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PAPER

Well-defined High Refractive Index Poly(monothiocarbonate) with Tunable Abbe's numbers and Glass-transition Temperatures via Terpolymerization

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The synthesis of thermoplastics with high refractive index (*n*) and high Abbe's number (V_d) is rarely reported. This work describes well-controlled synthesis of a soluble poly(monothiocarbonate) with high *n* and V_d values by using carbonyl sulfide (COS) as sulfur resource. The alternating COS/cyclohexene oxide (CHO)/propylene oxide (PO) terpolymerization was well performed by using a tetradentate Schiff base chromium chloride complex (SalenCrCl) and bis(triphenylphosphoranylidene) ammonium chloride (PPNCl) as catalyst at 40 °C, yielding terpolymers with 100 % poly(monothiocarbonate) selectivity based on the ^{1}H NMR spectra. The turnover frequency (TOF) of the SalenCrCl/PPNCl catalyst system was 323 h^{-1} for COS/PO/CHO terpolymerization at 40 °C. The terpolymers possess number-average molecular weight (M_n) up to 22.3 kg/mol with narrow polydispersity index (PDI) of 1.16. These terpolymers exhibited high refractive indices (*n*) of 1.55-1.56. Of importance, by varying the feeding ratio of PO and CHO, V_d of the resulting terpolymers was adjustable from 32.1 to 43.1, and the glass-transition temperature (T_g) varied from 43.7 to 93.4 °C. Such poly(monothiocarbonate) might be used as optical plastics with tailored optical and thermal properties.

Introduction

As an alternative of the inorganic glass, optical plastics have been reported for decades of years. Poly(methyl methacrylate) (PMMA), polystyrene (PS) and aromatic polycarbonate (PC) are three typical optical plastics. However, these conventional optical plastics with relatively high refractive indices (*n*) generally have low Abbe's number (V_d).[1] For example, PS and PC have high *n* of 1.59 and 1.58, respectively, but low V_ds of only 31 and 30, respectively, which are the minimum of V_d value for applying as visual optical material (generally, Vd is 30-60). Because the polymeric materials with small V_ds have intense chromatic dispersion, PS and PC with aromatic structure are seldom applied to visual optical materials, such as eyeglass lenses. PMMA has a high V_d of 58 but relatively low *n* of 1.49. As a result, it is valuable to design and synthesize novel soluble thermoplastics with high and balanced *n* and V_d values. However, the synthesis of thermoplastics with high-*n* and high-V_d values was rarely reported.[2]

Aliphatic poly(thiocarbonate), as an analogue of polycarbonate, is expected to have better optical properties. However, to date, very few of poly(thiocarbonate)s are reported.[3-12] The condensation of dithiol with phosgene in the presence of sodium hydroxide was reported to obtain poly(dithiocarbonate). However, the use of phosgene is dangerous to the operator and the environment once it was released. Nozaki et al reported a pioneer work that the alternating copolymerization of carbon disulfide (CS_2) with episulfide was catalyzed by bis(triphenylphosphoranylidene) ammonium chloride (PPNCl) and N,N'-bis(3,5-di-tert-buty- lsalicylidene)-1,2-benzenediamino chromium-(III) chloride [(Salen)CrCl], affording a poly(trithiocarbonate) with high *n* of 1.78 (22 °C, cast film, determined by Abbe refractometer).[3] But the V_d of this polymer was not measured. The copolymerization of CS_2 with epoxide was catalyzed by either (Salen)CrCl/PPNCl system[4,5] or zinc-cobalt (III) double metal cyanide complex [Zn-Co(III) DMCC],[6,7] the resulting polymers contained various disordered thiocarbonate linkages due to the inevitable oxygen/sulfur exchange reaction. The sulfur content of these polymers was high, however, the optical properties of them were not provided. Well-defined poly(thiocarbonate)s could also be synthesized by the ring-opening polymerization of five or six-membered cyclic monothiocarbonate, dithiocarbonates and trithiocarbonates.[8-10] However, the reactivity of these cyclic compounds was quite low, and the preparation of these cyclic compounds was difficult.

