Synthesis of Block Copolymers by Changing Living Anionic Polymerization into Living Ring Opening Metathesis Polymerization

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ABSTRACT: A series of AB diblock copolymers have been synthesized by transformation of living anionic polymerization into ring opening metathesis polymerization (ROMP). Ethylene oxide was polymerized anionically using diphenylmethylpotassium as the initiator and was terminated with vinylbenzyl chloride to produce a series of poly(ethylene oxide) (PEO) macromonomers with a terminal vinyl group. An alkylidene exchange reaction was then realized with ruthenium propylidene complex $RuCl_2({=}CHC_2H_5)(PCy_3)_2$, transforming PEO macromonomers into ruthenium ROMP macroinitiators. A variety of norbornene derivatives were then subjected to ROMP using PEO macroinitiators to synthesize well-defined block copolymers of varying molecular weights and compositions.

Introduction

Living polymerization techniques are powerful tools for the synthesis of polymers that are well-defined in terms of molecular weight and polydispersity.[1] Inherent termination and chain transfer reactions are either absent or insignificant, polymerization proceeds until all the monomer is consumed, and addition of further monomer results in continued polymerization.[2,3] Furthermore, these living techniques allow the synthesis of well-defined molecular architectures such as branched polymers[4,5] and block copolymers.[3,6] Block copolymers are defined as having a linear arrangement of blocks of different monomer composition.[7] By tethering together via covalent bonds two potentially incompatible polymers, macroscopic phase separation cannot occur and nanoscale self-organization results. It is this structural organization, which occurs in the melt, solid state, or micellar solution, which results in the unique and novel properties that make these materials so attractive for industrial applications. In the solid and rubbery states block copolymers are used as thermoplastic elastomers, with applications such as impact modification, compatibilization and adhesion. In solution, their surfactant properties are exploited in foams, oil additives, solubilizers, thickeners, and emulsion stabilizers.[8] The preparation of block copolymers by sequential addition of monomers using living polymerization is the method of choice for the production of well-defined materials.[9] In fact, Szwarc described this aspect of living polymerization in his seminal paper in 1956.[2]

Two examples of a living polymerization technique are anionic polymerization and ring opening metathesis polymerization (ROMP); both may be used to synthesize block copolymers[9,10] by sequential addition of monomers but both techniques are limited in the range of monomers that may be used. The former is limited to certain styrenes, dienes, (meth)acrylates, vinylpyridines, epoxides, cyclic siloxanes, and lactones.[9] However, any monomer featuring a functional group containing a relatively acidic proton (alcohol, carboxylic acid, amine) would terminate polymerization. ROMP can be carried out with ring-strained cyclic monomers such as cyclobutene and norbornene. Major advances achieved during recent years have resulted in the design of ROMP initiators that tolerate polar functional groups (aldehydes, acids, alcohols) and aqueous environments.[11,12]

Living anionic polymerization and living ROMP have been combined to prepare well-defined graft copolymers. Feast and Khosravi[13,14] undertook a program to make graft copolymers by first synthesizing living polystyrene via anionic polymerization, then subjecting the chains to a controlled termination reaction to prepare polystyrene macromonomers with a terminal norbornene unit. Finally the macromonomers were subjected to ROMP to produce well-defined graft copolymers with a norbornene backbone. Similarly Richards and Miller synthesized a series of graft copolymers with a norbornene backbone and poly(ethylene oxide) (PEO) grafts.[15] Gnanou et al.[16,17] have also worked extensively in the area of graft copolymers utilizing these two polymerization techniques.

