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Synthesis and Purification of Tunable High Tg Electro-Optical Polymers by Ring Opening Metathesis Polymerization

by Robert H. Lambeth, Joseph M. Dougherty, Joshua A. Orlicki, Adam M. Rawlett, Robert C. Hoffman, Timothy Pritchett, and Andrew G. Mott

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14. ABSTRACT

This report summarizes efforts to date toward preparing electro-optical polymer by ring opening metathesis polymerization. Initial work involved preparing model electro-optical polymers with tunable glass transitions. Random copolymerization of a norbornene ester tethered to E-O chromophore Disperse Red 1 (DR1) with various levels *exo*-*N*-Phenylnorbornene-5,6-dicarboxamide (NDI) and 5-carbomethoxy-2-norbornene produced materials with controlled T_gs. The T_g could be varied from 89 to 189 °C by modifying the feed ratio of the 3 monomers enabling materials to be produced according to desired processing conditions. The polymers were tested for electro-optical activity but displayed very little or no alignment along an electric field. The lack of activity is potentially the result of residual polymerization catalyst remaining in the final polymer product. To probe this further, a comprehensive investigation was performed to discover purification methods capable of reducing residual catalyst to acceptable levels. Initially, baseline levels were established for polymer purified via "traditional" methods involving multiple precipitations. The residual catalyst levels ranged from 240 to 140 ppm depending on the number precipitations. Several different strategies were employed to further reduce the trace metal remaining in the final polymer product. The first strategy involved the use of catalyst modifiers and various adsorbents. None of the methods explored reduced the catalyst level below 100 ppm while significantly reducing the yield of polymer due to adsorption of the polymer. The second strategy involved the use of heterogeneous functionalized particles to scavenge the catalyst from the solution. Filtration of the particles followed by precipitation produced polymers with 10–60 ppm residual catalyst, depending on the type of particle used, surface functional groups, and number of equivalents. The third strategy used small organic molecules that could coordinate to the metal species and modify the solubility of the catalyst, facilitating partitioning of the catalyst into the precipitation solvent. Several types of molecules with varied functionality reduced the residual catalyst level to 30–120 ppm, depending on the loading. Reducing the amount of trace catalyst significantly improved the oxidative stability of the polymer.

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ROMP, electro-optical polymers

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1. Introduction

Organic/polymer electro-optical (E-O) materials have been heavily studied in recent years due to their potential use in high speed photonic devices (*1*). Compared to their inorganic counterparts, polymeric E-O materials offer significant advantages including: faster switching speeds, tunability, and processability (*2*). E-O properties arise from the non-centrosymmetric alignment of non-linear optical (NLO) chromophores during application of an electric field. One of the challenges in preparing materials for practical applications involves preventing decay of the poling-induced order during device operation (*3*). This can be achieved by incorporating the E-O chromophores into high glass-transition (T_g) polymers either as a guest or by covalent attachment. Covalent attachment is generally preferred as the motion of the chromophores is more restricted and phase separation from the matrix is not an issue (*4*). Covalent attachment can be achieved either by post-polymerization modification of a functionalized polymer backbone or direct polymerization of a chromophore containing monomer. Post-polymerization modification enables the incorporation of different chromophores with constant molecular weight. However, the procedure can be difficult to quantify and reproduce in terms of the number of chromophores incorporated per chain and their distribution along the backbone (*5*). In certain cases, the chemistry to couple the chromophore to backbone is incompatible with chromophore itself. Direct polymerization of a chromophore containing monomer is easier to quantify and reproduce and requires less synthetic steps. However, many of the materials prepared in this regard require either demanding reaction conditions unsuitable for the E-O chromophores and produce polymers with broad molecular weight distributions (*6, 7*). Thus, preparation of thermally stable E-O materials via direct polymerization of chromophore containing monomers under mild reaction conditions is highly desirable. Ring opening metathesis polymerization (ROMP) is an attractive alternative to other modes of polymerization because well-defined, high molecular weight polymers can be obtained under mild reaction conditions with excellent functional group tolerance (*8*). Thus, ROMP would be a viable route to directly produce E-O polymers where the desired chromophore is incompatible with other polymerization methods.

Another important factor to consider is the processing and poling conditions of the material produced. In general, the poling induced order of the chromophores is better preserved with higher T_g. However, with higher T_g, the material becomes more difficult to process and thermal stability of the chromophores itself is an issue. Such constraints could limit the temperature range over which the materials would be applicable and necessitates control over the T_g. Varying comonomer feed ratios is a convenient method to control T_g and is easily employed in ROMP. In this report, we explain the synthesis, characterization, and purification of tunable high T_g E-O polymers by ROMP.

