2-Isopropenyl-2-Oxazoline: Well-defined Homopolymers and Block Copolymers via Living Anionic Polymerization

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ABSTRACT: Poly(2-isopropenyl-2-oxazoline) (PIPOx) has drawn significant attention for numerous applications. However, the successful living anionic polymerization of 2-isopropenyl-2-oxazoline has not been reported previously. Herein, we describe how well-defined PIPOx with quantitative yields, controlled molecular weights from 6,800 to over 100,000 g/mol, and low polydispersity indices (PDI ≤ 1.17) were synthesized successfully via living anionic polymerization using diphenyl methyl potassium/diethyl zinc (DPM-K/Et_2Zn) in tetrahydrofuran (THF) at 0 °C. In particular, we report the precise synthesis of well-defined PIPOx with the highest molecular weight ever reported (over 100,000 g/mol) and low PDI of 1.17. The resulting polymers were characterized by ^{1}H- and ^{13}C-nuclear magnetic resonance spectroscopy (NMR), along with size exclusion chromatography (SEC). Additionally, the reactivity of living PIPOx was investigated by crossover block copolymerization with styrene (St), 2-vinyl pyridine (2VP), and methyl methacrylate (MMA). It was found that the nucleophilicity of living PIPOx is of this order: living PS > living P2VP > living PMMA > living PIPOx. The self-assembly behavior in bulk of PIPOx-*b*-PS-*b*-PIPOx triblock copolymers having different block ratios of 10:80:10 and 25:50:25 was studied using transmission electron microscopy (TEM). The formation of spherical and lamellar nanostructures, respectively, was observed.

INTRODUCTION

Functional polymers containing heterocyclic units have received a great deal of attention and played critical roles in material science and polymer chemistry[1] because they demonstrate potentially exploitable properties such as optical, catalytic, electrochemical, sensory, photochemical, magnetic, and mechanical behavior.[2, 3] Among heterocycle-containing monomers, 2-isopropenyl-2-oxazoline (IPOx) is quite versatile because 2-isopropenyl-2-oxazoline (IPOx), as a dual-functional monomer, can undergo living cationic ring-opening polymerization via the oxazoline moiety resulting in poly(2-oxazoline)s, which have found multiple pharmaceutical and medical applications.[4] In addition, IPOx can be polymerized through the vinyl moiety leading to poly(2-isopropenyl-2-oxazoline) (PIPOx). PIPOxs are water-soluble, showing specific reactivity in quaternization and addition reactions with a variety of nucleophiles,[5] and they can serve as an electron transporting medium in organic electronic divices.[6] Moreover, PIPOx-containing copolymers and block copolymers have shown the ability to form self-assembled nanostructures, such as micelles and vesicles, which show great potential for drug and gene delivery.[7-10]

For the preparation of these interesting oxazole-containing polymers, several research groups have demonstrated free radical, anionic, and RAFT (reversible addition fragmentation chain transfer) polymerization via the α-carbon, and cationic ring opening polymerization (CROP) through the β-carbon.[11] In this regard, Jordan *et al.* produced cylindrical molecular brushes on a modified silicon substrate via surface-initiated radical polymerization and CROP of oxazoline units in PIPOx and thus studied their protein and cell adhesion behavior,[12] and Schubert *et al.* employed RAFT polymerization to synthesize PIPOx homopolymers and copolymers of IPOx with MMA and NiPAM (N-*iso*-propylacrylamide). The polydispersity indices (PDIs) of the resulting polymers were reduced significantly as compared with products of conventional free radical polymerization.[13] Atom-transfer radical polymerization (ATRP) of IPOx was also attempted, but it was not successful due to strong coordination of the Cu catalyst with the oxazoline moiety.[14]

Rieger *et al.* reported successful synthesis of well-controlled PIPOx materials (*M*W= 21,000 g/mol) with very low PDI and a yield of 95 % via rare earth metal-mediated group transfer polymerization (REM-GTP).[14] Recently, Kelland *et al.* studied the performance of a kinetic hydrate inhibitor using well-defined PIPOx synthesized anionically using the *n*-butyllithium (*n*-BuLi)/lithium chloride (LiCl) initiator system and obtained a maximum molecular weight (*M*W) of approximately 29,000 g/mol with PDI of 1.23.[15] To the best of our knowledge, none of these approaches have produced well-defined PIPOx with a combination of quantitative yield, very low PDI (≤ 1.15), and high *M*W (> 30,000 g/mol). Consequently, superior synthetic methods for the preparation of well-defined PIPOx and block copolymers containing PIPOx segments are required for specific applications and for creation of various nanostructures by self-assembly of amphiphilic homopolymers.[16-18]

Living anionic polymerizations has proven itself over the past 60 years to be the most powerful method for the synthesis of homopolymers and block copolymers with various tailored architectures and very low PDIs.[19, 20] In this study, we developed novel synthetic methods to produce well-defined PIPOx with controlled molecular weight and narrow polydispersity via anionic polymerization in tetrahydrofuran (THF) using different initiators based on alkyllithiums and aryl potassium, with additives including 1,1-diphenylethylene (DPE), LiCl, and Et_2Zn at -78, -41, 0, and 25 °C. Well-defined PIPOx homopolymers with MW up to 100,000 g/mol were synthesized. To understand the living nature and reactivity of PIPOx, crossover sequential block copolymerizations of IPOx with styrene, 2-vinyl pyridine, and methyl methacrylate were carried out. The microphase self-assembly of PIPOx-*b*-PS-*b*-PIPOx block copolymers in bulk was also examined.

EXPERIMENTAL SECTION

Materials. The monomers 2-isopropenyl-2-oxazoline (IPOx, 99%, Aldrich), 2-vinyl pyridine (2VP, 99% Aldrich), styrene (St, 99%, Aldrich) and methyl methacrylate (MMA, 99%, Aldrich) were passed through basic alumina columns, dried over CaH_2 and twice distilled under reduced pressures of 10^{-1} and 10^{-6} mm Hg. These monomers were diluted and transferred to pre-calibrated ampoules equipped with break-seals under high vacuum conditions and stored at -30°C. THF (Fisher scientific, HPLC grade) was distilled over potassium naphthalenide solution under reduced pressure (10^{-6} mm Hg) on a high vacuum line.

Initiators. *n*-Butyllithium (*n*-BuLi) solution (1.6 M in hexanes, Aldrich) and *sec*-butyllithium (*sec*-BuLi) solution (1.4 M in cyclohexane, Aldrich) were diluted and ampoulized on a high vacuum line. Lithium chloride (99.999%, LiCl, Aldrich) was dried at 130 °C for 2 days and then diluted to the target concentration in THF and ampoulized under a reduced pressure of 10^{-6} mm Hg. Sodium (Na-Naph) and potassium naphthalenide (K-Naph) were prepared by the reaction of the corresponding metal with naphthalene in THF at room temperature for 48 h. Diphenyl methyl potassium (DPM-K) was prepared by the reaction of K-Naph with diphenylmethane in THF under high vacuum conditions at room temperature for 72 h.[21, 22] (3-Methyl-1,1-diphenylpentyl)lithium was prepared by adding *s*-BuLi solution dropwise to 1,1-diphenylethylene (DPE). Triphenylmethyl potassium (TPM-K) was prepared by the reaction of triphenylmethane (TPM, Aldrich, 99%) and potassium in THF at room temperature for 2 days, and the excess K metal was removed by passing the solution through a glass filter under high vacuum conditions.[23] Concentrations of DPM-K and TPM-K were determined by titration using octyl alcohol and used for anionic polymerization. All initiators were sealed off under high vacuum into ampoules with break seals and stored at -30 °C.

Instrumentation. NMR spectra were recorded on a liquid state Varian VNMRS 500 MHz spectrometer at 25 °C. The internal standard was $CDCl_3$ at 7.26 ppm. Attenuated Total Reflection-IR (ATR-IR) spectra were obtained using a Nicolet iS50 FT-IR spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector. Size exclusion chromatography (SEC) was performed on a modular (Waters pump Model 515 HPLC, Knauer RI detector, Mini-DAWN multi-angle light scattering detector) using PSS columns as the stationary phase and *N,N*-dimethylformamide (DMF, T = 25 °C, 1 mL/min) as the mobile phase. The calculation of the weight-average molecular weight (M_w) and number-average molecular weight (M_n) was based on PS standards and, in some cases, light scattering. Before each SEC measurement, a solution of the polymer sample in DMF was prepared at a concentration of 2.0 mg/ml and filtered through a 0.2 μm pore size PTFE filter. The specific refractive index increment (dn/dc = 0.01048 mL/g) was determined using the Wyatt Optilab Rex in DMF at 25 °C with a laser, λ = 658.0 nm. Transmission electron microscopy (TEM) images were acquired using a ZEISS LIBRA 200 instrument. The TEM samples were first annealed at 180 °C under high vacuum for 4 days, trimmed and microtomed into ~40 nm thick slices. The thin slices were then loaded onto carbon coated TEM grids and stained with iodine vapor for 30 min before use. Differential scanning calorimetry (DSC) was performed on a TA Q2000 instrument with a scanning rate of 5 °C/min under N_2 atmosphere. In order to eliminate the effect of thermal history, the second heating cycle was selected for use in measuring the glass transition. Thermal gravimetric analysis (TGA) was performed on a TA Q50 instrument with a heating rate of 10 °C/min under N_2 flow.