ROMP has also been combined with other polymerization techniques to prepare block copolymers. Grubbs et al.[18,19] reported a methodology based on changing from ROMP to Ziegler−Natta polymerization resulting in the formation of norbornene-ethylene block copolymers. The integration of ROMP with controlled radical polymerization has also been reported leading to the synthesis of block copolymers of norbornene with styrene and methyl acrylate.[20,21] Recently Register et al.[22] produced block copolymers via termination of living ROMP, initiated with a Schrock molybdenum initiator, with anionically synthesized macromolecular aldehydes. This approach was successful in converting at least 95% of the living ROMP chains into diblock copolymers in some examples, although an excess of the macroterminating agent was required in all cases. Inevitably this resulted in contamination of the block copolymer with homopolymer (macromolecular aldehydes). This particular approach also seems to be limited in the choice of suitable monomers. The methodology used for the synthesis of macromolecular aldehydes was successful with styrene but less so for isoprene, which upon reaction with the living ROMP block gave a diblock yield of only 45%. Furthermore, the aldehyde terminated polymers were designed as macroterminating agents for molybdenum-initiated ROMP. Thus, this method is further limited in terms of the choice of suitable ROMP

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monomers since molybdenum initiators show limited tolerance toward functional groups in contrast to Grubbs' ruthenium initiators.[11,12,23]

In this paper, we describe a novel route to transform living anionic polymerization into living ROMP and thereby synthesize a series of novel well-defined block copolymers. To our knowledge, this is the first time that macroinitiators capable of initiating ROMP have been prepared from polymers produced by anionic polymerization. This has been accomplished via alkylidene exchange reactions. It is also the first report of the synthesis of block copolymers by the combination of living anionic polymerization and living ruthenium-initiated ROMP.

Experimental Section

Materials. Ethylene oxide (EO, Aldrich, 99.5+%) was purified by stirring over CaH_2 and then by distillation from $Mg(Bu)_2$ (Aldrich, 1.0 M solution in heptane) immediately before use. THF was dried over sodium/benzophenone. Diphenylmethylpotassium was synthesized in solution by the reaction of potassium naphthalene with diphenylmethane in THF.[24] 4-Vinylbenzyl chloride (4-VBC, Aldrich, 90%) was stated by the supplier to be likely to contain the impurities, α-chloromethylstyrene (2%), dichloromethylstyrene (3%), and 3-vinylbenzyl chloride (3-VBC, 5%). 4-VBC was purified by vacuum distillation from CaH_2 prior to use. CH_3I (Lancaster, 99%) was distilled from 4 Å molecular sieves prior to use. Grubbs ruthenium initiator ($RuCl_2(=CHPh)(PCy_3)_2$) was synthesized according to literature procedures.[25] *trans*-3-Hexene (Aldrich, 99+%) and ethyl vinyl ether (Aldrich, 99%) were used as received. CH_2Cl_2 was dried over calcium hydride and benzene was purified by passing the solvent through a system of columns designed to remove both protic impurities and oxygen.[26] *exo,exo*-*N*-Phenylbutylbicyclo[2.2.1]hept-5-ene-2,3-dicarboxyimide (**A**) was synthesized according to a literature procedure.[27] *endo,exo*-Bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid dimethyl ester (**B**) was produced via the Diels–Alder reaction between cyclopentadiene and dimethyl fumarate.[28] *endo,endo*-5,6-Bis(chloromethyl)bicyclo[2.2.1]hept-2-ene (**C**) was obtained from the Diels–Alder reaction of cyclopentadiene with 1,4-dichlorobut-2-ene according to the method described by Bowe[29] and modified by Shahada and Feast.[30] $CDCl_3$ (Aldrich, 99.9%D, 0.03% v/v TMS) was used as received, and C_6D_6 (Aldrich, 99.6% D, 0.03% v/v TMS) was purified by distillation from CaH_2.

Analytical Measurements. Molecular weight analysis was carried out by size exclusion chromatography (SEC) on a Viscotek TDA 302 refractive index detector, with a guard column and 2 × 300 mL PLgel 5 μm mixed C columns, DMF was used as the eluent at a flow rate of 1.0 mL/min and at a constant temperature of 80°C. Molecular weights were obtained using a conventional calibration curve generated from narrow molecular weight distribution poly(ethylene glycol) (PEG)/PEO standards (Polymer Laboratories) with molecular weights in the range 106–273 000 g mol^{-1}. Number-average molecular weight and block copolymer compositions were determined by ^1H NMR using a Varian Inova 500 MHz or Mercury 400 MHz spectrometer. All ^1H NMR resonances are quoted relative to TMS.