2. Experimental

General Methods and Materials. All solvents and reagents were purchased from Aldrich and used as received. Compounds **2**, **3**, **4**, 4-(dimethylamino) pyridinium 4-toluenesulfonate (DPTS) and *cis*-5-norbornene-*exo*-2,3-carboxylic anhydride were prepared according to the literature (*9–13*). ^{1}H NMR and ^{13}C NMR data were recorded on a Bruker 600 MHz instrument. All chemical shifts are reported in ppm relative to residual $CHCl_3$ or DMSO. Coupling constants (*J*) are expressed in hertz (Hz). The molecular weight and polydispersity of the polymers was estimated in THF at rt with a Waters 515 HPLC pump, Thermo Separations Products AS300 autosampler, Waters 2487 Dual wavelength absorbance detector, Wyatt Optilab DSP refractive index detector, Wyatt Dawn EOS MALLS detector, and two Polymer Laboratories PLgel 5 µm mixed D columns at a flow rate of 1.0 mL/min. Glass-transitions were obtained on a TA Instruments DSCQ1000 with a heat-cool-heat cycle from 25 to 250 °C at 10 °C/min.

2-(ethyl(4-((E)-(4-nitrophenyl)diazenyl)phenyl)amino)ethyl bicyclo[2.2.1]hept-5-ene-2-carboxylate (1). 5-norbornene-2-carboxylic acid (2.02 g, 15.94 mmol), Disperse Red 1 (5.51 g, 17.52 mmol), and DPTS (0.50 g, 1.59 mmol) were dissolved in CH_2Cl_2 (100 mL) and cooled in an ice bath. In a separate flask, DCC (3.94 g, 19.12 mmol) was dissolved in CH_2Cl_2 (25 mL) and transferred via cannula to the above mixture. The reaction mixture was allowed to gradually warm to rt and was stirred overnight (~18 h). The reaction mixture was filtered by vacuum filtration to remove dicyclohexylurea (DCU) and concentrated by rotary evaporation. The crude mixture was dissolved in ethyl acetate (100 mL) and placed in an ice bath for 1 h to crystallize any remaining DCU. Vacuum filtration, concentration and recrystallization from ethanol produced the title compound (6.1 g, 88 %) as a red solid. m.p. 86–88 °C; *endo*-norbornyl isomer: ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.27-130 (m, 4H), 1.37-1.47 (m, 2H), 1.93 (td, *J* = 3.7, 9.4, 1H), 2.93 (s, 1H), 2.97 (dt, *J* = 3.9, 9.4, 1H), 3.03 (s, 1H), 3.56 (dd, *J* = 7.1, 14.3, 2H), 3.68 (t, *J* = 6.3, 2H), 4.27 (t, *J* = 6.3, 2H), 5.91 (dd, *J* = 2.8, 5.6, 1H), 6.21 (dd, J = 2.9, 5.6, 1H), 6.83 (d, *J* = 9.1, 2H), 7.93 (m, 4H), 8.33 (d, *J* = 8.8, 2H) ^{13}C NMR (150 MHz, $CDCl_3$) δ 12.33, 29.33, 30.47, 41.65, 42.56, 43.11, 43.34, 45.74, 46.42, 46.59, 48.83, 49.72, 61.20, 111.51, 122.67, 124.69, 126.28, 132.20, 135.65, 138.05, 138.17, 143.86, 147.43, 151.33, 156.79, 174.74.

***exo*-*N*-(*p*-Carboxyphenyl) nadimide**. *cis*-5-norbornene-*exo*-2,3-carboxylic anhydride (19.14 g, 0.117 mol) was dissolved in acetone (70 ml) with slight heating. *p*-aminobenzoic acid (16.05g, 0.117 mol) was added in one portion and the mixture was allowed to stir for 30 min during which a white precipitate formed. The precipitate was collected by vacuum filtration and dried under high vacuum to yield 29.13 g of the amic acid.

The amic acid was dissolved in DMF (100 mL) at 100 °C. Acetic anhydride (14.8 g, 0.145 mol) and anhydrous sodium acetate (0.8 g, 0.01 mol) were added and the mixture was allowed to stir at 100 °C for 2 h. The solution was allowed to gradually cool to rt during which the product

crystallized. The crystals were collected by vacuum filtration, washed thoroughly with water, and dried under high vacuum at 80 °C to yield 20.96 g (63 %) of the title compound. m.p. 265–268 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.46 (q, *J* = 9.9, 2H), 2.87 (s, 2H), 3.22 (s, 2H), 6.36 (s, 2H), 7.42 (d, *J* = 8.5, 2H), 8.05 (d, *J* = 8.5, 2H), 13.13 (bs, 1H) ^{13}C NMR (150 MHz, $CDCl_3$) δ 42.55, 44.86, 47.47, 126.73, 129.71, 130.032, 135.73, 137.63, 166.40, 176.29.

