 h. After being cooled to room temperature, the tube was opened and the solution was diluted with THF (10 mL). The mixture was dropped into cold methanol (200 mL). The precipitates were filtered and then dried under vacuum for 24 h to give 0.153 g product. Yield: 81%. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 1.5−2.5 (CH_3CO), 0.5−1.5 (main chain CH_2), 3.0−3.8 (main chain CH), 4.0−6.2 (sugar), 6.2−8.5 (terphenyl).

Radical Polymerization of GPS. The radical polymerizations of GPS were carried out in DMSO and DMF, respectively. A representative procedure was described below: GPS (0.184 g, 0.3 mmol), AIBN (0.24 mg, 0.0015 mmol), and DMSO (2 mL) were added into a reaction tube. After three freeze−pump−thaw cycles, the tube was sealed under vacuum and put into an oil-bath thermostatted at 60 °C for 20 h. After being cooled to room temperature, the tube was opened and the solution was diluted with DMSO (10 mL). The mixture was dropped into cold DMF (200 mL). The precipitated solids were filtered and then dried under vacuum for 24 h to give 0.149 g product. Yield: 81%. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 3.0−3.8 and 5.0−5.2 (CH and CH_2 in sugar), 4.0−5.4 (OH in sugar), 5.6−8.0 (terphenyl).

Deacetylation of PTAGPS. A mixture of PTAGPS (0.50 g) and freshly prepared CH_3ONa in methanol (0.1 mol/L, 120 mL) was stirred at room temperature for 2 days. The solids were filtered and washed with methanol three times and then dried under vacuum. Thus, 0.29 g of white powder was obtained. Yield: 90%.

Enzyme Hydrolysis. First, 2.10 g of citric acid monohydrate and 6.94 g of disodium hydrogen phosphate dodecahydrate were added into 100 mL of water to give a buffer of pH 4.5. A mixture of PGPS (1.4 mg) and galactosidase (1.1 mg) in 10 mL of buffer was stirred at 30 °C for 24 h and ended with the addition of 1 mL of 0.5 M sodium carbonate aqueous solution. Water was removed under reduced pressure, and the residue was extracted with DMSO-d_6 for the characterization by ^{1}H NMR.

Results and Discussion

Synthesis. The monomers, TAGPS and GPS, were prepared via a multistep synthetic route as illuminated in Scheme 1. Bromination of 2,5-dibromotoluene by NBS in carbon tetrachloride yielded 2,5-dibromobenzyl bromide, which reacted with triphenylphosphine to give (2,5-dibromobenzyl)triphenylphosphonium bromide. The Wittig reaction of phosphonium salt with formaldehyde in aqueous solution under alkaline condition produced 2,5-dibromostyrene. Etherification of *p*-bromophenol with DHP followed by Grignard reaction with magnesium metal