Synthesis of a PEO Macromonomer. The anionic polymerization of EO was carried out using standard high vacuum techniques. EO (12.52 g, 0.28 mol) and THF (100 mL) were distilled into the reaction vessel, and polymerization was initiated by the addition of diphenylmethylpotassium (1.0 M solution in THF, 2.09 mL, 2.09 mmol). Polymerization proceeded over a period of 12 h at room temperature after which the temperature was increased to 35°C for a further 12 h before the mixture was allowed to reach room temperature. An aliquot (5 mL) of the solution was then removed from the reactor and terminated with CH_3I (0.01 mL, 1.60 mmol) in order to provide a sample of unfunctionalized PEO for molecular weight analysis. A slight molar excess of 4-VBC (0.34 mL, 2.39 mmol, 1.2 equiv) was added to the rest, and the mixture was stirred for 16 h at room temperature. The polymer was recovered by precipitation into hexane (800 mL), filtered, washed with hexane and dried in vacuo at room temperature for 16 h. The sample was then dissolved in CH_2Cl_2 (80 mL) and filtered through Celite (Aldrich grade 521) in order to remove the KCl formed as a byproduct of the coupling reaction of the living PEO with 4-VBC, and the solvent was evaporated off. Following this the product was redissolved in benzene (80 mL) and reprecipitated in hexane (640 mL) and dried in vacuo, twice to ensure the complete removal of unreacted 4-VBC. Yield = 11.33 g, 95%. DMF SEC: M_n = 4600, PDI = 1.04.

^1H NMR ($CDCl_3$): δ 7.39 (d, J_{HH} = 8.0 Hz, *o*-**H** of C_6H_4 relative to C**H**H=CH), 7.30 (d, J_{HH} = 8.0 Hz, *m*-**H** of C_6H_4 relative to C**H**H=CH), 7.28–7.23 and 7.18–7.15 (m, all PEO–$CH(C_6\mathbf{H_5})_2$), 6.71 (dd, CHH=C**H**-C_6H_4), 5.74 (dd, C**H**H=CH–C_6H_4), 5.24 (dd, CH**H**=CH–C_6H_4), 4.55 (s, C_6H_4–C$\mathbf{H_2}$–PEO), 4.10 (t, J_{HH} = 8.0 Hz, PEO–C**H**$(C_6H_5)_2$), 3.64 (s, C$\mathbf{H_2}$C$\mathbf{H_2}$O), 3.37 (t, J_{HH} = 6.5 Hz, PEO–OC$\mathbf{H_2}$$CH_2$–$CH(C_6H_5)_2$), 2.33 (q, J_{HH} = 8.0 Hz, PEO–OCH_2C$\mathbf{H_2}$–$CH(C_6H_5)_2$).

CH_3I-Terminated PEO. After being stirred with CH_3I for 16 h, the polymer was precipitated into hexane (40 mL). The sample was then dissolved in CH_2Cl_2 (10 mL) and filtered through Celite to remove KI, and the solvent was evaporated off. Following this the product was twice redissolved in benzene (7 mL) and reprecipitated in hexane (56 mL) and dried in vacuo. Yield = 0.19 g, 32%. DMF SEC: M_n = 4450, PDI = 1.03.