Anionic polymerization of IPOx with *n*-BuLi. The anionic polymerization of IPOx was performed in glassware equipped with break seals under high vacuum (10^{-6} mm Hg) for 120 min. *n*-BuLi (0.054 mmol) in heptane (2.50 mL) was transferred into the reaction flask and thermally equilibrated at -78 °C. Chilled solution of IPOx (5.01mmol) in THF (6.40 mL) was then added to the initiator solution. The polymerization mixture was kept at this temperature for 120 min and terminated with degassed methanol (1.00 mL). Then the reaction mixture was concentrated and dissolved in chloroform, precipitated from diethyl ether twice and dried in a vacuum oven at 40 °C.

Anionic polymerization of IPOx with DPM-K. The procedure of anionic polymerization and purification was followed as described above, except using DPM-K as an initiator instead of *n*-BuLi at -78 and 0 °C.

Anionic polymerization of IPOx with s-BuLi and DPE. DPE (0.15 mmol) in THF (1.53 mL) was added to *s*-BuLi (0.058 mmol) solution in heptane at -78 °C. The color turned from colorless to yellow indicating (3-methyl-1,1-diphenylpentyl)lithium was formed. The chilled solution of IPOx (5.18 mmol) in THF (6.60 mL) was then added to the initiator mixture after 30 min. Polymerization was terminated with degassed methanol. The purification procedure was performed as described above.

Anionic polymerization of IPOx with DPM-K and Et_2Zn. A typical polymerization procedure is described as follows. The solution of DPM-K (0.093 mmol) in THF (4 mL) was transferred to main reactor at -78 °C and the solution of Et_2Zn (1.76 mmol) in THF (2 mL) was added to DPM-K solution at -78 °C. The solution of IPOx monomer (7.28 mmol) in THF (9.30 mL) was then added to the initiator mixture and the solution was maintained at -78 °C for 30 min to allow for complete initiation. The propagation in anionic polymerization was performed for 10 to 24 h at -78, -41, 0, and 25 °C. The polymerizations were terminated with degassed methanol. The purification of the polymer was performed as described above. The resulting polymer was characterized by SEC, DSC, TGA, ^{1}H- and ^{13}C-NMR, and FT-IR. ^{1}H-NMR spectra (500 MHz, $CDCl_3$), δ (ppm) = 4.08 - 4.25 (2H, CH_2 of the pendant oxazoline), 3.65 - 3.85 (2H, CH_2 of the pendant oxazoline), 1.70 - 2.00 (2H, CH_2 of the polymer backbone), 1.01 - 1.56 (3H, α-CH_3). ^{13}C-NMR spectra (75 MHz, $CDCl_3$), δ (ppm) = 172.97 (C, N=C-O of the pendant oxazoline), 66.95 and 54.27 (CH_2-CH_2 of the pendant oxazoline), 40.11 (CH_2 of the polymer backbone), 20.00 and 18.00 (α-CH_3, heterotactic and syndiotactic). FT-TR (cm^{-1}): 2928 (C-H stretch, m), 1652 (C=N, stretch, s), 1125 (C-O (unconjugated), stretch, s), 991, 960, 928 (oxazoline ring skeleton vibration).

Anionic polymerization of IPOx with K-NaPh, Na-NaPh, and TPM-K. The solution of K-Naph, Na-Naph, and TPM-K in THF, respectively, was transferred into the reaction flask and then the solution was thermally equilibrated at –78 °C. The chilled solution of IPOx in THF was added to the initiator solution and polymerization was carried out at -78 °C for 10 and 12 h. After terminating with degassed methanol, the polymers were obtained as described above.

Block copolymerization of 2VP with IPOx using DPM-K and Et_2Zn. Living poly(2-vinylpyridine) was prepared via living anionic polymerization using DPM-K at -78 °C for 30 min in an all-glass apparatus under reduced pressure of 10^{-6} mm Hg, as reported previously.[24, 25] A small portion of living poly(2-vinyl pyridine) (P2VP) solution was transferred to an attached receiver and then characterized by SEC to determine M_n of first block P2VP. The solution of Et_2Zn in THF was then added to the remainder of the living P2VP solution, followed by addition of IPOx monomer. The monomer IPOx was initiated at -78 °C for 5 min and then the anionic polymerization was kept at 0 °C for 12 h. The polymers were obtained as described earlier. The resulting block copolymer was characterized by SEC, ^{1}H-NMR. ^{1}H-NMR spectra (500 MHz, $CDCl_3$), δ (ppm) = 8.51-8.08(pyridine), 7.51-6.98 (pyridine), 6.96-6.64 (pyridine), 6.55-6.10 (pyridine). 4.31-3.91 (CH_2 of the pendent oxazoline), 3.91-3.44 (CH_2 of the pendent oxazoline), 2.05-1.52 (CH_2 of the polymer backbone), 1.42-0.89(α-CH_3).

Block copolymerization of MMA with IPOx. The solution of DPM-K and Et_2Zn in THF was added to the glass apparatus and thermally equilibrated at -78 °C. The solution of MMA in THF was then added. After 30 min, a small portion of the living PMMA solution was transferred to an attached receiver, and the polymer was characterized by SEC to obtain M_n of first block, PMMA. The chilled solution of IPOx in THF was then added at -78 °C with vigorous shaking. After 5 min, the polymeric mixture was warmed to 0 °C, kept at 0 °C for 12 h, and terminated with degassed methanol. The polymers were obtained as described earlier. The resulting block copolymer was characterized by SEC and ^{1}H-NMR. ^{1}H-NMR spectra (500 MHz, $CDCl_3$), δ (ppm) = 4.31-4.07 (CH_2 of the pendent oxazoline), 3.88-3.68 (CH_2 of the pendent oxazoline), 3.62-3.53 (-O-CH_3, ester), 2.10-1.56 (CH_2 of the polymer backbone), 1.31-0.74 (α-CH_3).

Block copolymerization of Styrene with IPOx. The synthesis of PIPOx-*b*-PS-*b*-PIPOx (f_{PIPOx}=0.5) is described as follows. The solution of K-Naph (0.087 mmol) in THF (4.10 mL) was added to an all-glass apparatus at -78 °C and the chilled solution of St (14.10 mmol) in THF (19.80 mL) was then added. The polymerization was kept at -78 °C for 40 min. A portion of the living PS solution was transferred to an attached receiver and the polymer was characterized by SEC to obtain M_n of the first block, PS. The solution of DPE (0.23 mmol) in THF (2.40 mL) was then added to the living PS solution, followed by Et_2Zn (1.04 mmol in 4 mL THF). The reaction mixture maintained at -78 °C for 30 min. The chilled solution of IPOx (14.67 mmol) in THF was then added with vigorous shaking for complete initiation. After 5 min, the solution was warmed to 0 °C, kept at this temperature for for 12 h, and terminated with degassed methanol. The polymer purification procedure was performed as described earlier. The resulting block copolymer was characterized by SEC, DSC and ^1H-NMR. ^1H-NMR spectra (500 MHz, $CDCl_3$), δ (ppm) = 7.17-6.38 (phenyl), 4.21-4.03 (CH_2 of the pendent oxazoline), 3.86-3.61 (CH_2 of the pendent oxazoline), 2.05-1.33 (CH_2 of the polymer backbone), 1.31-0.97 (α-CH_3).

RESULTS AND DISCUSSION

Homopolymerization of IPOx with different initiation systems. All of the polymerizations in this work were carried out using high-vacuum and glass blowing techniques.[26] The conditions and results for homopolymerization using different initiators, additives, reaction time, and temperatures are summarized in **Table 1**.