Scheme 1. Synthetic Routes for Monomers and Polymers

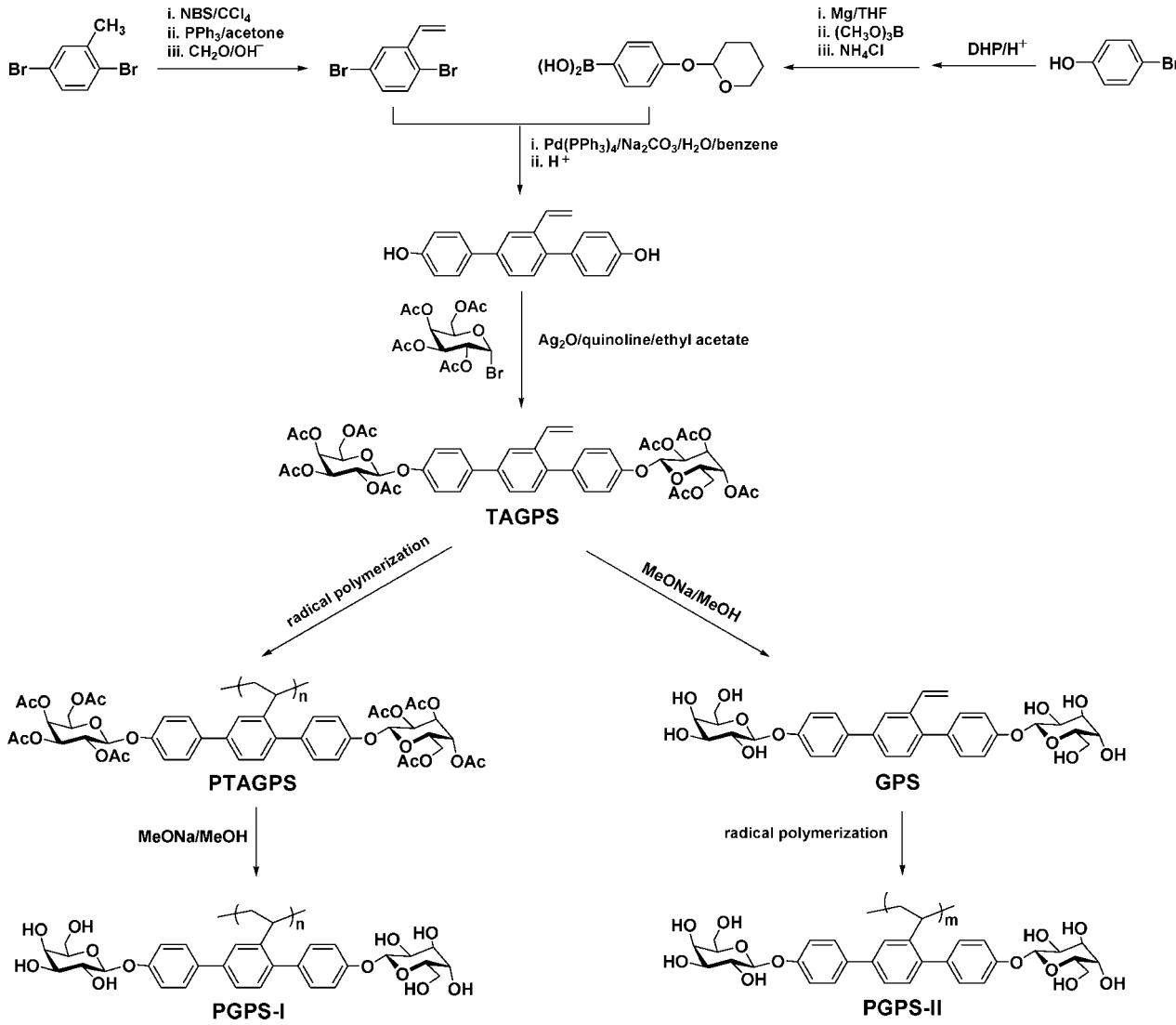
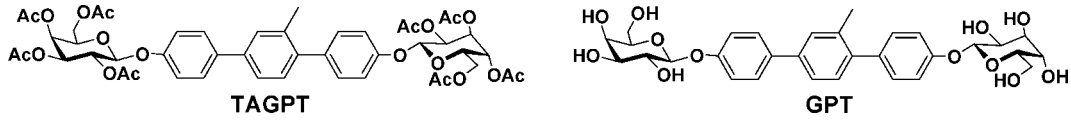


Chart 1. Chemical Structures of TAGPT and GPT



gave 4-(tetrahydro-2*H*-pyran-2-yloxy)phenylmagnesium bromide, which reacted with trimethylborate and NH_4Cl successively to yield 4-(tetrahydro-2*H*-pyran-2-yloxy)phenylboronic acid. Suzuki coupling reaction of 2,5-dibromostyrene and pyranyl protected *p*-hydroxyphenylboronic acid catalyzed by $Pd(PPh_3)_4$ resulted in 2,5-bis[4′-(tetrahydro-2*H*-pyran-2-yloxy)-phenyl]styrene. 2,5-Bis(4′-hydroxyphenyl)styrene was obtained after deprotection by diluted hydrochloric acid. TAGPS was obtained by glycosylation of 2,5-bis(4′-hydroxyphenyl)styrene with 2,3,4,6-tetra-*O*-acetyl-*β*-D-galactopyranosyl bromide, while GPS was prepared by deacetylation of TAGPS with freshly prepared CH_3ONa in CH_3OH. The two model compounds, TAGPT and GPT (Chart 1), were synthesized with a similar method except that 2,5-dibromotoluene was employed as the starting material of Suzuki coupling reaction instead of 2,5-dibromostyrene. The structures of all the intermediates and monomers were confirmed by proton NMR, mass spectrometry, and elementary analysis.

Free radical polymerizations of TAGPS and GPS were carried out in solution. In the case of TAGPS, the nature of solvents and the molar ratio of monomer to initiator were varied to investigate the effect of reaction condition on the chiroptical property of the resultant polymer. The results are summarized in Table 1. Anisole, DMF, and DMSO are good solvents for both TAGPS and PTAGPS. The polymerization mixture in these solvents kept clear during the whole polymerization process. Methanol is good solvent for TAGPS but not for PTAGPS. Therefore, during the early period of polymerization (about 6 h), the reaction mixture was homogeneous and gel formed gradually when the reaction time was longer.

The polymer PGPS was obtained via deacetylation of PTAGPS by CH_3ONa in methanol and direct radical polymerization of GPS carried out in DMF and DMSO, respectively (Table 2). For the sake of clarity, the deacetylized product of PTAGPS was named as PGPS-I, while that obtained directly from GPS was denoted as PGPS-II. Either GPS or PGPS is

Table 1. Summary of Polymerization Results and Chiroptical Properties of PTAGPS[a]

entry	solvent	[M]/[I]	yield (%)	$M_n \times 10^4$	M_w/M_n	$[\alpha]_{365}^{20}$ (deg)[b]
1	anisole	20:1	79	1.74	1.78	+895
2	anisole	50:1	68	2.79	2.45	+974
3	anisole	100:1	84	5.18	2.76	+1200
4	anisole	200:1	81	7.29	2.27	+1160
5	anisole	300:1	80	9.47	1.95	+1144
6	DMF	300:1	74	2.96	1.70	+1070
7	DMSO	300:1	25	2.40	1.68	+827
8	methanol	100:1	86	2.32	2.56	+1040

[a] Key: polymerization temperature, 60 °C; initiator, AIBN; concentration, 0.15 mol/L. [b] Estimated in THF ($c = 0.03$).