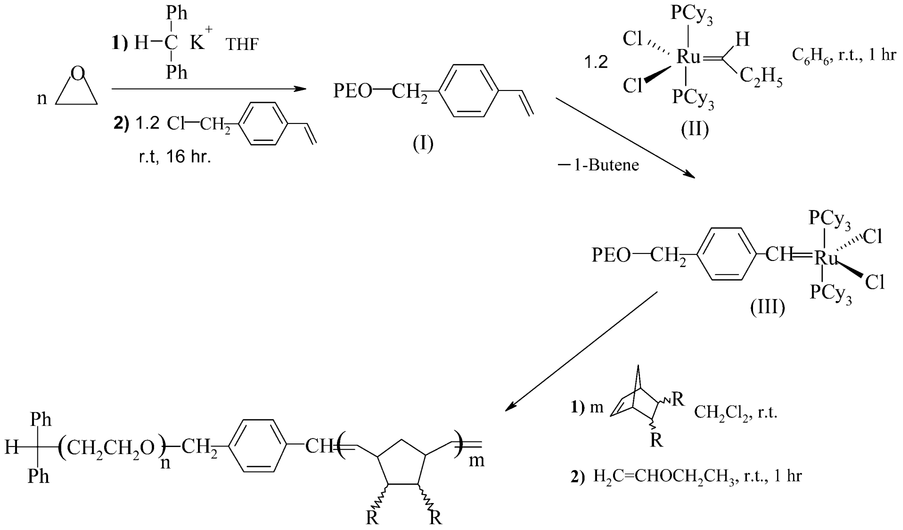
^1H NMR ($CDCl_3$): δ 7.28–7.23 and 7.18–7.15 (m, all PEO–$CH(C_6\mathbf{H_5})_2$), 4.10 (t, J_{HH} = 8.0 Hz, PEO–C**H**$(C_6H_5)_2$), 3.64 (s, C$\mathbf{H_2}$C$\mathbf{H_2}$O), 3.37 (t, J_{HH} = 6.5 Hz, PEO–OC$\mathbf{H_2}$$CH_2$–$CH(C_6H_5)_2$), 2.33 (q, J_{HH} = 8.0 Hz, PEO–OCH_2C$\mathbf{H_2}$–$CH(C_6H_5)_2$).

Synthesis of Propylidene Complex $RuCl_2(=CHC_2H_5)(PCy_3)_2$. A sample of ruthenium benzylidene $RuCl_2(=CHPh)(PCy_3)_2$ (0.50 g, 0.61 mmol) was dissolved in CH_2Cl_2 (6 mL) and placed in an ampule with a magnetic stirrer. Five equivalents of *trans*-3-hexene (0.38 mL, 3.06 mmol) was added and the mixture stirred for 6 h before removing the solvent under vacuum. When the product had the consistency of a thick paste, it was washed with acetone (chilled to −30 °C, 3 × 5 mL) and filtered to remove side products (1-phenylbutene) and other impurities before being dried at room temperature and a pressure of approximately 1 × 10^{-6} mbar in vacuo overnight. The acetone was chilled to minimize loss of the desired propylidene product, which is slightly soluble in acetone at room temperature. The solid was redissolved in CH_2Cl_2 (2 mL) and exposed to another five equivalents of *trans*-3-hexene (0.30 mL, 2.41 mmol) for 6 h and worked up as described above. This procedure was repeated once more with a further 5 equiv of *trans*-3-hexene (0.25 mL, 2.01 mmol) in order to achieve 100% conversion of benzylidene to propylidene, as shown by ^1H NMR spectroscopy. Yield = 0.34 g (73%).

^1H NMR (C_6D_6): δ 19.61 (t, J_{HH} = 5 Hz, 1H, Ru=C**H**), 3.08 (p, J_{HH} = 6.5 Hz, 2H, C$\mathbf{H_2}$$CH_3$), 2.79–2.74, 2.03–2.00, 1.79–1.77, 1.71–1.66 and 1.32–1.21 (all m, $P(C_6H_{11})_3$), 1.37 (t, J_{HH} = 7.5 Hz, 3H, CH_2C$\mathbf{H_3}$). ^{31}P NMR (C_6D_6): δ 37.10 (s, PCy_3).

Ruthenium PEO Macroinitiator. In a nitrogen-filled glovebox (M. Braun), PEO macromonomer (DMF SEC M_n = 2400, 500.0 mg, 166.7 mmol) was dissolved in C_6H_6 (2.5 mL) and placed in an ampule. $RuCl_2(=CHC_2H_5)(PCy_3)_2$ (155.0 mg, 200.0 mmol) and C_6H_6 (5.5 mL) were added to another ampule. Both ampules were transferred to a vacuum line and kept under argon. The solution of PEO macromonomer was then introduced via a cannula to the agitated solution of initiator under an argon purge. Argon was bubbled through the mixture and agitation continued for a further hour. The solution was concentrated to half its original volume under vacuum and the solution added dropwise to vigorously stirred, degassed hexane (chilled to −78° C, 40 mL), producing a red precipitate. The mixture was then filtered and washed thoroughly with chilled hexane (3 × 10 mL) using standard cannula techniques. The solid obtained was dried at room temperature and in vacuo (1 × 10^{-6} mbar) overnight. Yield = 394 mg (65%).