Our group reported the first example of well-controlled synthesis of a poly (propylene monothiocarbonate) (PPMTC) from direct copolymerization of carbonyl sulfide (COS) with propylene oxide (PO) by using (Salen)CrCl/PPNCl system.[11] The PPMTC possessed high *n* of 1.63 (22 °C, cast film, Abbe refractometer), the glass transition temperature (T_g) of 22.4 °C and 5% weight loss temperature ($T_{d,5wt\%}$) of 125 °C. We also studied the copolymerization of COS with cyclohexene oxide (CHO) by using Zn-Co(III) DMCC,[12] the resulting poly-

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Electronic Supplementary Information (ESI) available: NMR spectrum, DSC and TGA results of PCHMTC. See DOI: 10.1039/x0xx00000x (cyclohexene monothiocarbonate) (PCHMTC) had small amounts of contaminated ether units and carbonate units due to the homopolymerization of CHO and the oxygen/sulfur exchange reaction. This copolymer still presented high *n* of 1.705 (20 °C, cast film, Abbe refractometer), as well as high T_g (112 °C) and $T_{d,5wt\%}$ (214 °C). However, both PPMTC and PCHMTC had low V_d values (16 and 30, respectively) that would cause intense chromatic dispersion, limiting their application.

According to the Lorentz-Lorenz equations,[2,13] *n* defines the relationship between the refractive index and individual parameters of the polymer structure, given by,

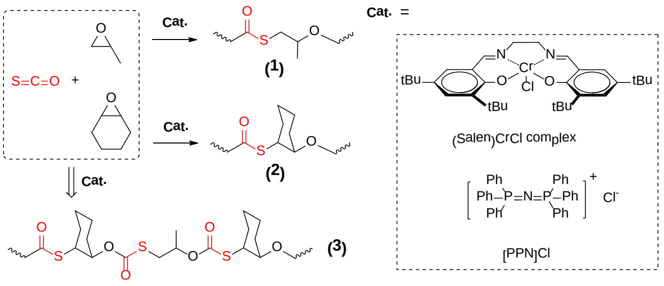
$$\mathbf{n} = \sqrt{\frac{1+2[R]/V_0}{1-[R]/V_0}} \qquad (1)$$

where [R] the molar refraction, and V_0 the molecular volume of the polymer repeat unit and ΔR the molar dispersion. V_d is defined as,

$$V_d = \frac{6n_d[R]}{(n_d^2+2)(n_d+1)[\Delta R]} \qquad (2)$$

According to the above equations, n_d (*n* value at wavelength 587.6 nm) and V_d are proportional to the molar refraction [R] that is proportional to the molecular polarizability. Generally, the higher *n* means that lower V_d, that is, a trade-off tendency is found between the *n* and V_d values for a polymer.[2] In equation (2), if the increase of [R]/[ΔR] could make up the decrease of *n*, V_d might be varied. For PO/COS copolymer with T-H linkages formed by selective attack of S to CH_2 site of PO,[11] the molecular polarizability of C-S bond was solely determined by the connection manner of COS with PO (Scheme 1), if another epoxide was randomly introduced into the PO/COS polymer, the chemical environment around C-S bond, i.e., the polarizability of C-S bond, will be changed depending on the structure change of the resulting terpolymer. As a consequence, the $[R]/V_0$ and [R]/[ΔR] values will vary, *n* and V_d values of the resulting terpolymer could be possibly tuned via changing the feeding ratio of PO/CHO (Scheme 1).

Aiming to verify the above hypothesis, we herein report the alternating copolymerization of COS/CHO and the terpolymerization of COS/CHO/PO catalyzed by the binary (Salen)CrCl/PPNCl catalyst (Scheme 1). It was found that the COS/CHO/PO terpolymers indeed exhibited improved *n* and V_d values in comparison with COS/CHO and COS/PO copolymers.



Scheme 1. The PO/COS copolymerization[11] and proposed CHO/COS copolymerization and CHO/PO/COS terpolymerization catalyzed by binary (Salen)CrCl/PPNCl catalyst.