Table 2. Summary of Polymerization Results and Chiroptical Properties of PGPS-II[a]

				$[\alpha]_{365}^{20}$ (deg)[c]	
polymer	solvent[b]	[M]/[I]	yield (%)	H_2O	DMSO[d]
PGPS-II-1	DMSO	200:1	81	−1349	−901
PGPS-II-2	DMF	200:1	86	+1660	+947

[a] Key: polymerization temperature, 60 °C; initiator, AIBN; concentration, 0.15 mol/L. [b] Polymerization solvent. [c] Estimated in H_2O and DMSO, respectively ($c = 0.03$). [d] A mixture of 3 mg of PGPS-II and 10 mL of DMSO in a volumetric flask was exposed to ultrasonic sound for 10 min at 20 °C to cause the sample to dissolve completely. Then the solution was transferred to a 1 dm cell and was measured instantly.

soluble in DMSO. DMF is a good solvent of GPS but not PGPS. As a result, the reaction mixture in DMSO kept clear throughout the polymerization, whereas the polymers precipitated during the polymerization of GPS in DMF.

Figure 1 shows the ^{1}H NMR spectra of TAGPS, PTAGPS, and PGPS-I. The presence of only one doublet with $J = 5.2$ Hz at 5.18 ppm for the anomeric protons of TAGPS (Figure 1a) indicated a pure β-galactosidic linkage.[61] The sharp characteristic signals of TAGPS became broad after polymerization (Figure 1b) due to the limited mobility of protons, accompanied by disappearance of the vinyl signals at 5.3, 5.9, and 6.7 ppm, respectively. The acetyl protons signals were present at about 2 ppm. After deacetylation, the peaks assigned to acetyl groups were completely absent, indicating the complete removal of acetyl groups (Figure 1c).[62] Figure 2exhibits the ^{1}H NMR spectra of GPS and PGPS-II, separately. As in PTAGPS, after polymerization, the resonance peaks of vinyl protons centered at 5.3, 5.9, and 6.7 ppm disappeared completely. In addition, PGPS-I and PGPS-II showed similar NMR patterns, suggesting identical chemical structures (Figure 1c and 2b).

Figure 3 displays the FT-IR spectra of PTAGPS, PGPS-I, and PGPS-II, respectively. It was evident that the C═O absorption peak of acetyl groups of PTAGPS at 1751 cm^{-1} disappeared after deacetylation and a broad absorption peak at 3392 cm^{-1} corresponding to hydroxy groups of PGPS were present. Furthermore, the spectrum of PGPS-I was the same with that of PGPS-II. Both of them showed sharp C−O−C absorption peak of glycosyl ring at 1077 cm^{-1}. This was another evidence that the O-protecting acetyl groups were removed quantitatively.

Effort was made to estimate the tacticities of both PTAGPS and PGPS by ^{13}C NMR under various conditions. Unfortunately, no valuable information was obtained due to the overlap of tertiary carbons, which are usually employed to characterizaed the tacticity of polystyrene.[63]

Chiroptical Properties. The monomer TAGPS and the model compound TAGPT displayed positive specific optical rotations ($[\alpha]_{365}^{20}$) of 105 and 106° in THF ($c = 0.03$), respectively. After polymerization, the resultant polymers had an $[\alpha]_{365}^{20}$ value more than 800°. It seemed that the strength of optical rotation

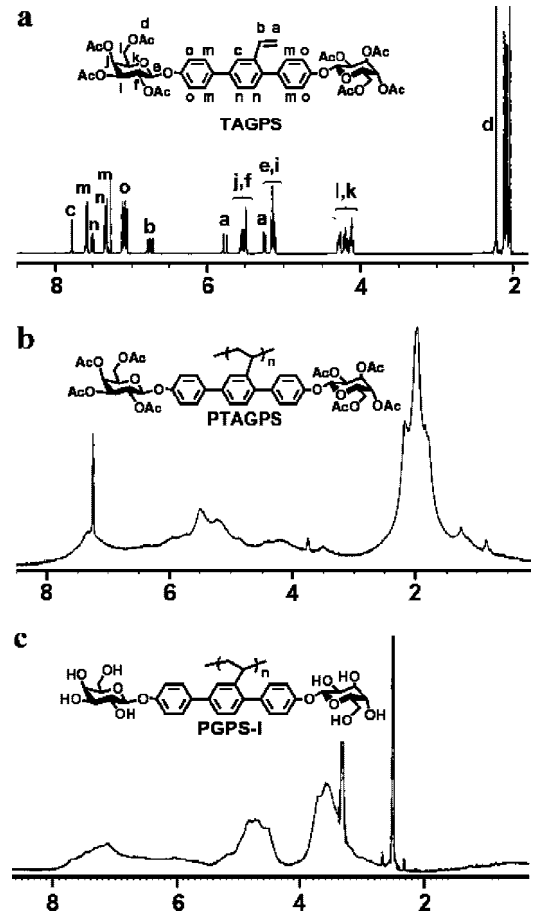


Figure 1. ^{1}H NMR spectra of TAGPS in $CDCl_3$ (a), PTAGPS in $CDCl_3$ (b), and PGPS-I in DMSO-d_6 (c), respectively, recorded at room temperature.