***exo*-*N*-[(E)-2-(ethyl(4-((4-nitrophenyl)diazenyl)phenyl)amino)ethyl benzoate] nadimide (5)**. DPTS (0.44 g, 1.41 mmol), *exo*-*N*-(*p*-Carboxyphenyl) nadimide (2.0 g, 7.06 mmol) and Disperse red 1 (2.26 g, 7.20 mmol) were dissolved in a mixture of THF (40 mL) and CH_2Cl_2 (40 mL) under N_2 atmosphere and cooled in an ice bath. In a separate flask, DCC (1.75 g, 8.47 mmol) was dissolved in CH_2Cl_2 (10 mL) and transferred via cannula to the above mixture. The reaction mixture was allowed to gradually warm to rt and was stirred overnight (~18 h). The reaction mixture was filtered by vacuum filtration to remove dicyclohexylurea (DCU) and concentrated by rotary evaporation. The product was purified by column chromatography (SiO_2: 1:1 ethyl acetate:hexanes). The product crystallized in the fraction tubes and was collected by vacuum filtration to yield 0.89 g (22 %) of the title compound as a deep red solid. m.p. 184 – 187 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.28 (t, *J* = 7.1, 14.16, 3H), 1.45 (d, *J* = 9.9, 1H), 1.62 (d, *J* = 10.0, 1H), 2.87 (s, 2H), 3.41 (s, 2H), 3.58 (q, *J* = 7.0, 2H), 3.83 (t, *J* = 6.2, 2H), 4.56 (t, *J* = 6.2, 2H), 6.36 (s, 2H), 6.86 (d, *J* = 8.5, 2H), 7.93 (m, 4H), 8.11 (d, *J* = 8.4, 2H), 8.32 (d, *J* = 8.9, 2H) ^{13}C NMR (150 MHz, $CDCl_3$) δ 12.39, 43.08, 45.80, 45.98, 47.97, 48.89, 62.28, 111.58, 122.71, 124.70, 126.23, 126.32, 129.50, 130.52, 136.15, 138.05, 143.97, 147.48, 151.25, 156.783, 165.62, 176.53

Representative Polymerization Procedure. A solution of **4** (11.1 mg, 0.013) in CH_2Cl_2 (1 mL) was rapidly injected via syringe into a vigorously stirred solution of **1** (150 mg, 0.34 mmol), **2** (75 mg, 0.49 mmol), and **3** (275 mg, 0.68 mmol) in CH_2Cl_2 (9 mL) at rt. After 30 min, a large excess of ethyl vinyl ether was added to quench the polymerization. The reaction mixture was poured into stirred methanol, and the resulting precipitate was collected by vacuum filtration and dried under high vacuum.

3. Results and Discussion

As stated previously, our goal is to explore the use of ROMP to directly prepare tunable, high T_g E-O polymers that would otherwise be difficult to prepare using polymerization methods where high temperatures or free-radicals are required. We envisioned copolymerizing an E-O chromophore tethered monomer such as **1** with norbornyl-monomers **2** and **3** via ROMP as a method for preparing polymers with controllable T_g values under mild reaction conditions. Polymers derived from nadimide **3** are thermally robust with T_g values exceeding 200 °C and are soluble in common organic solvents (*10*). Modification of the feed ratio between monomers **2**

and **3** with constant **1** should enable the preparation of polymers with pre-determined T_g values, allowing the material to be tuned according to the desired processing conditions.

Commercially available Disperse Red 1 (DR1) was used as a model chromophore for this study, which is attached to the polymerizable norbornene unit via DCC/DPTS coupling. Acrylic monomers containing DR1 are difficult to polymerize to high molecular weights by free radical polymerization (*14*). Lambeth and Moore have previously shown that similar azobenzene-tethered norbornyl-monomers are readily polymerized in a controlled fashion by complex **4** (*15*).

Monomers **1**, **2**, and **3** were initially homo-polymerized in the presence of complex **4** with target molecular weights of 40 kDa. Five copolymer samples were also prepared with target molecular weights of 40 kDa where the weight fraction of monomer **1** in the feedstock was held constant at 30% while the ratios of monomers **2** and **3** were varied. GPC characterization indicated the polymers were well-defined as evidenced by nearly mono-modal peak shapes and low PDIs (1.1-1.2).

The polymers were characterized by DSC heating from 25 to 250 °C at 10 °C/min with two heating cycles. The T_g values reported were taken from the 2nd heating scan. The T_gs of the homopolymers (Samples **P1**–**P3**, table 1) were used to estimate the T_g values of the copolymers (Samples **P4**–**P8**, table 1) using the Fox equation (*16*). As anticipated, the T_g of the copolymers increased as the ratio of monomer 2 to 3 was decreased. For a copolymer with 30 wt% of monomer **1**, the T_g can be manipulated from 89 to 189 °C simply by varying to ratios of **2** and **3** in the monomer feedstock. The measured T_g values are higher by 5–11% then those predicted by the Fox equation. The polymers are also soluble in a variety of common organic solvents and are easily processed under bulk conditions.

Table 1. Thermal data for E-O polymers prepared by ROMP.