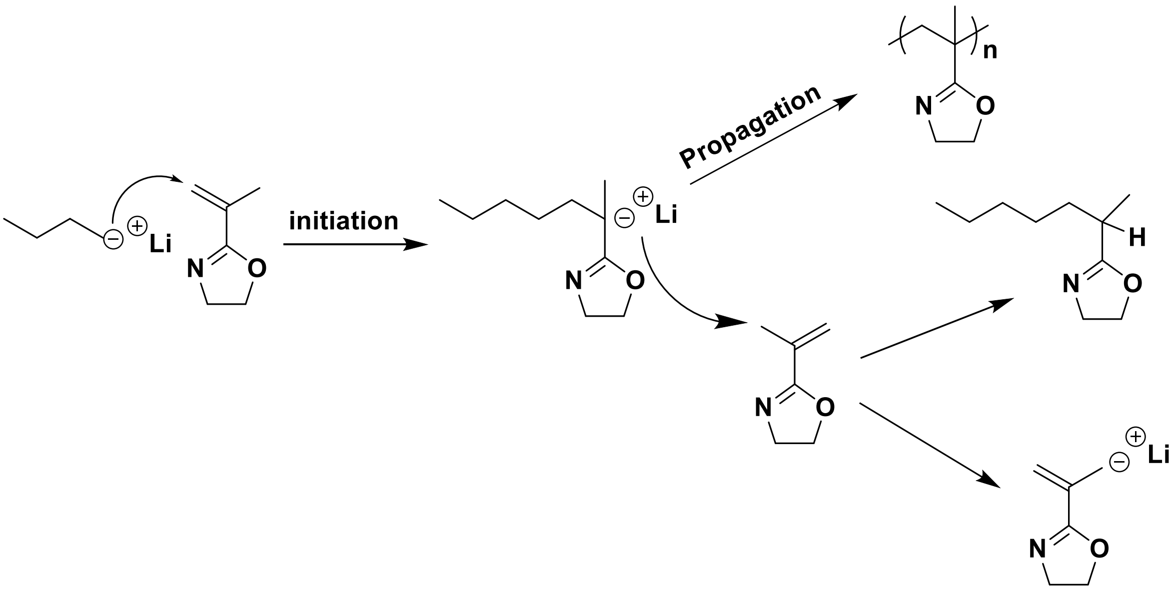
Table 1. Synthesis of poly(2-isopropenyl-2-oxazoline) with different initiation systems in THF.

run	IPOx	Initiator	Additive	Time	Temp	Yield[a]	M_n ($\times 10^{-3}$ g/mol)		PDI[c]
	mmol	mmol	mmol	h	°C	%	calcd[b]	obsd[c]	
1	5.01	*n*-BuLi, 0.054	None	2	-78	57.8	10.3	8.8	2.38
2	5.74	DPM-K, 0.065	None	2	-78	40.3	9.8	24.6	1.40
3	4.95	DPM-K, 0.071	None	2	0[d]	70.0	7.8	22.3	1.52
4	5.18	s-BuLi/DPE, 0.058/0.150	LiCl, 0.45	2	-78	40.0	7.7	6.80	1.13
5	6.72	s-BuLi/DPE, 0.073/0.293	LiCl, 0.49	10	-78	64.1	10.2	6.2	1.48
6	8.57	DPM-K, 0.076	Et_2Zn, 1.00	10	-78	73.0	12.7	9.6	1.12
7	9.23	DPM-K, 0.102	Et_2Zn, 1.00	24	-78	68.0	10.1	8.0	1.13
8	8.27	DPM-K, 0.087	Et_2Zn, 1.00	10	-45	60.4	10.6	7.8	1.15
9	7.28	DPM-K, 0.093	Et_2Zn, 1.76	10	0	100	6.9	6.8	1.10
10	10.20	DPM-K, 0.090	Et_2Zn, 1.35	12	25[e]	100	12.6	12.3	1.15
11	11.64	DPM-K, 0.023	Et_2Zn, 0.31	20	25	84.3	55.7	36.3	1.25
12	21.53	DPM-K, 0.031	Et_2Zn, 0.47	36	25	94.3	77.2	45.7	1.57
13	13.20	K-Naph, 0.189	None	12	0	100	15.5	14.0	1.30
14	9.10	Na-Naph, 0.180	None	10	0	100	11.2	16.0	1.50
15	8.85	TPM-K, 0.066	None	10	0	99.9	14.9	49.1	1.31

[a] Yield was calculated by the ^{1}H-NMR integration of corresponding peaks. [b] M_n(calcd)=(MW of IPOx) × [IPOx]/[initiator]× f × yield of polymer (%); f = 1 or 2, corresponding to functionality of the initiators. [c] M_n(obsd) and PDI were determined by SEC against narrow polystyrene standard in DMF at 25 °C. [d] 0: polymerization was initiated at -78 °C for 5 min and then temperature was increased to 0°C. [e] 25: the polymerization was initiated at -78 °C for 5 min and then the temperature was increased to 25 °C.

Initially, the effect of various initiation systems (initiators and combinations of initiator/additive) on homopolymerization of IPOx were investigated. The initiation systems include *n*-BuLi, DPM-K, TPM-K, *s*-BuLi/DPE/LiCl, and DPM-K/Et_2Zn. The homopolymerization of IPOx, which has the strong electron withdrawing oxazoline unit (N=C-O), using *n*-BuLi at -78 °C resulted in low yield (57.8%) and very high PDI (2.38) due to side reactions (Run 1 in **Table 1**). These side reactions could occur through the possible mechanisms of termination and/or chain transfer of the propagating species via H^+ abstraction during the polymerization, as shown in **Scheme 1**.[6, 11, 27] To circumvent such nucleophilic attack, DPM-K, a weaker nucleophile, was used to initiate the anionic polymerization of IPOx. However, this polymerization also showed low yield (40.3%) and rather high PDI (1.40) at -78 °C. The conversion was improved to 70% by increasing the reaction temperature from -78 °C to 0 °C (Run 2 in **Table 1**). The polymerization initiated by the even bulkier initiator of TPM-K exhibited quantitative yield. However, the observed M_n is almost three times higher than calculated M_n and the PDI was high (1.31, Run 15 in **Table 1**). It was thus concluded that the TPM-K is not sufficiently nucleophilic to completely initiate the polymerization of IPOx and that possible side reactions still occurred.

Scheme 1. The mechanism of possible side reactions via termination and chain transfer by H^+ abstraction in the polymerization of IPOx using *n*-BuLi as initiator.[6, 11, 27]



To further suppress the side reactions during the polymerization, additives such as DPE, LiCl, and Et_2Zn were employed as coordinating ligands along with *s*-BuLi and DPM-K. The *s*-BuLi/DPE system with ~15 eq of LiCl (*s*-BuLi/DPE/LiCl), regarded as an efficient initiation system for the synthesis of living PMMA,[28, 29] was used for the polymerization of IPOx. The polymerizations at -78 °C were controlled with rather low PDI (1.13) but the yield was only 40% after 2 h (Run 4 in **Table 1**). In order to obtain quantitative conversion, the reaction time was increased to 10 h. Unfortunately, a low yield (64.1%) was still obtained and the PDI turned out to be even higher (Run 5 in **Table 1**).

On the other hand, polymerization initiated by DPM-K/Et_2Zn at -78°C was well-controlled even with increased polymerization times (Run 6 and 7 in **Table 1**). This could be attributed to the polarizability of the carbanion/K^+ ion pair being higher than that of the carbanion/Li^+ and carbanion/Na^+ ion pairs during propagation, caused by the different radii of the couterrions (K^+>Na^+>Li^+).[29] Reaction time was further increased to 24 h but the yield was only 68% (Run 7 **in Table 1**). It should be noted that the polymeric mixture became turbid during propagation. This heterogeneous solution of the polymeric mixture caused by the low solubility of PIPOx in THF at -78 °C limited the synthesis of polymer having molecular weight over 9,600 g/mol. We speculate that the propagating chains were trapped in the aggregates so that it was difficult for the chain end carbanion to attack the incoming monomer, leading to low conversion.

Additionally, to investigate the effect of polymerization temperature, the polymerizations were carried out at -45, 0, and 25 °C, respectively (Runs 8, 9, & 10 in **Table 1**). Surprisingly, the low PDI (1.10) and quantitative yield (100%) could be achieved via anionic polymerization even at 0 °C (Run 9 in **Table 1**). This polymerization was monitored by ^{1}H-NMR spectroscopy to study kinetics of reaction (See **Figure S3** in Supporting Information). The polymerization using 20 eq of Et_2Zn at 25 °C also produced polymer with low PDI and in quantitative yield within 10 h (Run 10 in **Table 1**). It thus appears that Et_2Zn is an effective ligand to suppress side reactions during anionic polymerization of these monomers. However, as the polymerization time was increased to over 12 h at 25 °C, side reactions turned to be substantial as indicated by large PDIs (Runs 11 and 12 in **Table 1**). The polymerization mixture was hazy in appearance with a gel-like substance present. It is thus concluded that temperature should not be above 0 °C in order to produce well-defined PIPOx.

Furthermore, to demonstrate the unique merit of our anionic polymerization method, PIPOx was also synthesized via RAFT polymerization. In contrast to RAFT polymerization in toluene at 70 °C (See Supporting Information for the synthesis detail, **Figure 1b** blue line), RAFT polymerization reported elsewhere,[13, 15] and anionic polymerization initiated by *n*-BuLi (Run 1 in **Table 1**, **Figure 1c** red line), our synthetic approach produced well-defined polymers as shown in **Figure 1a** (black line). In particular, anionic polymerization using DPM-K/Et_2Zn in THF at 0 °C showed quantitative yield.