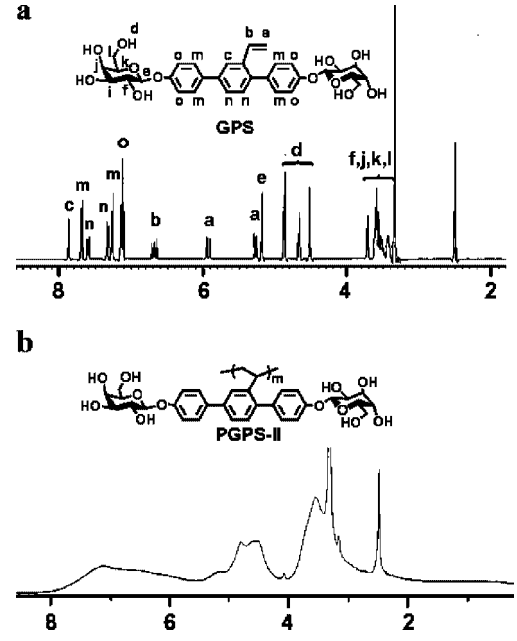


Figure 2. ^{1}H NMR spectra of GPS (a) and PGPS-II-1 (b) in DMSO-d_6, respectively, recorded at room temperature.

increased with molecular weight and leveled off at 1100−1200° when M_n was higher than 5.18×10^4 Da (entries 3−5 in Table 1). The similar optical rotation values (ORVs) of the monomer and the model compound suggested that the reaction at vinyl group did not influence the optical properties of such molecules

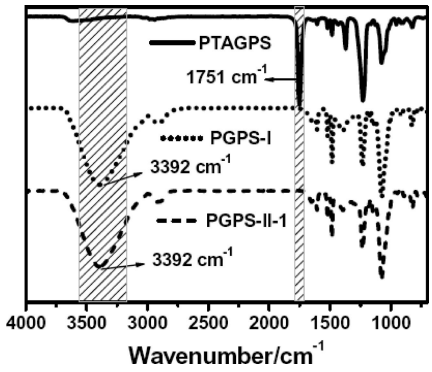


Figure 3. FT-IR spectra of PTAGPS, PGPS-I, and PGPS-II-1.

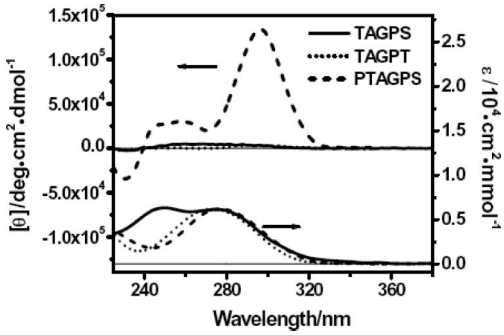


Figure 4. CD and UV−vis absorption spectra of TAGPS, TAGPT, and PTAGPS in THF at a concentration of 2×10^{-5} mol/L.

significantly. So the large increase in ORV of the polymer compared to TAGPS and TAGPT implied that the optical activity of the polymer did not arise solely from the configurational chirality of side groups, and a chiral higher structure should be generated. By analogy to **1a** and other polymers with similar architectures,[47,64,65] the most probable chiral higher structure of PTAGPS was helical polymer backbone.

CD spectroscopy was used to further characterize the chiroptical properties of PTAGPS. Figure 4 shows UV−vis and CD spectra of TAGPS, TAGPT, and PTAGPS in THF, respectively. The polymer absorbed intensively in the range from 245 to 315 nm, indicating the electronic transitions of the side-groups. Its CD spectrum exhibited two positive Cotton effects centered at 258 and 298 nm, respectively, and one negative Cotton effect at 230 nm. The monomer had two intensive absorption peaks centered at 245 and 278 nm, separately. The later represented the absorption of terphenyl chromophore as PTAGPS, while the former represented that of vinyl group. In contrast to PTAGPS, TAGPS displayed only neglectable Cotton effect. The major electronic transitions of the model compound, TAGPT, were essentially those of the polymer. However, its CD spectrum was quite like monomer, showing no discernible Cotton effects in the wavelength range concerned.

It is a commonly used method to approach macromolecular conformations of proteins and helical polyolefins by incorporation of aromatic chromophores into the chains of polymers as probes.[1,36] Due to the asymmetrical microenvironment of helical main-chain, achiral aromatic group show strong optical activity of $\pi-\pi^*$ transition. Therefore, the presence of Cotton effects of PTAGPS was consistent with a chiral secondary structure, which positioned *p*-terphenyl groups in a skewed way. And for a linear polymer chain like PTAGPS, the reasonable chiral secondary structure is a helical conformartion with one prevailing screw sense.