Results and discussion

COS/CHO copolymerization was firstly investigated in detail. Because CHO is a symmetrical molecule, when it copolymerizes with COS, only one kind of repeating unit will be formed, as shown in Scheme 1. Binary (Salen)CrCl/PPNCl catalyst was employed to catalyze COS/CHO copolymerization with a [Cr]/[CHO] molar ratio of 1/1000 under various reaction conditions, as summarized in Table 1. Blank reactions (entries 1, 2 in Table 1) indicated that the sole employment of (Salen)CrCl or PPNCl failed to catalyze the copolymerization. The combination of (Salen)CrCl with PPNCl could effectively catalyze COS/CHO copolymerization (entries 4-10 in Table 1). The chain structure of the resulting copolymer was analyzed by nuclear magnetic resonance (NMR) spectroscopy. Figure 1 shows the ^1H NMR spectrum of the typical COS/CHO copolymer (entry 6 in Table 1). Peak **a** at 4.94-4.87 ppm and peak **b** at 3.51-3.46 ppm were ascribed to the two single methine protons connecting with O and S atoms of the monothiocarbonate unit [-SC(=O)O-], respectively. And the integral area of peaks **a** and **b** was equal and consistent with the unit structure. Unlike early reported COS/CHO and CS_2/CHO copolymerization,[7,12] no other linkages such as ether, carbonate, dithiocarbonate and trithiocarbonate linkages were observed, indicating a completely alternating structure. That is, the O/S exchange reaction was totally prohibited. In correspondence, the carbonyl region in ^{13}C NMR spectrum (Figure 2) of the copolymer only presented the resonance peak for the monothiocarbonate linkage, which split into two peaks at 169.0 ppm and 168.7 ppm and could be ascribed to the isotactic and syndiotactic chain structure,[12] respectively.

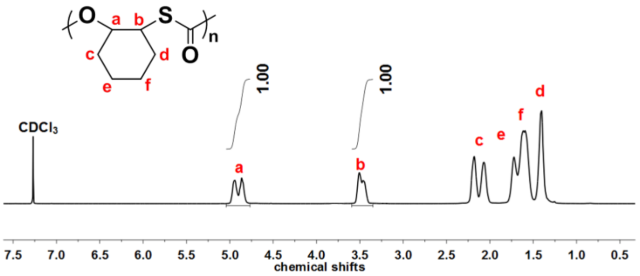


Figure 1. ^1H NMR spectrum for the copolymer of the entry 6 in Table 1.

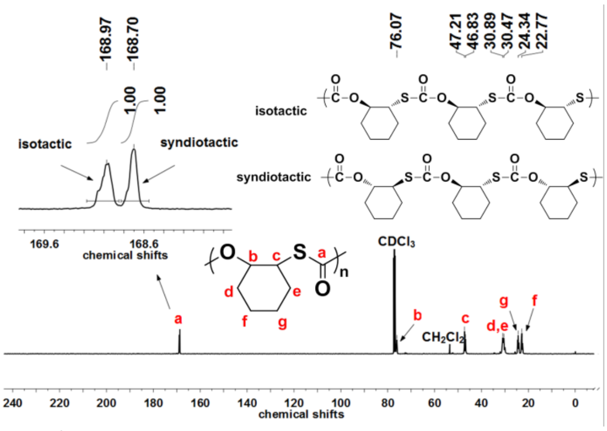
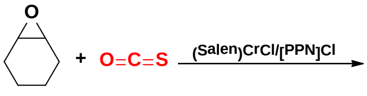


Figure 2. ^{13}C NMR spectrum for the copolymer of the entry 6 in Table 1.

Table 1. CHO/COS copolymerization results [a]



Entry	n_{COS}/n_{CHO}	T (°C)	Copolymer Selectivity[b]	CHO Conv.[b] (%)	TOF[c] (h^{-1})	PCHMTC linkages[b] (%)	O/S ER product[d]	M_n[e] (kg/mol)	PDI[e] (M_w/M_n)
1[f]	2:1	40	-	-	-	-	-	-	-
2[g]	2:1	40	-	-	-	-	-	-	-
3	2:1	0	-	-	-	-	-	-	-
4	2:1	20	>99	77.8	260	99	N.F	11.3	1.10
5	2:1	30	>99	89.1	297	99	N.F	12.2	1.09
6	2:1	40	>99	97.7	325	99	N.F	12.3	1.10
7	2:1	50	>99	92.3	307	99	N.F	12.3	1.10
8	2:1	60	>99	76.8	257	99	N.F	9.2	1.57
9	1:1	40	>99	74.9	250	99	N.F	8.9	1.10
10	4:1	40	>99	88.4	295	99	N.F	12.5	1.13

[a] The reaction was performed in neat CHO (2.0 mL, 19.7 mmol; (Salen)CrCl/[PPN]Cl, catalyst/CHO = 1/1000, all in molar ratio) in a 10 mL autoclave for 3 h. [b] Determined by ^1H NMR spectroscopy. [c] TOF = Turnover frequency of CHO to products. (Mol epoxide consumed)/(mol Cr h). [d] Determined by using ^{13}C NMR spectroscopy. N.F = not found, and F = found. [e] Determined by gel permeation chromatography in THF, calibrated with polystyrene standards. [f] Only (Salen)CrCl was used. [g] Only [PPN]Cl was used.