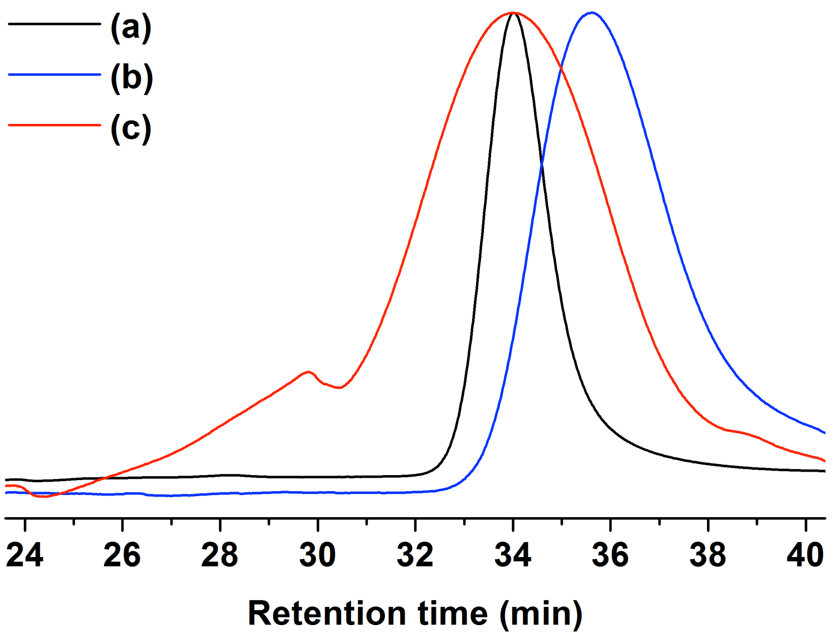


Figure 1. SEC curves of PIPOx synthesized by (a) anionic polymerization using DPM-K/Et_2Zn in THF at 0 °C (M_n = 6,800 g/mol and PDI = 1.10), (b) RAFT in toluene at 70 °C (M_n = 1,900 g/mol and PDI = 1.23) and (c) anionic polymerization using *n*-BuLi in THF at -78 °C (M_n = 8,800 g/mol and PDI = 2.38).

The resulting homopolymers of PIPOx were characterized by ^{1}H-NMR (**Figure 2**) and FT-IR spectra (**Figure S1**). The ^{1}H-NMR spectra of PIPOx demonstrated the successful anionic polymerization. The vinyl proton signals at 5.76 and 5.39 ppm disappeared completely and new peaks at 1.76-2.13 ppm emerged from protons of methylene on the polymer backbone. On the other hand, the signals corresponding to protons of the oxazoline ring shift slightly from 3.92 and 4.26 ppm to 3.76 and 4.16 ppm, respectively. Moreover, detailed analysis of α-methyl protons reveals that the tacticity ratio of isotactic (i): heterotactic (h): syndiotactic (s) = 13.6: 39.7:46.7. In ^{13}C-NMR spectra of PIPOx homopolymer (See **Figure S2** in Supporting Information), the 121.52 ppm and 132.65 ppm peaks of vinyl groups disappeared completely after living anionic polymerization and 40.27, 19.96, and 17.80 ppm peaks of main chain of PIPOx polymer were generated. FT-IR spectra also verified that the ring skeleton vibration (991, 958 and 930 cm^{-1}) was intact after polymerization as shown in **Figure S1**. Two characteristic absorption peaks of monomer at 1606 cm^{-1} (C=C, stretch) and 1281 cm^{-1} (C=O (conjugated), stretch) were disappeared after polymerization indicating the isopropenyl group was reacted completely. Thus, it was confirmed that well-defined PIPOx was synthesized by living anionic polymerization with DPM-K/Et_2Zn as the initiation system.

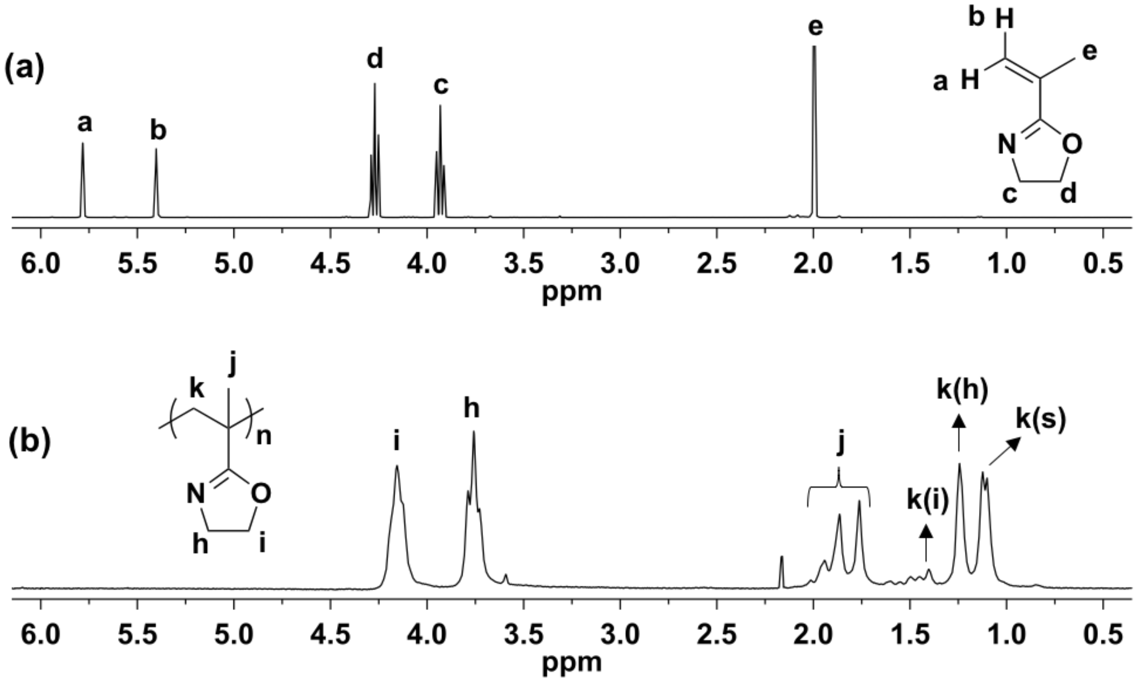


Figure 2. ^{1}H-NMR spectra of (a) IPOx and (b) PIPOx. Denote: (i) isotactic, (h) heterotactic, and (s) syndiotactic.

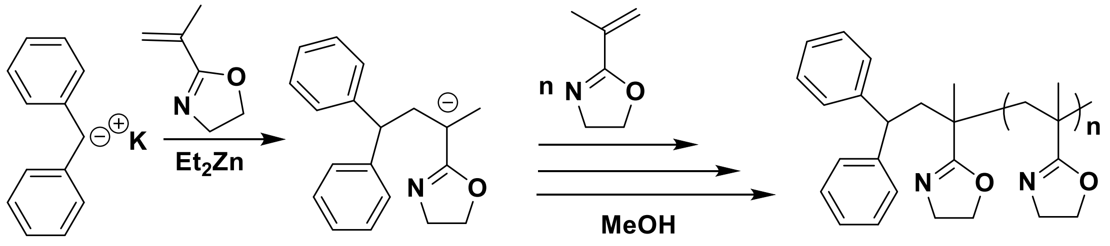
Several anionic polymerizations targeting different *M*Ws were carried out using the optimized reaction condition as shown in **Table 2** and **Scheme 2**. Well-defined polymers with molecular weights from 6,800 to 104,400 g/mol and low PDIs from 1.12 to 1.17 were synthesized successfully by controlling the molar ratios of the IPOx to DPM-K/Et_2Zn, and their SEC profiles are shown in **Figure 3**. The synthesis of PIPOx with very high molecular weight ($M_n > 100{,}000$ g/mol) is reported for the first time to, the best of our knowledge. The theoretical molecular weights (calcd M_n) are in good agreement with values from SEC, and a linear relationship between M_n and the feed ratio of monomer to initiation system is observed as shown in **Figure 3**.

Table 2. Living anionic polymerization of IPOx in THF at 0 °C using DPM-K in the presence of Et_2Zn.

run	IPOx	DPM-K[d]	Et_2Zn	Time	Yield[e]	M_n ($\times 10^{-3}$ g/mol)			PDI[b]
	mmol	mmol	mmol	h	%	calcd[a]	obsd[b]	obsd[c]	
1	8.57	0.0928	1.00	10	100	10.3	9.6	13.7	1.09
2	11.53	0.0756	1.32	10	100	18.7	16.2	20.9	1.13
3	11.54	0.0419	0.63	10	100	28.2	24.6	28.5	1.15
4	12.50	0.0323	0.47	15	100	43.0	38.0	50.3	1.15
5	15.83	0.0230	0.30	21	100	76.5	76.2	105.1	1.12
6	18.56	0.0190	0.30	24	100	108.6	104.4	133.2	1.17

[a] M_n(calcd)=(MW of IPOx)×[IPOx]×yield/[initiator]. [b] M_n(obsd) and PDI were determined by SEC with calibration using narrow polystyrene standard in DMF as eluent at 25°C. [c] M_n(obsd) was determined using light scattering detection in DMF at 25°C. The value of dn/dc is 0.01048 mL/g. [d] DPM-K: diphenylmethyl potassium. [e] Yield was calculated from the ^{1}H-NMR integration of corresponding peaks.