Figure 5 presents UV−vis and CD spectra of the monomer GPS, the model compound GPT, and the corresponding

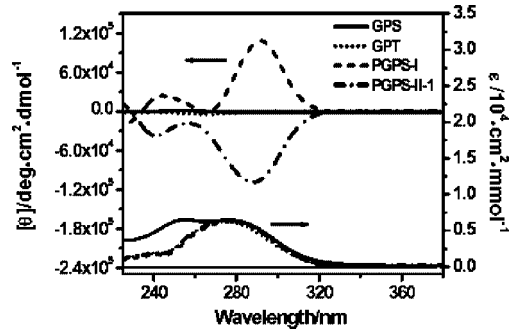


Figure 5. CD and UV−vis absorption spectra of GPS, GPT, PGPS-I, and PGPS-II-1 in H_2O at a concentration of 2×10^{-5} mol/L.

Table 3. Chiroptical Properties of PGPS and Its Annealing Product[a]

	$[\alpha]_{365}^{20}$ (deg)[b]	
polymer	H_2O	DMSO[c]
PGPS-I	+1700	+986
a-PGPS-I[d]	−1850	−1248
PGPS-II-2	+1660	+947
a-PGPS-II-2[d]	−1713	−1164

[a] PGPS-I: freshly deacetylated product of PTAGPS (entry 4 Table 1). Annealing procedure: 90 °C, DMSO, and 2 days. [b] Estimated in H_2O and DMSO, respectively ($c = 0.03$). [c] A mixture of 3 mg of sample and 10 mL of DMSO in a volumetric flask was dealt with ultrasonic sound for 10 min at 20 °C to make sure the sample to dissolve completely. Afterward, the solution was transferred to a 1 dm cell and then was measured instantly. [d] a-PGPS-I and a-PGPS-II-2 are PGPS-I and PGPS-II-2 annealed in DMSO at 90 °C for 48 h.

polymers. GPS and GPT had similar electronic transitions to TAGPS and TAGPT, respectively, absorbing in the range from 245 to 318 nm. Both of them displayed no discernible Cotton effect, suggesting achiral nature of terphenyl chromophore because the stereocenters in sugar moieties were remote. PGPS-I and PGPS-II-1 exhibited UV−vis absorption spectra similar to that of GPT and PTAGPS, indicating the identical structures of terphenyl group in these compounds. It is interesting to note that PGPS-I had similar CD spectrum with its precursor, suggesting that the side terphenyl groups packed in a similar way with that of PTAGPS. However, the CD spectrum of PGPS-II-1 was almost mirror image of PGPS-I, an indication of chiral secondary structure with opposite screw sense.

Mutarotation. The mutarotation of sugar or glycopolymer is a frequently observed phenomenon.[43,66] To test the stability of optical activities of the resultant polymers, PTAGPS and the two types PGPS were dissolved in DMSO and annealed at various temperatures. At a certain temperature, the ORVs of PTAGPS and PGPS-II kept almost constant, indicating no significant structural variation happened to them under the condition chosen. For PGPS-I, however, a remarkable change in ORV was observed with annealing under the identical condition. As can be seen from Table 3, PGPS-I showed a positive optical rotation ($[\alpha]_{365}^{20} = 986°$) in DMSO as PTAGPS ($[\alpha]_{365}^{20} = 1160°$) at beginning, which decreased to a constant value of −1248° after being annealed for 48 h at 90 °C. Figure 6 displays the time dependent UV−vis and CD spectra of PGPS-I at 70 °C in DMSO. The UV−vis absorption spectrum of PGPS-I kept almost unchanged, while the CD spectrum of PGPS-I changed significantly with annealing time. Initially, the polymer showed two positive Cotton effects centered at 258 and 300 nm, respectively. With an increase in annealing time, the strength of the Cotton effects decreased and finally became essential of that of PGPS-II. This was consistent with optical rotation observation.

PGPS-I and PGPS-II-1 had identical chemical structures and differed only by the way in which they were obtained. The

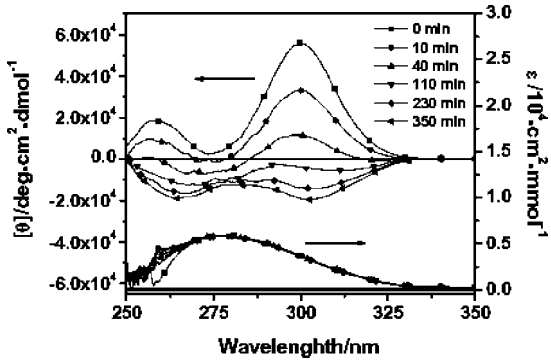
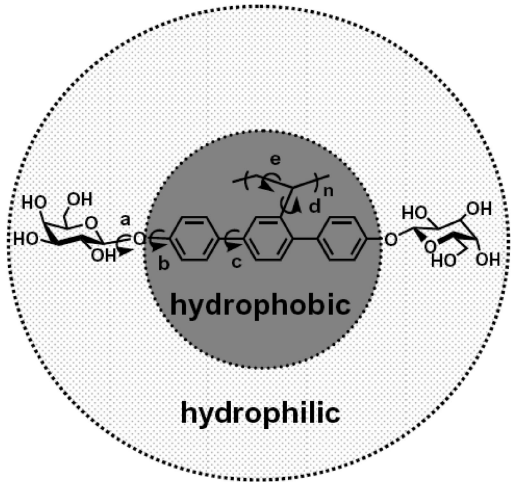