The effects of reaction temperature and CHO/COS feeding ratio were investigated. The results were shown in Table 1. Notably, cyclic products were not observed from 20 to 60 °C. The optimized condition was 40 °C and with a feeding ratio of 2/1 for COS/CHO (entry 6 in Table 1). The turnover frequency (TOF) on this condition reached 325 h^{-1} with a CHO conversion of 98%. However, TOF decreased with increasing reaction temperature from 40 to 60 °C. Moreover, both low and high COS/CHO loading ratio resulted in lower CHO conversion (entries 9, 10 in Table 1). The obtained COS/CHO copolymers showed M_ns of 11.3-12.5 kg/mol with narrow polydispersity index (PDI) of 1.09-1.13. To the best of our knowledge, it is the first report for synthesizing fully alternating poly(cyclohexene monothiocarbonate) (PCHMTC).

The obtained PCHMTC was a highly transparent colorless amorphous solid when it was casted into film. It was highly soluble in many common organic solvents such as dichloromethane, chloroform, tetrahydrofuran, dimethyl sulphoxide, etc. The refractive index of PCHMTC was measured to be 1.548 by Spectroscopic Ellipsometer.[14] It was close to those of PS and PC (1.58-1.59) and higher than that of PMMA (1.49). Therefore, PCHMTC could be classified into polymers with relatively high refractive index. V_d of PCHMTC was 32.2 and not high enough to be a visual optical material. Moreover, T_g of PCHMTC (entry 6 in Table 1) was 114.6 °C (Figure S2) which was higher than those of PS and PMMA. $T_{d,5wt\%}$ of the pure PCHMTC (entry 6 in Table 1) were 244 °C (Figure S3) that could meet the requirement for processing and application. However, such PCHMTC was brittle, which limited its application as a material.

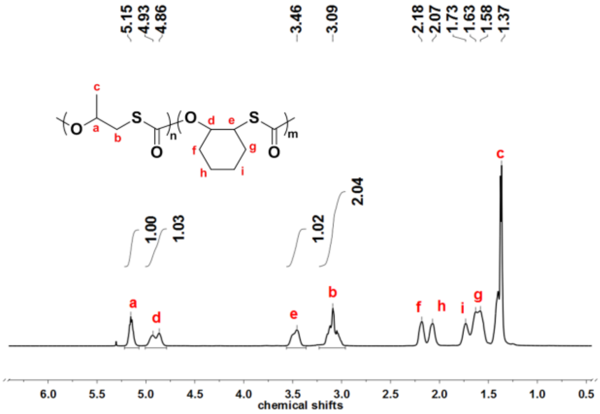


Figure 3. ^1H NMR spectrum for the copolymer of entry 3 in Table 2.

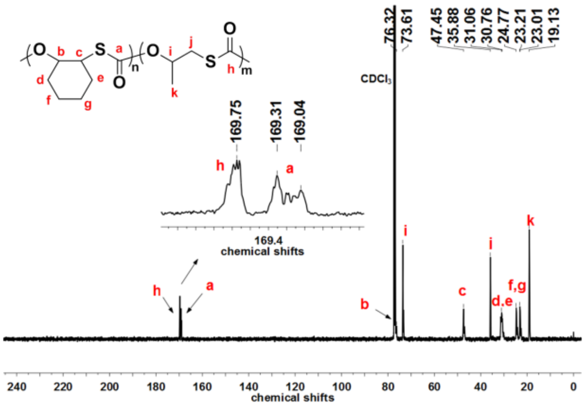
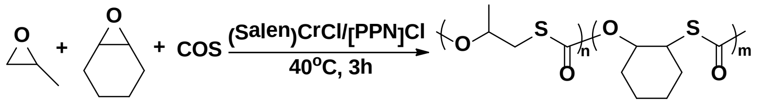


Figure 4. ^{13}C NMR spectrum for the copolymer of entry 3 in Table 2.

Table 2. COS/CHO/PO terpolymerization result [a].