	Monomer Feedstock				
Sample	**w_1**	**w_2**	**w_3**	**T_g (°C) (calc)[a]**	**T_g (°C) (DSC)[b]**
P1	1	0	0	–	103.8
P2	0	1	0	–	78.8
P3	0	0	1	–	234.8
P4	0.3	0.7	0	84.9	89.3
P5	0.3	0.55	0.15	95.1	106.64
P6	0.3	0.35	0.35	113.3	132.9
P7	0.3	0.15	0.55	140.1	163.1
P8	0.3	0	0.7	170.3	189.2

[a]Calculated according to the Fox equation. [b]Value reported is from 2nd heating cycle.

To further enhance the possible T_g range that could be accessed, a polymer where the entire backbone was derived from a nadimide type monomer was synthesized. To this end, *exo-N*-(p-carboxyphenyl) nadimide was prepared which provided an attachment point for DR1 (*17*). The chromophore was added via DCC/DPTS coupling to produce nadimide monomer **5**. Co-polymerization with nadimide **3** (70 wt%) was conducted at room temperature in the presence of complex **4** to produce **P9** in quantitative yield after 15 min. The polymer was not able to be characterized by GPC due to insolubility in THF. The material was characterized thermally by DSC giving a value of 212 °C for T_g. The polymer was also soluble in chlorinated solvents such as CH_2Cl_2 or $CHCl_3$ and polar, aprotic solvents such as DMF, NMP, or cyclopentanone. The structures of the various monomers and catalyst used are summarized in figure 1.

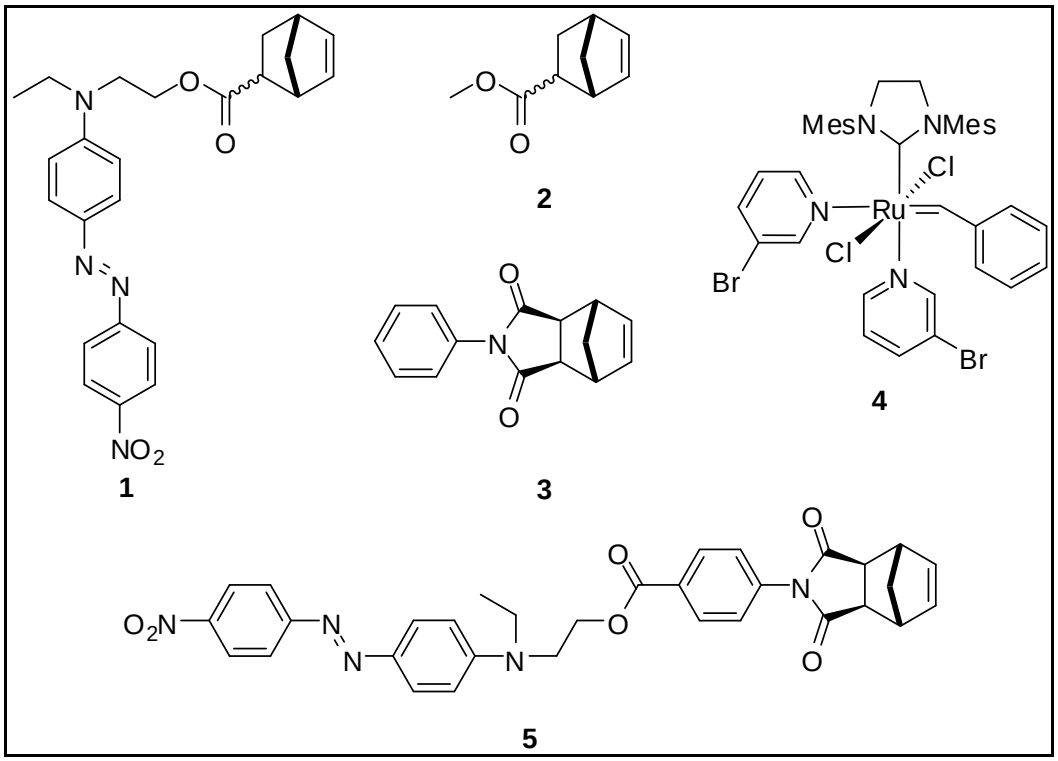


Figure 1. Structures of monomers and catalyst used in this study.

Having demonstrated the ability to prepare tunable high T_g E-O polymers in a mild fashion by ROMP, the polymerization method was scaled up (10 g) to test the material for E-O activity. The polymer was prepared from a feed ratio of 10 % **1**, 45 % **2**, and 45 % **3** target T_g of 140 °C. Characterization by DSC confirmed a T_g of 141 °C. The material was spin-coated from solution to form a thin film on an ITO coated glass substrate. The top surface was coated with gold and the material poled in the range of 200–400 V with peak temperatures ranging from 142 to 145 °C. Teng-Man analysis of the films indicated very low poling efficiency with the E-O coefficient r_{33} ranging from 0.3 to 1.1 pm/V at 1320 nm. For comparison, the highest recorded value for a DR1 tethered polymer system is 7.5 pm/V at 810 nm.