Figure 6. Variation of CD (a) and UV−vis absorption (b) spectra of PGPS-I in DMSO at 2×10^{-5} mol/L with annealing time at 70 °C. Procedure: a mixture of 3 mg of sample and 10 mL of DMSO in volumetric flask was dealt with ultrasonic sound for 10 min at 20 °C to make the sample dissolve completely and then the solution was transferred into a 1 cm cell thermostatted at the desired temperature. Once the sample was put into the cell, the spectrum was recorded instantly.

Scheme 2. Amphiphilic Structure and Molecular Motions of PGPS



former was prepared by deacetylation of PTAGPS with CH_3ONa in methanol, where neither the starting material nor the product dissolved, while the later was directly derived from GPS via radical polymerization in DMSO. It is reasonable to consider that PGPS-I reserved the essential structural characteristics of PTAGPS, which were different from those of PGPS-II-1 and were also not thermodynamically stable in DMSO and would undergo adjustment under suitable condition.

Scheme 2. shows the possible molecular motions that may lead to the mutarotation of PGPS-I in DMSO. The first is the configurational adjustment of sugar moieties. It is well-known that galactose undergoes mutarotation due to the equilibrium of various proportions (mainly α-form and β-form) through ring opening.[66] However, once it is transferred to glycoside, such conformation variation is forbidden because of the high stability of β-galactosidic linkage. It seemed that configurational change from the β- to the α-form was not responsible for the mutarotation of PGPS-I. The absence of mutarotation in GPS under the identical condition also supported this speculation.

The second is the conformation variation of sugar moieties caused by the rotation around C−O bonds a and b of the ether linkage. Kobayashi et al. found that the conformation adjustment of glycosidic linkages of poly(glycosyl phenyl isocyanide) due to deacetylation altered the minimum potential energy of the glycopolymer and therefore TCC. The fact that the $[\alpha]_{365}^{20}$

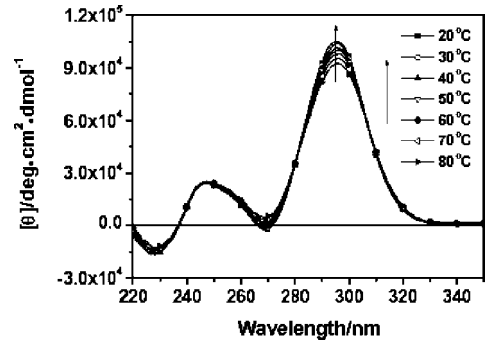


Figure 7. Temperature variable CD spectra of PGPS-I in H_2O at 2×10^{-5} mol/L.

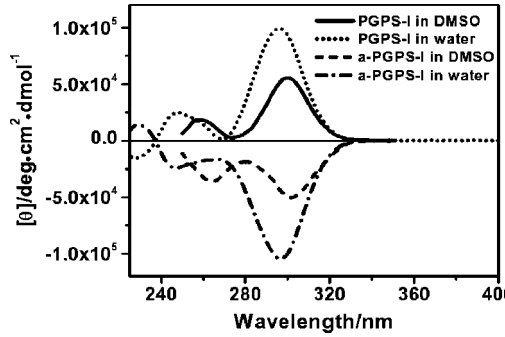


Figure 8. CD spectra of PGPS-I in DMSO (solid line), water (short dot), and a-PGPS-I in DMSO (short dash) and water (short dash dot) at 2×10^{-5} mol/L. a-PGPS-I was the product of PGPS-I annealed in DMSO for two days at 90 °C.

values of the monomer TAGPS and the model compound TAGPT in DMSO changed from 106 and 105° to −61 (GPS) and −69° (GPT) after deacetylation, respectively, seemed to support such speculation. To test this possibility, PGPS-I was dissolved in deionized water and annealed at various temperatures. Although the ORV of PGPS-I changed significantly with time in DMSO, it was quite stable in water. The ORV of PGPS-I decreased no more than 10% even after annealing at 90 °C for a week (from 1700 to 1580°). By a contrast, PGPS-I annealed in DMSO for 48 h at 90 °C displayed a strong negative optical rotation in H_2O (a-PGPS-1 in Table 3, $[\alpha]_{365}^{20} = -1850°$). Figure 7 shows temperature variable CD spectra of PGPS-I in water in the range from 20 to 80 °C. It was evident that though the intensity of the Cotton effects at 80° was a little weaker than those at 20 °C, the pattern of CD spectra remained almost unchanged. Moreover, upon cooling to 20 °C again, the signals returned to the original values. Figure 8 exhibits the CD spectra of PGPS-I and a-PGPS-1 in both DMSO and water, respectively. Freshly prepared PGPS-I presented positive Cotton effects in either water or DMSO, while annealed sample gave negative Cotton effects. Moreover, the CD spectrum of a-PGPS-I was independent of temperature and time. As a result, it was considered that the conformation of a-PGPS-I was stable in DMSO and water.