Entry	PO/CHO (molar ratio)	TOF[b] (h^{-1})	CHMTC Linkages[c] (%)	M_n[d] (kg/mol)	PDI[d] (M_w/M_n)	T_g[e] (°C)	$T_{d,5wt\%}$[f] (°C)	n_d[g]	V_d[h]
1	1/0	310	0	21.9	1.47	22.4	137.3	1.524	15.9
2	3/1	320	27.5	22.1	1.16	43.7	226.7	1.552	32.1
3	1/1	323	50.7	22.3	1.16	55.9	236.1	1.556	43.1
4	1/3	321	83.1	21.7	1.14	93.4	237.3	1.554	36.9
5	0/1	325	99	12.3	1.10	114.6	243.9	1.548	32.2

[a] The reaction was performed in the neat mixture of PO and CHO (28.6 mmol in total; (Salen)CrCl/[PPN]Cl = 1/1, catalyst/epoxides = 1/1000) in a 10 mL autoclave at 40 °C for 3 h. [b] TOF = Turnover frequency of epoxides to products. (Mol epoxide consumed)/(mol Cr h). [c] Determined by ^1H NMR spectroscopy. [d] Determined by gel permeation chromatography in THF, calibrated with polystyrene standards. [e] Determined by DSC. [f] Temperature at polymer decomposition of 5% in mass fraction measured by TGA. [g] n_d is the refractive index, determined by Spectroscopic Ellipsometer. [h] V_d is Abbe number. The Abbe number was calculated according to the following equation: $V_d = (n_d-1)/(n_F-n_C)$, where n_C, n_d, and n_F are the refractive indices of the polymer film at 656.3, 587.6, and 486.1 nm, respectively.

We expected to improve the V_d value and mechanical property via introducing PO as the third monomer.

The COS/CHO/PO terpolymerization was then carried out at 40 °C with the PO/CHO molar ratio of 3/1, 1/1 and 1/3, respectively. M_ns of the resulting terpolymers were 21.7-22.3 kDa with narrow PDIs of 1.14-1.16, as listed in Table 2 (entries 2-4). Only two monothiocarbonate units were observed in the ^1H and ^{13}C NMR spectra (Figure 3, 4), and the percentage of two monothiocarbonate units was estimated to be 100% based on the ^1H NMR spectrum. This terpolymerization exhibited 100% selectivity for monothiocarbonate linkages over other linkages or any cyclic products.

The percentage of the CHO/COS linkages in the terpolymer increased with increasing the CHO/PO feeding ratio (entries 2-4 in Table 2). Moreover, the differential scanning calorimetry (DSC) analysis and thermogravimetry (TG) results showed that COS/CHO/PO terpolymers had one T_g (Figure S4) and one thermolysis peak (Figure S5-S7), indicating that the resulting terpolymer possessed a random structure, rather than a diblock polymer, or a blend of two polymers. T_g of the terpolymer was adjustable from 43.7 to 93.4 °C by tuning the feeding ratio of CHO/PO. T_g was approximately proportional to the percentage of CHO/COS linkage (Figure 5) in the terpolymer. $T_{d,5wt\%}$ of the resulting polymer was significantly enhanced with increasing CHO loading in comparison with that of COS/PO copolymer. As shown in Figure 5, when 27.5 mol % CHMTC unit was introduced into the terpolymer, $T_{d,5wt\%}$ of the terpolymer increased from 137 °C to 227 °C. The obtained terpolymer was a highly transparent and colorless solid, which could be dissolved into common organic solvents, such as dichloromethane, chloroform, tetrahydrofuran, dimethyl sulphoxide. The dissolution of terpolymer in common solvents made it easy to be processing.

The distribution of the refractive indices of the obtained copolymers and terpolymers in the wavelength range of 400-800 nm were shown in Table 2 and Figure 6. The n_d (i.e., the refractive index at 587.6 nm) of the COS/CHO copolymer was 1.548 and higher than that of COS/PO copolymer (1.524) because of the aliphatic ring in the backbone of COS/CHO copol-

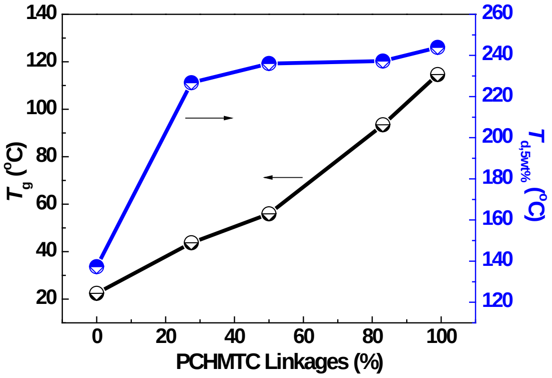


Figure 5. Plots of the T_g (left) and $T_{d,5wt\%}$ (right) versus PCHMTC linkages percentages in the COS/CHO/PO terpolymers.