We postulate the very low poling efficiency could be due to several factors including residual catalyst from the polymerization or oxidative instability of the polymer backbone. In ROMP, the polymerization involves initial coordination of the monomer to catalyst followed by a [2+2] cycloaddition between the strained double bond in the monomer and the metal alkylidene in the catalyst forming a metallocyclobutane intermediate. This intermediate ring opens to form a new metal alkylidene complex which can undergo reaction with another monomer. This process continues until all the monomer is consumed. Reaction with a terminating agent such as ethyl vinyl ether liberates the metal complex from the polymer chain and produces a metathesis inactive catalyst species (*18*). The polymer is then typically purified and isolated by multiple precipitations in a non-solvent for the polymer. Despite the many reports of the use of ROMP to prepare a wide variety of materials for various applications, authors rarely analyze the amount of residual Ru present. The presence of trace levels of Ru could be detrimental in a number of applications, especially for biomedical or optoelectronic applications. In our own application, the presence of trace metal species increases the conductivity of the material reducing the poling efficiency of the material. In an effort to increase the poling efficiency, we quantitated the amount of residual Ru present after standard purification procedures and explored alternative approaches to removing trace Ru.

Model polymers where prepared from monomers **2** and **3,** which mimicked the structure of the E-O polymers. Initially, the polymers where purified by repeated precipitation from methanol and the level of residual Ru analyzed by inductively coupled plasma mass spectrometry (ICP-MS). The analysis indicated significant levels of Ru present after three precipitations (140 ppm). This suggested the poor poling efficiency observed may have been the result of the presence of trace Ru species. To reduce the levels of Ru further, new purification protocols were investigated, some of which had been shown to be effective for the removal of Ru from products produced by ring closing metathesis in small molecule synthesis.

To further decrease the residual Ru, Soxhlet extraction was performed with MeOH. The resulting material contained 110 ppm Ru, an improvement over repeated precipitations but still relatively high for many applications. In small molecule organic synthesis, a variety of methods have been employed to remove trace Ru from the final product in reactions such as ring closing metathesis (RCM). Several authors reported successfully scavenging Ru based metathesis catalysts with activated carbon (*19, 20*). After isolation of the polymer by precipitation, the material was redissolved in CH_2Cl_2 and stirred with activated charcoal for 24 h. Filtration of the charcoal and precipitation in MeOH yielded polymer with 160 ppm Ru indicating the charcoal had no effect relative to simple repeated precipitation. Use of charcoal also significantly reduced the yield of polymer isolated suggesting the polymer is adsorbed.

Maynard and Grubbs used a polar, water soluble phosphine ligand to bind Ru and partition the complex into water via extraction (*21*). Alternatively, the solubility enhanced catalyst can be absorbed onto silica gel with heating and subsequently filtered (*22*). For our material, we choose to explore the second method employing silica gel to scavenge the catalyst from solution prior to

precipitation. The resulting material contained 100 ppm Ru in the final product accompanied with a reduction in isolated yield. The yield could be improved with additional washing of the filtered silica gel. However, we observed the colored Ru complex to slowly migrate from the silica gel to the filtrate resulting in increased residual catalyst in the final product.

Ahn et al. and Haack et al. found treatment of the catalyst with DMSO and/or PPh_3=O followed by silica gel filtration to be an effective method for catalyst removal (*23, 24*). This method has the advantage of using cheap, readily available compounds. For our material, the quenched polymerization medium was treated with DMSO and silica gel followed by filtration over a pad of silica. Surprisingly, the resulting material contained a higher level of residual Ru (260 ppm) then a single precipitation. This may have been partially the result of using a more polar mobile phase (4 % MeOH in CH_2Cl_2) to effectively elute the polymer from the silica.

Paquette and coworkers used $Pb(OAc)_4$ to aid in the removal of the Grubbs 1st generation catalyst from a variety of products prepared by RCM (*25*). Treatment of the polymerization medium with 1.5 eq $Pb(OAc)_4$ followed by filtration over a pad of silica and precipitation gave a polymer containing 100 ppm residual catalyst accompanied with a reduction in the isolated yield. As before, continued washing of the silica gel caused migration of the colored Ru byproduct from the silica gel to the filtrate. The results are summarized in table 2.

Table 2. Yields and residual catalyst for various purification protocols.