PGPS is unique in its amphiphilic structure consisting of hydrophobic backbone and side *p*-terphenyl groups and hydrophilic galactosyl residue in the two ends of *p*-terphenyl group. It was reasonable to think that the motion of polymer backbone and the appended *p*-terphenyl was frozen in water. Consequently, the stability of chiroptical property of PGPS-I in water implied that the structural adjustment in sugar moieties could not have large contribution to the mutarotation of PGPS-I in DMSO.

The next effect that may cause mutarotation of PGPS-I is conformational change of terphenyl group. *p*-Terphenyl has three

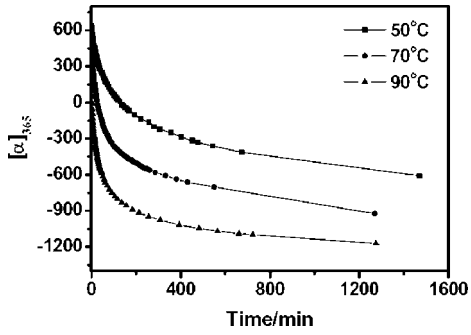


Figure 9. Annealing time dependence of specific optical rotation of PGPS-I in DMSO with a concentration of 0.3 mg/mL at 50 °C (■), 70 °C (●), and 90 °C (▲), respectively. Procedure: a mixture of 3 mg of powdered sample and 10 mL of DMSO in a volumetric flask was irradiated with ultrasonic sound for 10 min at 20 °C to make sure that the sample had dissolved completely, and then the resulting solution was transferred into a water-jacketed 1 dm cell with set temperature. The zero-time was selected artificially for the point where $[\alpha]_{365}$ of the solution was 640°.

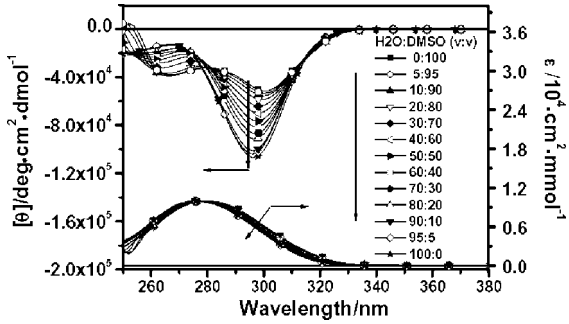


Figure 10. Variation of CD and UV−vis spectra of a-PGPS-I in H_2O/DMSO (v:v) with different ratios. $c = 2 \times 10^{-5}$ mol/L.

benzene rings linked by two inter-ring C−C bonds. The competition between the conjugative and steric effects results in helical conformers and alternately twisted conformers around the inter-ring C−C bonds. The variation in the population of different conformers might tune the chiroptical property of PGPS-I in DMSO. However, since the interconversion barrier is much low and different conformers interconvert rapidly in solution and in isotropic melt,[67] the 2′-substituted *p*-terphenyl cannot form one dominant conformation as in bridged biaryl compounds with atropisomers and is not able to influence efficiently the chiroptical property of the polymer.[68] On the other hand, if the dihedral angles between phenyl rings be changed, the maximum absorption of *p*-terphenyl would shift due to the variation in the conjugation length.[69] This contrasted with the observation from Figure 4.

Therefore, the irreversible evolution of PGPS-I in DMSO should result from the C−C bond rotation between side groups and backbone (d) and the C−C bond rotation in backbone (e), which might induce conformational adjustment of PGPS. Furthermore, the mutarotation of PGPS-I in DMSO at different temperatures (Figure 9) gave an activation barrier of 21 kcal/mol by the Arrhenius equation. It seemed to be congruous to the energy for the conformation change of the main chain.[46]

The CD spectra of a-PGPS-I in water were similar in the concentration range from 1×10^{-3} to 1×10^{-6} mol/L based on the repeating unit, although the solution became opalescence when the concentration was 1×10^{-3} mol/L. It indicated that aggregation did not affect the chiroptical property of PGPS significantly. But the chiroptical property of PGPS was dependent on the nature of solvent. Figure 10 shows the CD spectra of a-PGPS-I in water and DMSO mixture. With increasing water