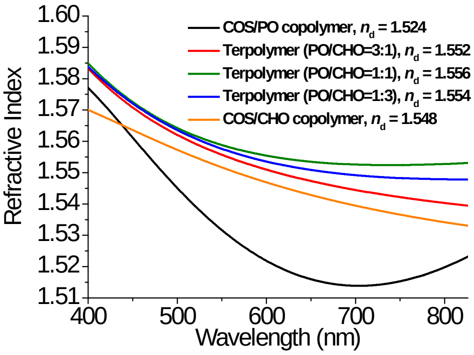


Figure 6. The variation of the refractive indices (n) (entries 1-5 in Table 2) via the wavelength from 400 to 800 nm. (n_d is refractive index at wavelength 587.6 nm)

ymer. As shown in Figure 6, the refractive index of COS/PO copolymer changed very dramatically along with the wavelength, which indicated the chromatic dispersion of this polymer was very severe, and its Abbe number (V_d) was calculated to be 15.9. The n_ds of the COS/CHO/PO terpolymers maintained at a high value (1.552-1.556), and V_d values were calculated to be 32.1-43.1.

Of interest, the terpolymer from equivalent PO/CHO feeding ratio exhibited a maximum V_d of 43.1. In this terpolymer, because of random terpolymerization of three monomers, maximum amounts of the COS/CHO/PO linkages were generated, leading to the maximum increase of the polarizability of C-S bond and thus the molar refraction [R] when PO/CHO feeding ratio was 1. Here, n_ds of the terpolymers were slightly higher than that of CHO/COS copolymer because the relationship of n_d is proportional to the square root of $[R]/V_0$ based on equation (1). While V_ds of the terpolymers with 50.7% and 83.1% COS/CHO linkage content (entries 3 and 4 in Table 2) were 43.1 and 36.9, respectively and higher than those of pure COS/CHO copolymer (32.2), indicating that the increase of [R] had decisive influence on V_ds based on equation (2). Note that the terpolymer of entry 3 in Table 2 had n_d of 1.556 and V_d of 43.1 was more suitable to apply as visual optical material in comparison with COS/PO copolymer and COS/CHO copolymer. The COS/CHO/PO terpolymer had a good balance of optical and thermal properties, making it a potential optical material.

Conclusions

In conclusion, fully alternating COS/CHO copolymers and COS/CHO/PO terpolymers have been synthesized from COS and CHO and/or PO by binary (Salen)CrCl/PPNCl catalyst. These polymers exhibited high refractive index and good thermal property, and COS/PO/CHO terpolymers had adjustable optical and thermal properties depending on the PO/CHO feeding ratios. Thanks to its good solubility, the terpolymer might be a new applicable optical material. Of significance, random terpolymerization of COS and different epoxides is an effective method to promote the optical property.

Experimental Section

Materials

All manipulations involving air- and/or moisture-sensitive compounds were carried out in a glove box under dry argon atmosphere or with the standard Schlenk technique under dry argon. Cyclohexene Oxide (CHO) and propylene oxide (PO) were distilled under a nitrogen atmosphere after drying over CaH_2. Carbonyl sulfide (COS) (99.5%) was purchased from the Mixed Gases Company of Hangzhou New Century and used as received. All the solvents used were distilled under a nitrogen atmosphere from CaH_2 prior to use. Most of other reagents were used without further purification unless otherwise specified.

Characterization

^1H and ^{13}C nuclear magnetic resonance (NMR) spectra of the polymers were recorded on a Bruker Advance DMX 400-MHz spectrometer. Chemical shift values were referenced to TMS as internal standard at 0.0 ppm for ^1H NMR (400 MHz) and against $CDCl_3$ at 77.16 ppm for ^{13}C NMR (125 MHz). Molecular weights and molecular weight distributions of polymers were determined with a PL-GPC220 chromatograph (Polymer Laboratories Ltd.) equipped with an HP 1100 pump from Agilent Technologies. The GPC columns were eluted with THF at 1.0 ml/min at 40 °C. The sample concentration was 0.5 wt. % and the injection volume was 50 µL. Calibration was performed using monodisperse polystyrene standards covering the molecular weight range from 580 to 460,000 Da. Infrared spectra were measured by using a Brucker Vector 22 FT-IR spectrophotometer.