Scheme 1. Synthesis of a PEO−PNB Block Copolymer[a]



[a] PEO = poly(ethylene oxide), PNB = polynorbornene, and Cy = cyclohexyl.

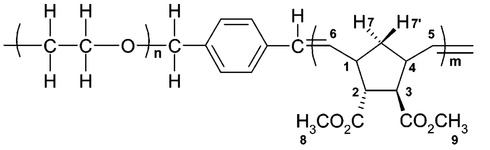


Figure 1. Numbering scheme for ^{1}H NMR assignments of poly(ethylene oxide)-*co*-(*endo,exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid dimethyl ester).

^{1}H NMR (C_6D_6): δ 20.56 (s, Ru=C**H**), 8.74 (d, J_{HH} = 7.0 Hz, *o*-**H** of C_6H_4 relative to Ru=CH), 7.31 (d, J_{HH} = 8.5 Hz, *m*-**H** of C_6H_4 relative to Ru=CH), 7.21−7.13 and 7.06−7.00 (m, all PEO−CH($C_6\mathbf{H}_5$)$_2$), 4.22 (t, J_{HH} = 8.0 Hz, PEO−C**H**(C_6H_5)$_2$), 4.09 (s, C_6H_4−C$\mathbf{H}_2$−PEO, 3.50 (m, C$\mathbf{H}_2$C$\mathbf{H}_2$O), 3.27 (t, J_{HH} = 6.5 Hz, PEO−OC$\mathbf{H}_2$CH$_2$−CH(C_6H_5)$_2$), 2.88, 1.99−1.97, 1.74−1.71, 1.66−1.55, 1.32−1.16 (all m, P($C_6\mathbf{H}_{11}$)$_3$), 2.26 (q, J_{HH} = 7.5 Hz, PEO−OCH$_2$C$\mathbf{H}_2$−CH(C_6H_5)$_2$).

^{31}P NMR (C_6D_6): δ 37.14 (s, PCy_3).

A Typical Block Copolymer Preparation. The Synthesis of Poly(ethylene oxide)-*co*-(*endo,exo*-bicyclo[2.2.1]-hept-5-ene-2,3-dicarboxylic acid dimethyl ester). Typically all ROMP reactions were performed in a nitrogen-filled glovebox (M. Braun) in screw top vials. *endo,exo*-Bicyclo[2.2.1]-hept-5-ene-2,3-dicarboxylic acid dimethyl ester (monomer **B**, 66.4 mg, 0.3 mmol) was dissolved in CH_2Cl_2 (2 mL). This solution was added to a stirred solution of a ruthenium PEO macroinitiator (20.0 mg, 3×10^{-3} mmol, PEO macromonomer M_n = 4600) dissolved in CH_2Cl_2 (1 mL). After 24 h, the living polymer was terminated by the addition of ethyl vinyl ether (0.1 mL, 1.1 mmol) under a stream of N_2. The solution was stirred for a further h, after which it was concentrated to approximately 0.5 mL using a stream of N_2 and precipitated with vigorous agitation in hexane (5 mL). The resulting precipitate was recovered by filtration, washed with hexane, and dried in vacuo at room temperature overnight. The block copolymer was then purified by dissolving it in CH_2Cl_2 and precipitating it in hexane twice. Yield = 0.035 g (42%). The low yield was due to the difficulty in recovering small quantities of samples efficiently. In larger scale ROMP reactions that used 700 mg of norbornene derivative monomers, the yield of the recovered block copolymer samples increased to approximately 96% after purification. DMF SEC: M_n = 15 300, PDI = 1.14.