Scheme 2. Synthesis of PIPOx using DPM-K/Et_2Zn initiation system in THF at 0 °C.



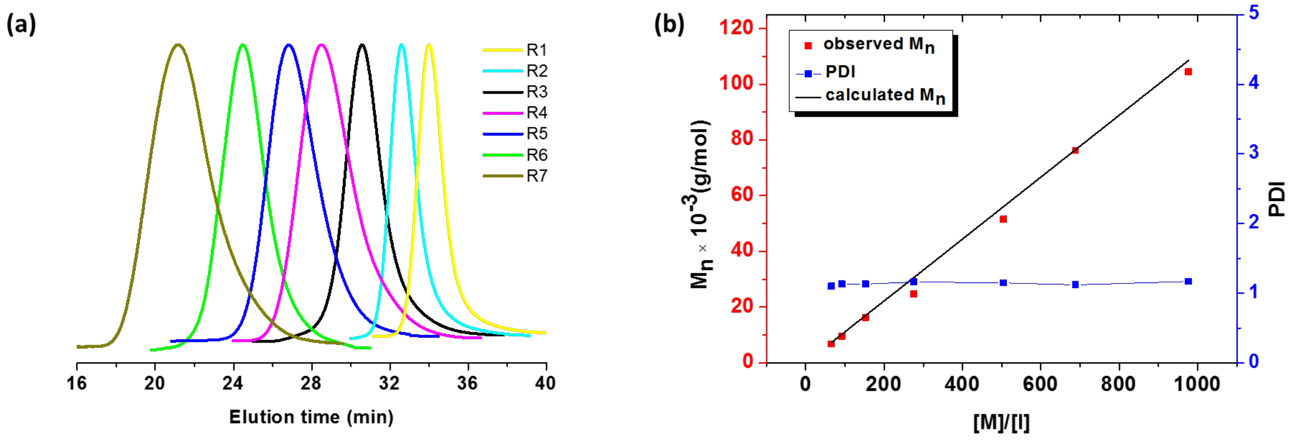


Figure 3. (a) SEC curves of homopolymer PIPOx. (R1: 6,800 g/mol (Run9 in Table1), R2: 9,600 g/mol, R3: 16,200 g/mol, R4: 24,600 g/mol, R5: 38,000 g/mol, R6: 76,200 g/mol and R7: 104,000

g/mol in Table 2). (b) Plot of molecular weight (M_n) and PDI vs feed ratio of IPOx monomer to DPM-K initiator.

The glass transition temperatures (T_g) of PIPOx homopolymers were characterized using DSC. **Figure 4a** shows DSC curves of six samples of PIPOx homopolymer with M_n ranging from 6,800 to 104,400 g/mole. The plot of T_g vs M_n plot (**Figure 4b**) shows that at high M_n (> 24,600 g/mol) there is no dependence of the T_g on M_n. However, as M_n decreases (<24,600 g/mol), there is a sharp drop of T_g from 173.1°C to 165.5 °C at M_n of 6,800 g/mol. As compared with other nitrogen-containing polymers, the T_g of PIPOx is much higher than the T_g of poly(*N*-isopropylacrylamide) (PNiPAM) (110 to 150 ºC)[30], similar to the T_g of poly(*N*-methacryloylazetidine) (PNMAA) (168°C)[31],and lower than that of poly(2-isopropenylbenzoxazole) (PIPBOz) (195°C)[6]. The thermal stability of PIPOx was examined by TGA and showed a single step decomposition at 294.09 °C for 5% weight loss (See **Figure S4** in Supporting Information).

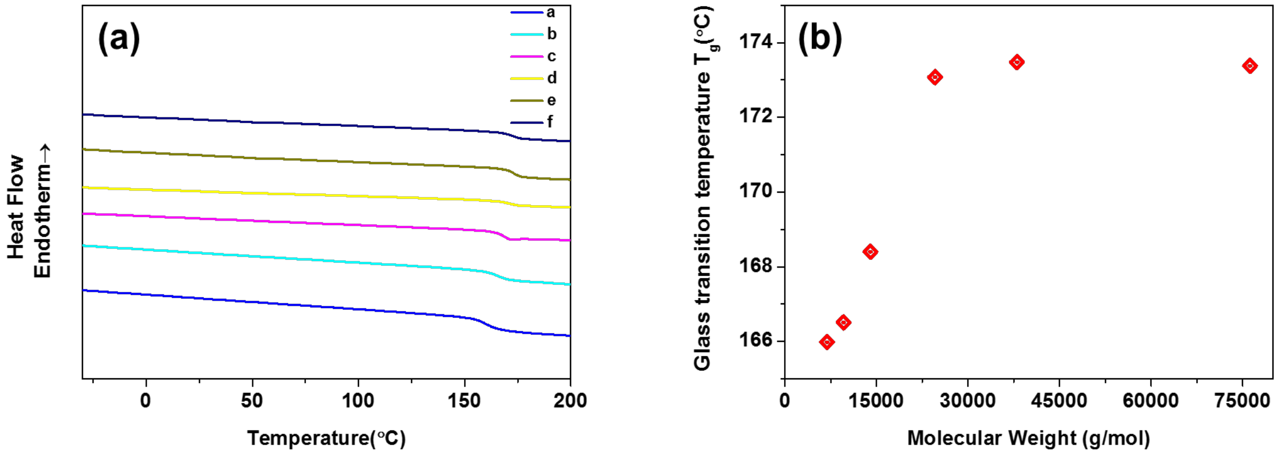


Figure 4. (a) DSC curves of PIPOx homopolymer with a) 6,800 g/mol (T_g=165.9 °C), b) 9,600 g/mol (T_g=166.5 °C), c) 16,200 (T_g=168.4 °C), d) with 24,600 (T_g=173.1 °C), e) 38,000 g/mol (T_g=173.5 °C), and f) 76,200 g/mol (T_g=173.4 °C) and (b) relationship between molecular weight and glass transition temperature.

Block copolymerization of IPOx with 2VP, MMA and St. A key advantage of sequential living anionic polymerization is the facile preparation of various precisely tailored block copolymers.

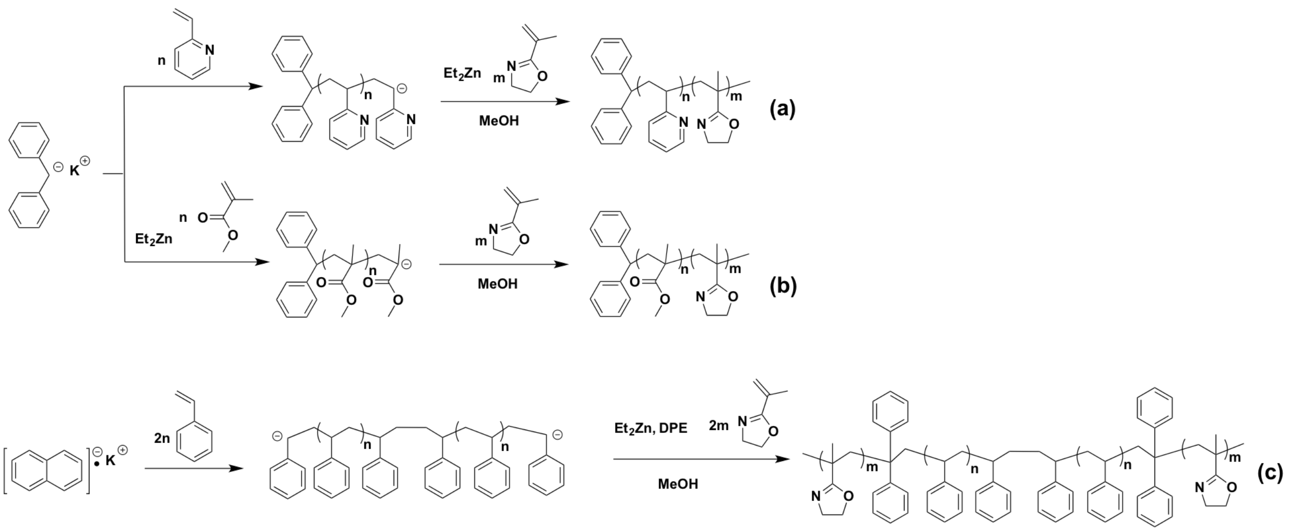
Block copolymerizations of IPOx with 2VP and MMA were thus conducted using the optimized initiation system of DPM-K/Et_2Zn in THF at 0 °C. The sequential block copolymerization of IPOx as the first monomer with 2VP and MMA as the second monomer only afforded homopolymers of PIPOx (Runs 2 and 4 in **Table 3**). This indicates that the nucleophilicity of living PIPOx is not strong enough to initiate 2VP and MMA, and therefore reactivity of the carbanions is in the order of living PIPOx < living PMMA < living P2VP. Sequential block copolymerization with IPOx as the second monomer thus yielded well-defined diblock copolymers of P2VP-*b*-PIPOx and PMMA-*b*-PIPOx (Runs 1 and 3 in **Table 3**), as shown in **Scheme 3a** and **3b**.