The glass transition temperature (T_g) of the polymer was determined by differential scanning calorimetry (DSC) on a TA DSC-Q200 instrument. The sample was heated in two cycles from room temperature to 130 °C at a rate of 5 °C /min in a nitrogen atmosphere. T_g was determined from the second run. Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer Pyris 1 instrument under an N_2 atmosphere at a heating rate of 10 °C/min from room temperature to 400°C. Samples for thermal analyses were all purified. The refractive index (n) was measured by Spectroscopic Ellipsometer, the copolymer was dissolved in CH_2Cl_2 (10 mg/mL) and then spin-coated at 3000 rpm on a silicon wafer for 50 s, then the coated film was measured by Spectroscopic Ellipsometer, the thicknesses of the prepared thin films are in the range of 300-800 nm.

Representative Procedure for the Copolymerization of Cyclohexene Oxide (CHO) with COS.

The copolymerization of CHO/COS was performed in a 10 ml autoclave equipped with a magnetic stirrer and a barometer. *N,N'*-Bis (3,5-di-*tert*-butylsalicylidene)-1,2-ethylenediamino chromium(III) chloride [(Salen)CrCl] was synthesized according to the literature method. The (Salen)CrCl complex (11.4 mg, 19.7×10^{-3} mmol), PPNCl (11.3 mg, 19.7×10^{-3} mmol), cyclohexene oxide (CHO) (2.00 ml, 19.7 mmol) were transferred into the autoclave, which was completely dried in advance. The autoclave was pressurized to appropriate pressure with COS, the reaction mixture was stirred at a specified temperature for 3 h. After copolymerization, the autoclave was cooled down and the pressure was slowly vented. A sample of crude product was sent to ^1H NMR analysis. The mixture was dried in vacuum at 100 °C for isolating the unreacted reactants and then weighed to calculate the productivity of this copolymerization. Afterward, an aliquot was taken from the resulting crude product for a ^1H NMR spectroscopy to determine the ratio of copolymer/cyclic product. Afterwards, the crude product was dissolved in CH_2Cl_2 (5 ml) and precipitated from methanol (100 ml) for 3 or more times. White precipitate was collected and dried in vacuum at 70 °C to constant weight. The obtained copolymer was analyzed by ^1H NMR, ^{13}C NMR, FT-IR spectroscopy and GPC.

Representative Procedure for CHO/PO/COS Terpolymerization

For a typical terpolymerization, the terpolymerization of CHO/PO/COS was performed in a 10 ml autoclave equipped with a magnetic stirrer and a barometer. The (Salen)CrCl complex (11.4 mg, 19.7×10^{-3} mmol), PPNCl (11.3 mg, 19.7×10^{-3} mmol), cyclohexene oxide (CHO) (1.00 ml, 9.85 mmol) and propylene oxide (0.7 ml, 9.85 mmol) were transferred into the autoclave, which was completely dried in advance. The autoclave was pressurized to appropriate pressure with COS, the reaction mixture was stirred at a specified temperature for 3 h. After copolymerization, the autoclave was cooled down and the pressure was slowly vented. A sample of crude product was dissolved in dichloromethane and sent to ^{1}H NMR analysis. The mixture was dried in vacuum at 100°C for isolating the unreacted reactants and then weighed to calculate the productivity of this copolymerization. An aliquot was taken from the resulting crude product for a ^{1}H NMR spectroscopy to determine the ratio of copolymer/cyclic product. Afterwards, the crude product was dissolved in CH_2Cl_2 (5 ml) and precipitated from methanol (100 ml) for 3 or more times. White precipitate was collected and dried in vacuum at 70 °C to constant weight. The obtained copolymer was analyzed by ^{1}H NMR, ^{13}C NMR, FT-IR spectroscopy and GPC.

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14 This *n* value measured from Spectroscopic Ellipsometer is generally lower than that from Abbe refractometer, for example, for the PCHMTC, *n* was measured 1.705 from Abbe refractometer, see ref 12, but measured 1.548 from Spectroscopic Ellipsometer. The data from Spectroscopic Ellipsometer is more accurate than Abbe refractometer, it can offer the *n* values of a material varies along with different wavelength of the incident light, you can exactly find the n value at specific wavelength. And the Abbe number can also be accurately calculated.