^{1}H NMR ($CDCl_3$, for numbering scheme of ROMP block see Figure 1): δ 7.34−7.30 (m, CH=CH−$C_6\mathbf{H}_4$−CH$_2$−O), 7.28−7.23 and 7.18−7.15 (m, all PEO−CH($C_6\mathbf{H}_5$)$_2$), 5.48−5.19 ($\mathbf{H}_{5,6}$), 4.54 (s, C_6H_4−C$\mathbf{H}_2$−PEO), 4.11 (t, J_{HH} = 8.0 Hz, PEO−C**H**(C_6H_5)$_2$), 3.67 ($\mathbf{H}_{8,9}$), 3.65 (C$\mathbf{H}_2$C$\mathbf{H}_2$O), 3.38 (t, J_{HH} = 7.0 Hz, PEO−OC$\mathbf{H}_2$CH$_2$−CH(C_6H_5)$_2$), 3.24 (br, $\mathbf{H}_{2,3}$), 2.98−2.94 (br, $\mathbf{H}_{1,4\ \mathrm{and}\ 2,3}$), 2.70 (br, $\mathbf{H}_{1,4}$), 2.33 (q, J_{HH} = 8.0 Hz, PEO−OCH$_2$C$\mathbf{H}_2$−CH(C_6H_5)$_2$), 1.97 (br, $\mathbf{H}_7$) 1.48 (br, $\mathbf{H}_{7'}$). M_n by ^{1}H NMR = 22 900.

Results and Discussion

A series of novel well-defined block copolymers have been synthesized by the transformation of living anionic polymerization into living ROMP (Scheme 1). Ethylene oxide (EO) was polymerized anionically, initiated by diphenylmethylpotassium and was end-functionalized by a controlled termination reaction with a slight excess of 4-vinylbenzyl chloride (4-VBC) to produce a poly(ethylene oxide) (PEO) macromonomer with a terminal vinyl group (**I**, Scheme 1). In each case a sample of PEO was removed prior to addition of 4-VBC and the molecular weight obtained by SEC (Table 1). ^{1}H NMR analysis of the macromonomers indicated the degree of vinyl functionalization was at least 95%. The macromonomer (**I**) was transformed into a ROMP macroinitiator (**III**) by an alkylidene exchange reaction between propylidene complex $RuCl_2(=CHC_2H_5)(PCy_3)_2$ (**II**) and the PEO macromonomer. Such alkylidene exchange reactions, as with most metathesis reactions that involve olefin substrates, are reversible, and to drive the reaction to completion it is necessary to remove the byproduct of the forward reaction.[10] In a preliminary experiment, Grubbs benzylidene initiator $RuCl_2(=CHPh)(PCy_3)_2$ was used for the macroinitiator synthesis. However, the byproduct of the forward reaction in this exchange is styrene and in order to drive the reaction to completion the styrene had to be distilled from the reaction mixture, followed by addition of fresh solvent. This process was repeated six times until no further exchange was observed. While ^{1}H NMR indicated that complete exchange did occur, it was a slow and laborious process. The synthesis of $RuCl_2(=CHC_2H_5)(PCy_3)_2$ has been reported previously in the literature[25] by reaction of the ruthenium benzylidene $RuCl_2(=CHPh)(PCy_3)_2$ with an excess (10 equiv) of 1-butene (bp −6.3 °C). The authors of this work also indicated that the same species could be obtained by a similar reaction with *cis*-3-hexene, a more facile reaction since *cis*-3-hexene is a liquid at room temperature. The kinetics of the formation of propylidene via the reaction of *cis*-3-hexene and *trans*-3-hexene with benzylidene have also been compared by ^{1}H NMR studies.[31] Although these kinetic

Table 1. Molecular Weight and Composition Data for a Series of Diblock Copolymers Synthesized by Combining the Anionic Polymerization of Ethylene Oxide (EO) and Ring Opening Metathesis Polymerization (ROMP)