Table 3. Cross-over block copolymerization of IPOx with 2VP and MMA using DPM-K in the presence of Et_2Zn in THF.

run	Monomer1		Monomer2		DPM-K/Et_2Zn[c]	time	Temp.	M_n($\times 10^{-3}$g/mol)		
		mmol		mmol	mmol/mmol	h	°C	calcd[a]	obsd[b]	PDI[c]
1	2VP[c]	3.21	IPOx	9.50	0.115/1.81	2/11	-78/0[d]	12.1(2.9)	12.5(3.0)	1.16
2	IPOx	7.65	2VP	3.60	0.104/1.85	11/2	0/-78	11.8(8.1)	8.1(8.1)	1.12
3	MMA[c]	5.00	IPOx	19.6	0.123/1.85	1/10	-78/0	21.8(4.1)	22.5(4.9)	1.13
4	IPOx	12.25	MMA	5.00	0.112/2.01	10/1	0/-78	16.6(12.2)	9.5(9.5)	1.10

[a] M_n(calcd) = (MW of Monomer1) × [Monomer1]/[initiator] + (MW of Monomer2) × [Monomer2]/[initiator] × yield. [b] M_n(obsd) of the block copolymer and PDI of block copolymer were determined by SEC with calibration using narrow polystyrene standards in *N*,*N*-dimethylformamide (DMF) as eluent at 25 °C. [c] 2VP: 2-vinylpyridine, MMA: methylmethacrylate, DPM-K: diphenylmethyl potassium, and Et_2Zn: diethylzinc. [d] Polymerization was initiated at -78°C for 5 min and the temperature was then increased to 0 °C.

Scheme 3. The synthetic routine of (a) P2VP-*b*-PIPOx, (b) PMMA-*b*-PIPOx and (c) PIPOx-*b*-PS-*b*-PIPOx.



In addition, amphiphilic triblock copolymers of PIPOx-*b*-PS-*b*-PIPOx with different block compositions (PIPOx:PS:PIPOx = 25:50:25, 10:80:10 and 40:20:40) were synthesized via sequential living anionic polymerization using the bi-directional initiator of K-Naph with DPE in the presence of Et_2Zn as shown in **Scheme 3c**. The results of triblock copolymerizations are summarized in **Table 4**.

Table 4. Synthesis of PIPOx-*b*-PS-*b*-PIPOx triblock copolymers with different block ratios.

Run	St^d	IPOx	K-Naph^d	DPE/Et_2Zn^{d}	Time	Temp.	M_n($\times 10^{-3}$g/mol)				Block ratio
	mmol	mmol	mmol	mmol	min	°C	calcd^a	obsd^b	obsd^c	PDI^b	
1	14.40	14.67	0.087	0.230/1.040	40/720	-78/0^e	61.9	63.2	74.6	1.14	25:50:25
2	11.47	2.84	0.055	0.155/0.750	40/720	-78/0	54.9	76.7	60.9	1.17	10:80:10
3	3.84	15.28	0.065	0.222/0.910	40/720	-78/0	64.6	76.3	66.4	1.12	40:20:40

$^a M_n$(calcd) = (MW of Monomer1) × [Monomer1]/[initiator] + (MW of Monomer2) × [Monomer2]/[initiator]. $^b M_n$(obsd) and ^{b}PDI of block copolymer were determined by SEC with calibration using narrow polystyrene standards in DMF at 25 °C. M_n(obsd)^c was determined by light scattering. dn/dc of PS=0.16 ml/g ^{d}St: styrene, K-Naph: Potassium naphthalenide, DPE: 1,1-diphenylethylene, and Et_2Zn: diethylzinc. ^{e}Polymerization was initiated at -78 °C for 5 min and then the temperature was increased to 0 °C.

The successful sequential block copolymerization was proven by the shift of the SEC profile from homopolymer PS of 11,900 g/mol and PDI = 1.06 to PIPOx-*b*-PS-*b*-PIPOx of 76,300 g/mol and PDI = 1.12 (Run 3 in **Table 4**), as shown in **Figure 5a**. Moreover, the block ratio was determined by ^{1}H-NMR (**Figure b).** The successful synthesis of these block copolymers based on IPOx are the first reported via living anionic polymerization. Upon introducing the polystyrene block, the DSC profile of PIPOx-*b*-PS-*b*-PIPOx (f_{IPOx} = 0.5) showed two T_gs, 106.5 °C and 171.3 °C, corresponding to the T_g of PS and T_g of PIPOx, respectively, as shown in **Figure 6**.

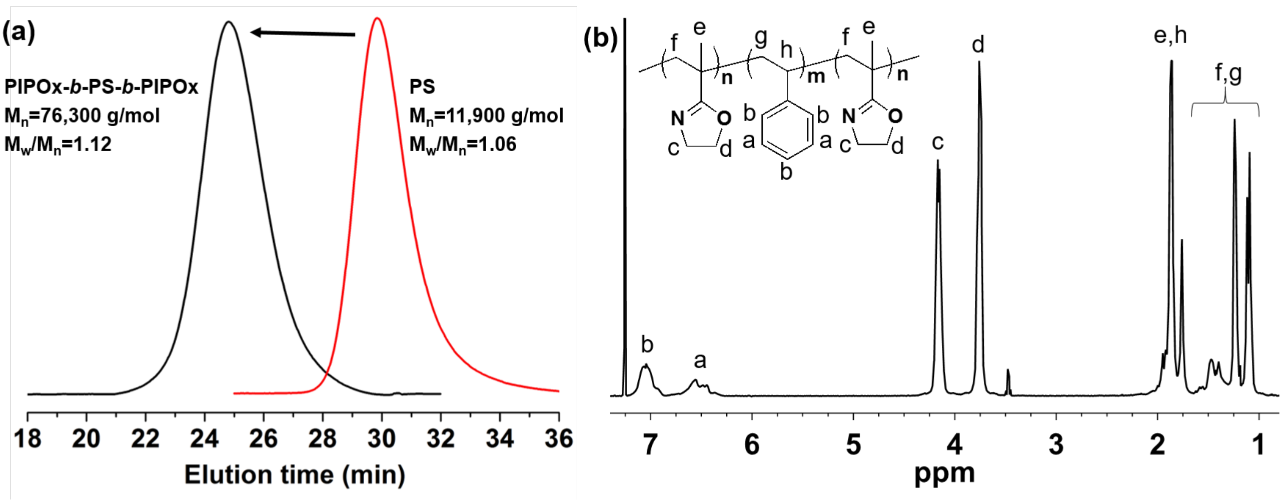


Figure 5. a) SEC profile of PS homopolymer (red curve) and PIPOx-*b*-PS-*b*-PIPOx (f_{IPOx} = 0.8) (black curve) (Run 7 in Table 3) and b) ^{1}H-NMR spectrum of corresponding PIPOx-*b*-PS-*b*-PIPOx (f_{IPOx} = 0.8).

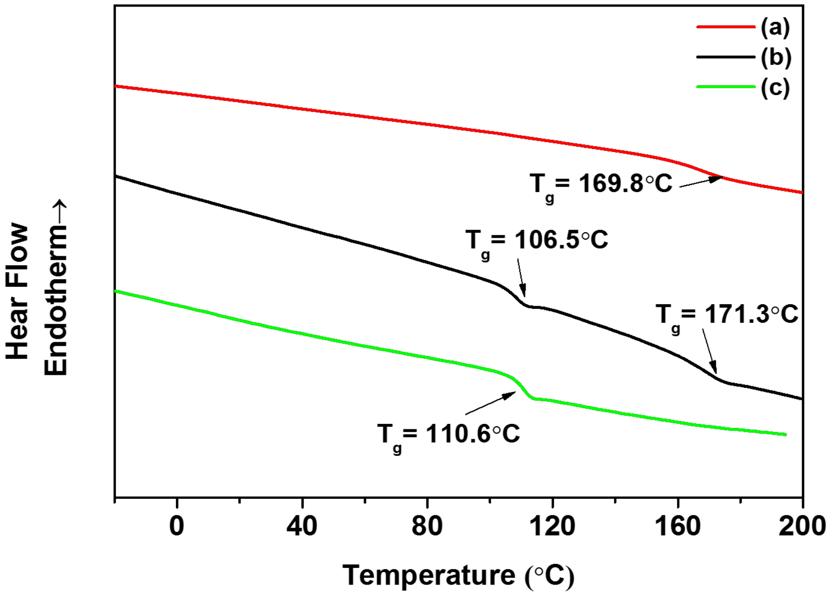


Figure 6. DSC profiles of (a) PIPOx-*b*-PS-*b*-PIPOx (f_{IPOx} = 0.8), (b) PIPOx-*b*-PS-*b*-PIPOx (f_{IPOx} = 0.5) and (c) PIPOx-*b*-PS-*b*-PIPOx (f_{IPOx} = 0.2).