Entry	Method	Yield	Residual Ru (ppm)
1	Once precipitated	97	240
2	Twice precipitated	91	160
3	Thrice precipitated	77	140
4	Precipitate, Soxhlet extraction, precipitate	86	110
5	Precipitate, activated charcoal, precipitate	53	160
6	$P(CH_2OH)_3$ and SiO_2 at 40 °C, filter over SiO_2, precipitate	69	100
7	DMSO and SiO_2, filter over SiO_2, precipitate	63	260
8	$Pb(OAc)_4$, filter over SiO_2, precipitate	65	100

Despite the success of several of the methods for removing the catalyst to a satisfactory content in small molecule synthesis, none of the preceding methods employed reduced the remaining metal below 100 ppm. For many applications, this amount would present several issues for product stability and toxicity. We subsequently explored new strategies to further reduce the level of residual catalyst. The first strategy explored involved using heterogeneous particles bearing various functional groups. The functional groups on the surface of the particle can coordinate to the metal species, allowing the metal to be removed by a simple filtration of the particles from the reaction mixture. The polymer is then isolated by precipitating the polymer from the filtrate. The second method involves post-polymerization addition of a solubility modifier to enhance the solubility of the Ru catalyst in a particular solvent. Upon precipitation of the polymer in a non-solvent, the modified solubility of the Ru species will allow it to stay in solution and be washed away from the polymer during filtration. These two methods have been

used by chemists to remove metal catalysts used to effect various chemical transformations in small molecule synthesis for the pharmaceutical industry (*21*, *26*, *27*). However, these techniques have yet to be applied in the removal of residual catalyst species in polymer synthesis.

The effectiveness of heterogeneous scavengers depends on a number of factors such as the affinity of the surface functional group toward the metal, the spatial arrangement of the functional groups, and compatibility of the particle with reaction conditions. Thus, a wide range of scavengers were tested with different surface functionalities and compositions at 500 eq relative to catalyst. Several different particle types were investigated, consisting of silica particles, polystyrene beads, polysiloxane beads, and grafted polyolefin fibres. Surface functional groups consisted of imidazole, thiourea, dimercaptotriazine (DMT), pyridine, amine, triaminetetraacetic acid (TAAcOH), tetrasodium triaminetetraacetate (TAAcONa), and isothiouronium. From our initial screening, four candidates were identified for further investigation. Three of the four candidates consisted of silica functionalized with DMT, thiol, or TAAcONa. The fourth candidate was thiol-functionalized polysiloxane beads. The scavengers were tested at two additional levels: 100, and 50 molar equivalents to catalyst. The results are summarized in table 3.

Table 3. Heterogeneous scavengers used in study.

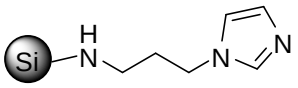
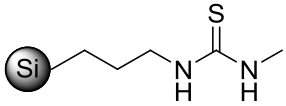
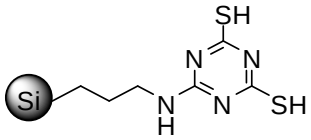
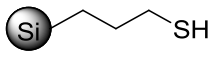
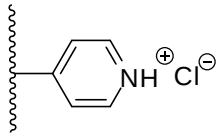
Additive Name	**Structure**	**Residual Ru Level (ppm)**		
		500 eq	**100eq**	**50 eq**
Siliabond® imidazole		20		
Siliabond® thriourea		20		
Siliabond® DMT		10	30	20
Siliabond® thiol		20		
Smopex-105 Pyridine		20		

Table 3. Heterogeneous scavengers used in study (continued).

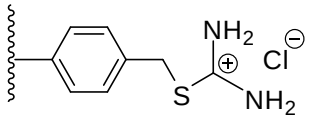
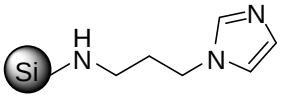
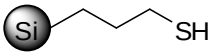
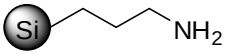
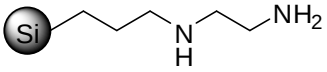
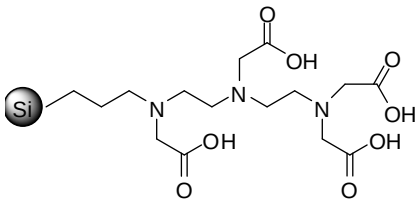
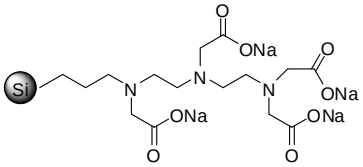
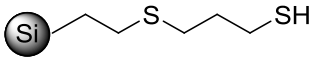
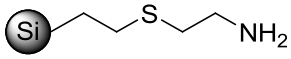
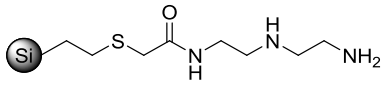
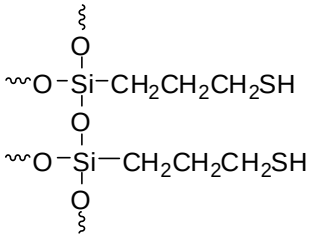
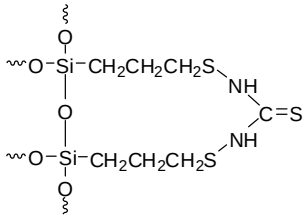
Additive Name	Structure	Residual Ru Level (ppm)		
		500 eq	**100eq**	**50 eq**
Smopex-110		100		
Quadrapure™ IMDAZ		20		
QuadraSil™ MP		<10	10	20
QuadraSil™ AP		20		
Siliabond® diamine		110		
Siliabond® TAAcOH		30		
Siliabond® TAAcONa		10	10	<10
PhosphonicS™ SPM36		20		
PhosphonicS™ SEA		20		