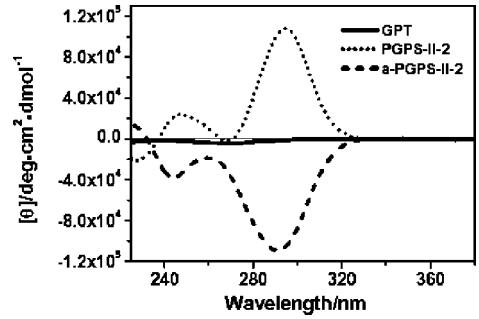


Figure 11. CD spectra of GPT (solid line), PGPS-II-2 (short dot) and a-PGPS-II-2 (short dash) in water at 2×10^{-5} mol/L. a-PGPS-II-2 was the product of PGPS-II-2 annealed in DMSO for 2 days at 90 °C.

content, the Cotton signals at 265 nm became weaker while those at 300 nm became stronger and showed a blue shift. The absorption of the model compound GPT also exhibited an obvious blue shift under identical condition but no discernible change in CD spectra (not shown). It suggested that the dependence of the chiroptical property of PGPS on the composition of solvent did not originate from the side group alone. The large increase in the CD effects at 300 nm could be rationalized by the variation of main chain conformation. Due to its amphiphilic structure, PGPS had a looser conformation in DMSO than that in water. With increasing water content, the helical chain of PGPS was contracted, which shortened the screw pitch (*P*) and therefore enhanced the optical activity.

TCC vs KCC. On the basis of the above-mentioned results, it is apparent that TCCs were generated in PTAGPS and PGPS-II-1 during radical polymerization since their chiroptical properties did not obviously change upon annealing. In addition, the freshly prepared PGPS-I kept the characteristic secondary structure of its O-protected precursor. The opposite sign of optical rotation of the freshly prepared PGPS-I and PGPS-II-1 and the gradual changes of the optical rotation of the former from positive to negative implied that the thermodynamically stable secondary structure of PTAGPS was different from that of PGPS. It was notable that deacetylation did not cause any change in the configurations of steteocenters of both monomer (TAGPS) and polymer (PTAGPS). It is reasonable to think that PTAGPS and PGPS had identical chiral secondary structures. One possibility of the conflicting observation is that the KCC of PGPS formed is different from its TCC and is evolved to TCC during polymerization. To shed light on this point, GPS was polymerized in DMF, a good solvent for GPS but a precipitant for PGPS. It was expected that the KCC of PGPS formed in DMF could be quenched. As shown in Table 2, the polymer obtained via polymerization of GPS in DMF, i.e., PGPS-II-2, showed a positive ORV ($[\alpha]_{365}^{20} = 1660°$) in water and a strong positive Cotton signal as illuminated in Figure 11. After the sample was annealed at 70 °C in DMSO for 24 h, the ORV of PGPS-II-2 also changed to negative (−1713°, c 0.03 in water) and the CD spectrum changed in a similar way.

Enzyme Hydrolysis. The polymer **1a** was reported to show a remarkable "memory effect" of optical activity; i.e., the polymer kept large optical rotation and intensive Cotton effects after the removal of the stereogenic centers, which were important in inducing a dominant helical sense. To test if the "memory effect" exists in the polymers concerned in this work, the hydrolization was carried out under alkaline condition. The resultant polymer displayed no optical activity at all. It was doubted that the static repulsion of the resultant polyanions and rigorous hydrolization condition caused racemization. As a result, a wild hydrolysis by galactosidase was tried in a buffer with a pH value of 4.5 at 30 °C. The process was monitored by ^{1}H NMR spectroscopy.

Although galactosidase is a quite active hydrolysis enzyme toward (4-nitro-phenyl)-β-D-galactopyranoside, no hydrolyzed product was identified after 24 h. Kobayashi and co-workers found the rigid helical conformation of poly(glycosyl phenyl isocyanide)s blocked the specific interaction between galacosyl and lectins.[43] It may also account for the failure of hydrolization of PGPS by galactosidase in the present work.

Conclusion

We have demonstrated that the sugar moieties in TAGPS and GPS molecules are able to dictate the polymer chain growth in radical polymerizations. The resultant macromolecules have adopted chiral secondary structures, most probable helical conformations of polymer main chains with a prevailing screw sense. The KCC and TCC of PTAGPS are essentially the same no matter what the polymerization condition is employed. However, the radical polymerization of GPS in DMSO yields the polymer with TCC while that in DMF with KCC. An evolution from KCC to TCC is observed by annealing the polymer in DMSO at various temperatures. The PGPS derived from PTAGPS in nonsolvent shows the chiroptical characteristics of its precursor and its counterpart arisen directly from radical polymerization of GPS in DMF, which undergoes mutarotation under suitable condition. The same sign in optical rotations and Cotton effects of PTAGPS and PGPS with KCC indicates that both acetylated and free saccharides, as chaperones appended to polymer backbone, have an identical guidance in distinguishing otherwise equal amount of right- and left-handed conformation. The failure in the hydrolysis of the polymer by galactosidase suggested the glycosidic section buried in highly crowded polymer chain is rather hard to attack. This stability is useful when the polymer is applied as chiral separation media. It may also provide another reasonable evidence that not only structural compatibility but also the relative spatial compatibility of oligosaccharides is important for molecular recognition.

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