Microphase separation of PIPOx-*b*-PS-*b*-PIPOx triblock copolymers. Block copolymers consisting of thermodynamically incompatible components usually show microphase separation behavior, with the particular morphology controlled by the properties of the polymers such as chemical composition and molecular weight, as well as by the solvent used for film casting, annealing temperature, *etc*.[32] The microphase separation behavior of the amphiphilic triblock copolymers PIPOx-*b*-PS-*b*-PIPOx (f_{IPOx} = 0.2) and PIPOx-*b* PS-*b*-PIPOx (f_{IPOx} = 0.5) were studied in the bulk. TEM images of PIPOx-*b*-PS-*b*-PIPOx (f_{IPOx} = 0.2) and PIPOx-*b*-PS-*b*-PIPOx (f_{IPOx} = 0.5) exhibited spherical (**Figure 7a**) and lamellar structure with long-range order (**Figure 7b**), respectively. In TEM images of **Figure 7a and b**, the dark domains represent iodine stained PIPOx block and the gray domains are PS blocks in the resulting block copolymer nanostructures. From molecular length consideration, the effective length of one vinyl unit is roughly 0.2 nm. The fully extended length of PIPOx unit in PIPOx-*b*-PS-*b*-PIPOx (f_{IPOx} = 0.2) is close to 22 nm and for the PS block the fully extended length is roughly 122 nm. TEM analysis using Gatan software[33] shows that the dark zone is not regular in shape, the average size is in range of 17± 2 nm and it is surrounded by 22 ± 1.5 nm gray zone of PS block, which is 18 percent of fully extended length of PS block. This indicates that the PS segments are bent due to their flexible coil nature to accommodate intrachain interactions among PIPOx chain (**Figure 7c**).

Owing to the short chain length of PIPOx, it not able the balance to long chain hydrophobic interaction of the PS blocks and makes first globular micelles and later these micelles aggregate due to high concentration and ultimately form networks as shown in **Figure 7c**. However, as the chain length of PIPOx in PIPOx-*b*-PS-*b*-PIPOx (f_{IPOx} = 0.5) is increased, a long-range lamellar structure is observed due to balance in interactions between PIPOx and PS blocks. Furthermore, detailed analysis of **Figure 7b**, the average domain size of PIPOx and PS is in range of 18.9 ± 2.0 for both blocks, which is roughly equal to 30 percent length of the fully extended chain lengths of the blocks as shown in **Figure 7c**. The fully extended length of the three blocks in PIPOx-*b*-PS-*b*-PIPOx (f_{IPOx} = 0.5) is roughly 60 nm.

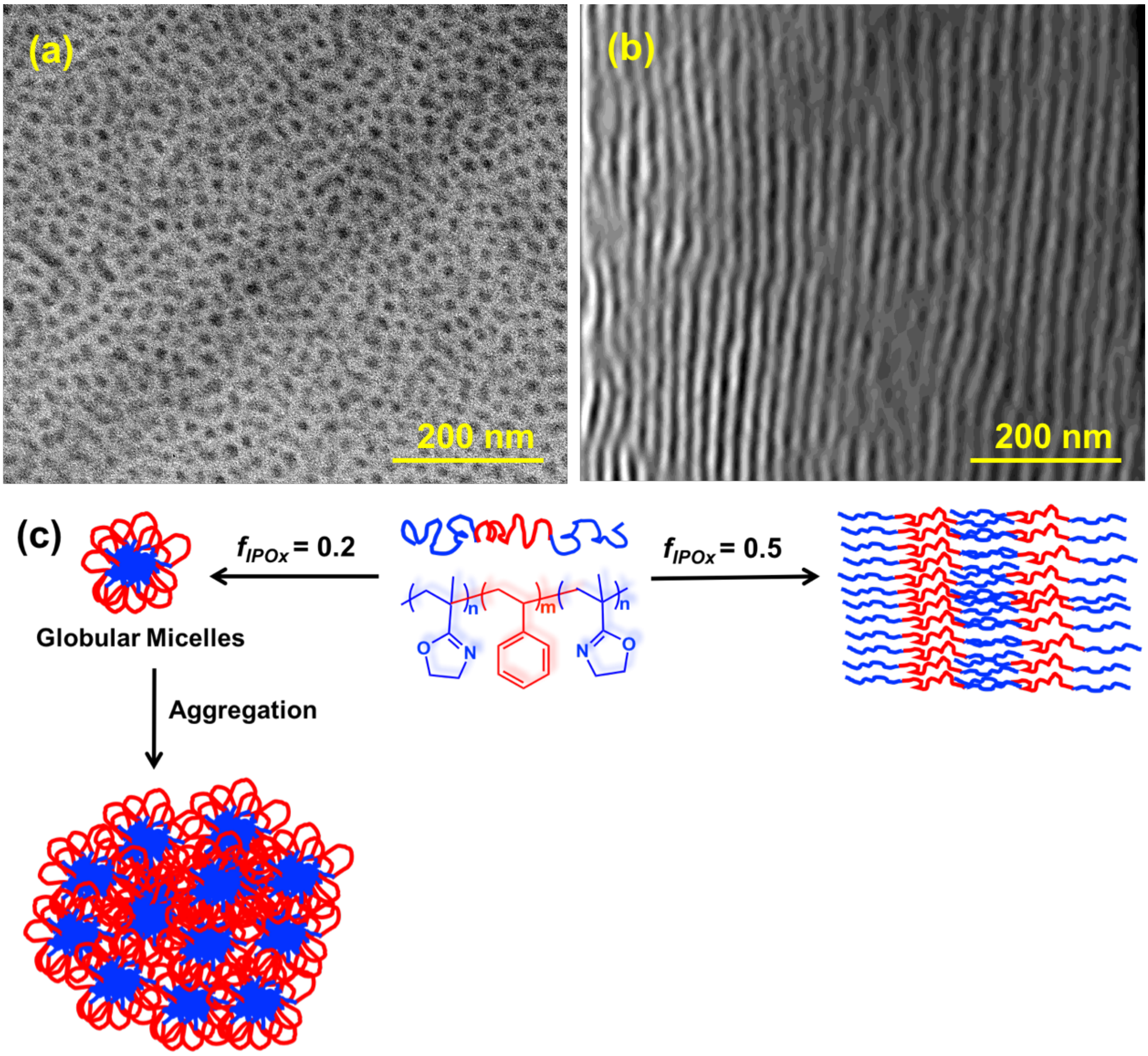


Figure 7. TEM images of PIPOx-*b*-PS-*b*-PIPOx triblock copolymers: (a) $f_{\text{IPOx}} = 0.2$ and (b) $f_{\text{IPOx}} = 0.5$. The dark regions represent IPOx domain stained with iodine vapor and the PIPOx domain size is 18.9 ± 2.0 nm, and (c) model for self-assembly into spherical and lamellar nanostructures.

CONCLUSION

We report a superior and effective synthetic method to prepare well-defined poly(2-isopropenyl-2-oxazoline) via living anionic polymerization through the use of high vacuum and glass blowing techniques. The optimized initiator system for living anionic homopolymerization of IPOx was found: DPM-K/Et_2Zn ($[Et_2Zn]/[\text{DPM-K}] = 20$), temperature: 0 °C, and time: 10 h. Well-defined PIPOx with MW as high as 100,000 g/mol and PDI of 1.15 was synthesized for the first time. The linear relationship between molecular weight and [monomer]/[initiator] ratio verified the living nature of these polymerizations. The living nature of this polymerization was further confirmed by block copolymer synthesis. The anionic polymerization reactivity order of IPOx < MMA < 2VP < St, attributed to the stability of carbanions, was established via block copolymerizations using IPOx as the first or second monomer. It was observed that films of amphiphilic triblock copolymers PIPOx-*b*-PS-*b*-PIPOx with $f_{\mathrm{IPOx}} = 0.2$ formed a spherical morphology while a lamellar structure was formed by PIPOx-*b*-PS-*b*-PIPOx with $f_{\mathrm{IPOx}} = 0.5$. Both systems exhibit good long-range order.