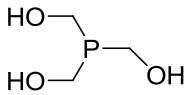
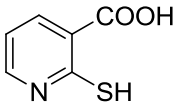
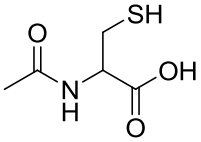
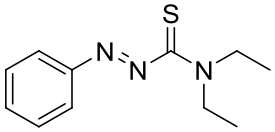
Table 3. Heterogeneous scavengers used in study (continued).

Additive Name	Structure	Residual Ru Level (ppm)		
		500 eq	100eq	50 eq
PhosphonicS™ STA3		30		
Deloxan® MP		<10	40	60
Deloxan® THP II		30		

The selected scavengers significantly reduced the residual catalyst levels compared to multiple precipitations in MeOH. Of the selected scavengers, the TAAcONa- and thiol-functionalized silica particles were the most effective, reducing the residual Ru level to 10 and 20 ppm, when 100 and 50 eq, respectively, relative in G3, were added to the polymerization medium after quenching the polymerization.

For the second strategy, several compounds were investigated that had been previously successfully employed as solubilizing agents for Ru or Pd catalysts in small molecule synthesis. The results are summarized in table 4. 2-mercaptonicotinic acid (MNA) was previously shown to be an effective solubilizing agent for a Ru-based catalyst when extracted with aqueous sodium bicarbonate (*28*, *29*). We reasoned that MNA could enhance the solubility of the metathesis inactive G3 catalyst in MeOH. After precipitation of the polymer in MeOH, the residual catalyst would be effectively washed away with the filtrate. Gratifyingly, the Ru level was reduced from 190 ppm to 30 ppm in a single precipitation when 50 eq of MNA relative to G3 was added to the polymerization medium prior to precipitating the polymer in MeOH. Tris(hydroxymethyl) phosphine (THP) was previously shown to be an effective compound for modifying the solubility of metathesis catalysts to facilitate removal of the residual catalyst during purification in both RCM and ROMP processes (*21*, *22*). For comparison, THP was also used in this study. The addition of 100 eq THP relative to G3 to the polymerization medium prior to precipitation resulted in a polymer containing 50 ppm Ru.

Table 4. Residual Ru levels for ROMP polymers purified with catalyst solubilizing agents.

Scavenger	Structure	Residual Ru Level (ppm)	
		100 eq	50 eq
Tris(hydroxymethyl) phosphine		50	110
2-mercaptonicotinic acid		30	30
N-acetyl-L-cysteine		70	120
Diethylphenylazothioformamide		30	30

Next, we turned our attention to solubilizing agents that had previously shown efficacy in reducing residual catalyst levels in Pd-catalyzed reactions. N-acetyl-L-cysteine was demonstrated to be an effective scavenging agent for Pd during the crystallization of an active pharmaceutical ingredient intermediate from ethanol (*30*). N,N-diethylphenylazothioformamide (DEPATF) was shown to be an effective solubilizing agent for Pd(0) during the precipitation of conjugated polymers in MeOH (*31*). Given the success of other thiol-functionalized compounds and particles in scavenging Ru, we reasoned N-acetyl-L-cysteine and DEPATF could be effective solubilizing agents for metathesis inactive G3 as well. As anticipated, both compounds were effective in reducing the residual catalyst level compared to simple precipitation in MeOH. The addition of 100 eq of N-acetyl-L-cysteine reduced the Ru level to 70 ppm while the addition of 50 eq DEPATF reduced the Ru level to 30 ppm.

When the two strategies investigated in this report are compared, each method has advantages and disadvantages. The surface functionalized particles were more effective in removing Ru as evidenced by lower levels of residual catalyst at similar equivalents. However, removal of the particles by filtration added an extra step to the process. Use of solubilizing agents is a simple modification to the traditional purification process but is not as effective as using functionalized heterogeneous particles at comparable equivalents.

To demonstrate the effect of the residual catalyst on material properties, the oxidative stability of a polymer purified by simple precipitation was compared to a polymer purified with DEPATF by differential scanning calorimetry (DSC). It was previously suggested that the presence of

residual Ru in polymers prepared by ROMP limited the oxidative stability of the polymer (*32*). Samples were heated from room temperature to 300 °C under an atmosphere derived from a compressed air tank. The DSC curves are shown in figure 2. The first sample was purified by a single precipitation in MeOH and contained 190 ppm Ru. During heating under an air atmosphere, the sample began to decompose ca. 86 °C. The second sample was purified using the solubility agent DEPATF and contained 30 ppm Ru. During heating under an air atmosphere, the sample began to decompose ca. 107 °C. Reduction of the residual Ru level from 190 ppm to 30 ppm resulted in a 21 °C increase in the oxidation induction temperature. This simple experiment demonstrates the importance of considering the presence of trace catalyst species on materials properties and performance.

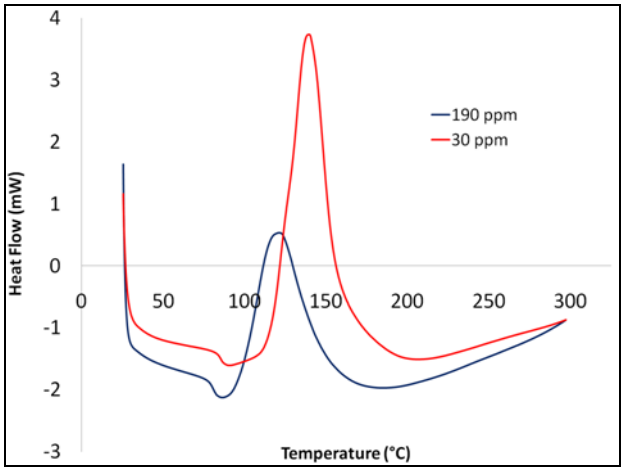


Figure 2. Oxidative stability of polymer with varying levels of residual Ru.

4. Summary and Conclusions

We report a new method for directly preparing tunable, thermally stable E-O polymers via ROMP. Polymers containing 30 wt% DR1 were prepared in quantitative yields under undemanding reaction conditions. The materials were characterized by DSC indicating that the T_g could be controlled from 89 to 189 °C by varying the feed ratio of monomers **1**, **2**, **3**. The T_g could be increased above 200 °C by using a backbone derived entirely from nadimide type monomers. The materials were soluble in a range of solvents and could easily be processed in the bulk. These characteristics make ROMP a highly attractive method for preparing E-O polymers. Preparation of materials that combine high thermal stability and processability were previously difficult to obtain without post-polymerization modification or lattice hardening procedures during poling. The use of ROMP should greatly simplify the overall process and provide materials capable of realizing stable E-O coefficients. Unfortunately the polymers did not display the anticipated poling behavior. This was potentially attributed to residual polymerization catalyst present in the final product. A comprehensive study was undertaken to

determine levels of residual catalyst present in ROMP based materials when isolated using typical protocols. Catalyst levels ranged from 240 to 140 ppm depending on the number of precipitations. The difficulty in complete removal of the catalyst may be the result of coordination of the metal species to double bonds located along the polymer backbone. Hydrogenation of the double bonds in the polymer backbone using diimide generated in-situ produced polymer containing 10 ppm residual Ru upon precipitation. Since saturation of the polymer backbone may not always be a suitable strategy to facilitate removal of residual metal, additional strategies were explored. Several methods were explored that previously had been used in small molecule synthesis to remove residual Ru that were based on the use of various catalyst modifiers and adsorbents. None of these methods succeeded in reducing the level of trace metal below 100 ppm while also significantly reducing the yield of the polymerization. Various functionalized heterogeneous particles and fibers were tested, several of which successfully reduced the catalyst levels to 10–30 ppm using 50–100 equivalents relative catalyst. The use of solubility agents was also explored, which could coordinate to the metal species and help partition the catalyst into the precipitation solvent, facilitating removal during isolation of the polymer via filtration. The presence of residual catalyst on the oxidative stability of ROMP-based polymer was also explored to demonstrate the detrimental effects the presence of the metal can have on material properties. A 20 °C increase in the oxidative induction temperature was observed when the level of Ru was reduced from 190 ppm to 30 ppm. Recently, we have prepared a series of ROMP based polymers containing various E-O chromophores where some of the methods previously described were used to remove any residual catalyst from the final polymer product. These materials are currently undergoing testing for E-O activity.

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List of Symbols, Abbreviations, and Acronyms

DCU	dicyclohexylurea
DEPATF	diethylphenylazothioformamide
DMT	dimercaptotriazine
DPTS	(dimethylamino) pyridinium 4-toluenesulfonate
DR1	Disperse Red 1
DSC	differential scanning calorimetry
E-O	electro-optical
Hz	hertz
ICP-MS	inductively coupled plasma mass spectrometry
MNA	mercaptonicotinic acid
NLO	non-linear optical
RCM	ring closing metathesis
ROMP	ring opening metathesis polymerization
TAAcOH	triaminetetraacetic acid
TAAcONa	tetrasodium triaminetetraacetate
T_g	glass-transition
THP	Tris(hydroxymethyl) phosphine

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