ASSOCIATED CONTENT

Supporting Information. Figures S1–S4 correspond to the synthesis and characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Darbre, T.; Reymond, J.-L. Peptide Dendrimers as Artificial Enzymes, Receptors, and Drug-Delivery Agents. *Accounts of Chemical Research* **2006,** *39*, 925-934.

(2) Koh, H.-D.; Kang, N.-G.; Lee, J.-S. Fabrication of an Open Au/Nanoporous Film by Water-in-Oil Emulsion-Induced Block Copolymer Micelles. *Langmuir* **2007,** *23*, 12817-12820.

(3) Koh, H.-D.; Kang, N.-G.; Lee, J.-S. Location Control of Au/Cds Nanoparticles in Block Copolymer Micelles. *Langmuir* **2007,** *23*, 11425-11429.

(4) Viegas, T. X.; Bentley, M. D.; Harris, J. M.; Fang, Z.; Yoon, K.; Dizman, B.; Weimer, R.; Mero, A.; Pasut, G.; Veronese, F. M. Polyoxazoline: Chemistry, Properties, and Applications in Drug Delivery. *Bioconjugate Chemistry* **2011,** *22*, 976-86.

(5) Culbertson, B. M. Cyclic Imino Ethers in Step-Growth Polymerizations. *Progress in Polymer Science* **2002,** *27*, 579-626.

(6) Ishizone, T.; Oka, N.; Hirao, A.; Nakahama, S. Anionic Polymerizations of 2-Vinylbenzoxazole and 2-Isopropenylbenzoxazole. *Macromolecules* **1996,** *29*, 528-534.

(7) Pack, D. W.; Hoffman, A. S.; Pun, S.; Stayton, P. S. Design and Development of Polymers for Gene Delivery. *Nature Reviews Drug Discovery* **2005,** *4*, 581-593.

(8) Kwon, G. S.; Forrest, M. L. Amphiphilic Block Copolymer Micelles for Nanoscale Drug Delivery. *Drug Development Research* **2006,** *67*, 15-22.

(9) Adams, M. L.; Lavasanifar, A.; Kwon, G. S. Amphiphilic Block Copolymers for Drug Delivery. *Journal of Pharmaceutical Sciences* **2003,** *92*, 1343-1355.

(10) Hoogenboom, R. Poly(2-Oxazoline)S: A Polymer Class with Numerous Potential Applications. *Angewandte Chemie International Edition* **2009,** *48*, 7978-7994.

(11) Tomalia, D.; Thill, B.; Fazio, M. Ionic Oligomerization and Polymerization of 2-Alkenyl-2-Oxazolines. *Polymer Journal* **1980,** *12*, 661-675.

(12) Zhang, N.; Pompe, T.; Amin, I.; Luxenhofer, R.; Werner, C.; Jordan, R. Tailored Poly(2-Oxazoline) Polymer Brushes to Control Protein Adsorption and Cell Adhesion. *Macromolecular Bioscience* **2012,** *12*, 926-936.

(13) Weber, C.; Neuwirth, T.; Kempe, K.; Ozkahraman, B.; Tamahkar, E.; Mert, H.; Becer, C. R.; Schubert, U. S. 2-Isopropenyl-2-Oxazoline: A Versatile Monomer for Functionalization of Polymers Obtained via RAFT. *Macromolecules* **2012,** *45*, 20-27.

(14) Zhang, N.; Salzinger, S.; Soller, B. S.; Rieger, B. Rare Earth Metal-Mediated Group-Transfer Polymerization: From Defined Polymer Microstructures to High-Precision Nano-Scaled Objects. *Journal of the American Chemical Society* **2013,** *135*, 8810-3.

(15) Reyes, F. T.; Malins, E. L.; Becer, C. R.; Kelland, M. A. Non-Amide Kinetic Hydrate Inhibitors: Performance of a Series of Polymers of Isopropenyloxazoline on Structure II Gas Hydrates. *Energy & Fuels* **2013,** *27*, 3154-3160.

(16) Zhang, J.; Liu, K.; Müllen, K.; Yin, M. Self-Assemblies of Amphiphilic Homopolymers: Synthesis, Morphology Studies and Biomedical Applications. *Chemical Communications* **2015,** *51*, 11541-11555.

(17) Changez, M.; Kang, N. G.; Lee, C. H.; Lee, J. S. Reversible and Ph-Sensitive Vesicles from Amphiphilic Homopolymer Poly(2-(4-Vinylphenyl)Pyridine). *Small* **2010,** *6*, 63-68.

(18) Changez, M.; Kang, N. G.; Lee, J. S. Uni-Molecular Hollow Micelles from Amphiphilic Homopolymer Poly(2-(4-Vinylphenyl)Pyridine). *Small* **2012,** *8*, 1173-1179.

(19) Hong, K.; Uhrig, D.; Mays, J. W. Living Anionic Polymerization. *Current Opinion in Solid State and Materials Science* **1999,** *4*, 531-538.

(20) Wang, W.; Schlegel, R.; White, B. T.; Williams, K.; Voyloy, D.; Steren, C. A.; Goodwin, A.; Coughlin, E. B.; Gido, S.; Beiner, M. High Temperature Thermoplastic Elastomers Synthesized by Living Anionic Polymerization in Hydrocarbon Solvent at Room Temperature. *Macromolecules* **2016,** *49*, 2646-2655.

(21) Candau, F.; Afchar-Taromi, F.; Rempp, P. Synthesis and Characterization of Polystyrene-Poly (Ethylene Oxide) Graft Copolymers. *Polymer* **1977,** *18*, 1253-1257.

(22) Ishizone, T.; Yanase, E.; Matsushita, T.; Nakahama, S. Controlled Anionic Polymerization of Methacrylonitrile with Diphenylmethylpotassium in the Presence of Triethylborane. *Macromolecules* **2001,** *34*, 6551-6553.

(23) Ji, H.; Farmer, B. S.; Nonidez, W. K.; Advincula, R. C.; Smith, G. D.; Kilbey, S. M.; Dadmun, M. D.; Mays, J. W. Anionic Synthesis of Epoxy End-Capped Polymers. *Macromolecular Chemistry and Physics* **2007,** *208*, 807-814.

(24) Kang, N.-G.; Changez, M.; Kim, M.-J.; Lee, J.-S. Effect of Biphenyl Spacers on the Anionic Polymerization of 2-(4′-Vinylbiphenyl-4-yl)Pyridine. *Macromolecules* **2014,** *47*, 6706-6714.

(25) Kang, N.-G.; Changez, M.; Lee, J.-S. Living Anionic Polymerization of the Amphiphilic Monomer 2-(4-Vinylphenyl)Pyridine. *Macromolecules* **2007,** *40*, 8553-8559.

(26) Uhrig, D.; Mays, J. W. Experimental Techniques in High-Vacuum Anionic Polymerization. *Journal of Polymer Science Part A: Polymer Chemistry* **2005,** *43*, 6179-6222.

(27) Whitney, S. E.; Rickborn, B. Substituted Oxazoles: Syntheses via Lithio Intermediates. *The Journal of Organic Chemistry* **1991,** *56*, 3058-3063.

(28) Varshney, S. K.; Hautekeer, J.; Fayt, R.; Jérôme, R.; Teyssié, P. Anionic Polymerization of (Meth) Acrylic Monomers. 4. Effect of Lithium Salts as Ligands on the "Living" Polymerization of Methyl Methacrylate Using Monofunctional Initiators. *Macromolecules* **1990,** *23*, 2618-2622.

(29) Baskaran, D. Strategic Developments in Living Anionic Polymerization of Alkyl(Meth) Acrylates. *Progress in Polymer Science* **2003,** *28*, 521-581.

(30) Hirano, T.; Okumura, Y.; Kitajima, H.; Seno, M.; Sato, T. Dual Roles of Alkyl Alcohols as Syndiotactic-Specificity Inducers and Accelerators in the Radical Polymerization of N-Isopropylacrylamide and Some Properties of Syndiotactic Poly (N-Isopropylacrylamide). *Journal of Polymer Science Part A: Polymer Chemistry* **2006,** *44*, 4450-4460.

(31) Fuchise, K.; Sakai, R.; Satoh, T.; Sato, S.-i.; Narumi, A.; Kawaguchi, S.; Kakuchi, T. Group Transfer Polymerization of N,N-Dimethylacrylamide Using Nobel Efficient System Consisting of Dialkylamino Silyl Enol Ether as an Initiator and Strong Brønsted Acid as an Organocatalyst. *Macromolecules* **2010,** *43*, 5589-5594.

(32) Bates, F. S. Polymer-Polymer Phase Behavior. *Science* **1991,** *251*, 898-905.

(33) Liu, Z.; Suenaga, K.; Harris, P. J.; Iijima, S. Open and Closed Edges of Graphene Layers. *Physical Review Letters* **2009,** *102*, 015501.

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2-Isopropenyl-2-Oxazoline: Well-defined Homopolymers and Block Copolymers via Living Anionic Polymerization

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