	PEO block[a]			ROMP block[b]		block copolymer[c]			
sample	M_n	M_w	PDI	monomer	DP	M_n/Pred	M_n/SEC	PDI	M_n/NMR
1	2400	2500	1.06	**A**	100	31 900	16 400	1.10	30 400
2					200	61 500	28 400	1.21	56 300
3					500	150 100	63 100	1.21	140 500
4	4600	4800	1.04	**A**	100	34 100	18 900	1.12	30 500
5	10 400	10 600	1.04	**A**	100	39 900	23 000	1.11	36 600
6					200	69 500	35 500	1.15	63 500
7	38 800	41 200	1.06	**A**	200	97 900	62 900	1.28	88 300
8	2400	2500	1.06	**B**	100	23 400	14 400	1.10	23 500
9	4600	4800	1.04	**B**	100	25 600	15 300	1.14	22 900
10	10 400	10 800	1.04	**B**	100	31 400	20 700	1.13	31 400
11	2400	2500	1.06	**C**	100	21 500	10 000	1.32	23 700

[a] EO was polymerized in THF over the course of 24−144 h depending on the desired M_n. Molecular weight data for the resulting poly(ethylene oxide) (PEO) block was obtained by DMF SEC. [b] The ROMP monomer was polymerized in CH_2Cl_2 over the course of 1−5 h in the case of monomer **A**, depending on the required DP (degree of polymerization) of the ROMP block. For monomer **B** polymerization proceeded over 24 h and 1 h for monomer **C**. The DP was calculated by the ratio of molar equivalents of monomer to macroinitiator. [c] M_n by ^1H NMR calculated by comparing the integrals of the methylene protons of the PEO block (3.64 ppm) and the olefinic protons (protons 5 and 6 in the case of poly **A** − Figure 1), which fall in the region 5.75−5.51 for blocks formed from monomer **A**, 5.48−5.19 ppm for monomer **B** and 5.62−5.29 for monomer **C**.

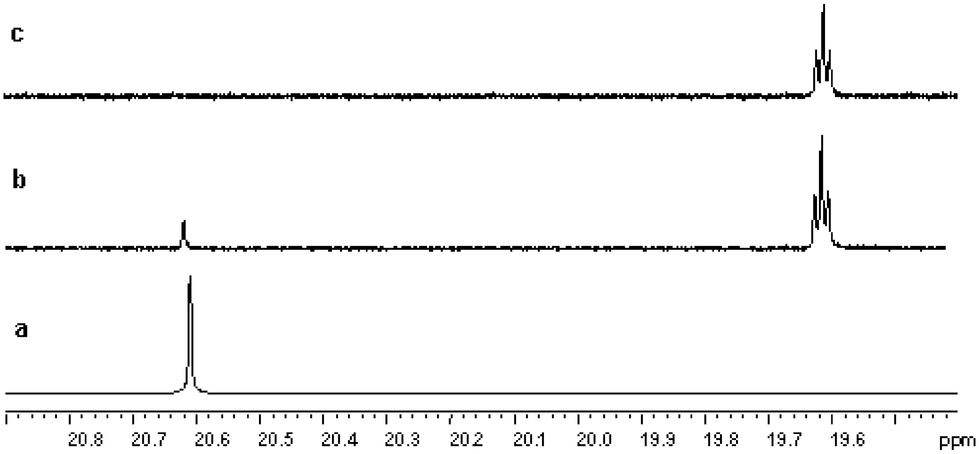
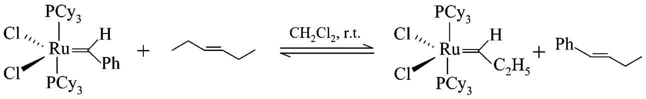


Figure 2. ^1H NMR analysis of alkylidene exchange reaction in the synthesis of bis(tricyclohexylphosphine) propylidene ruthenium dichloride. Spectra recorded in C_6D_6, at a concentration of 14 mg/mL, referenced against TMS: (a) ruthenium benzylidene initiator. (b) alkylidene region after addition of 5 equiv of *trans*-3-hexene to the benzylidene initiator. (c) same region after performing three additions of 5 equiv of *trans*-3-hexene.

Scheme 2. Synthesis of Bis(tricyclohexylphosphine) Propylidene Ruthenium Dichloride[a]



[a] Cy = cyclohexyl.

studies indicate that the cis isomer is more reactive than the trans isomer, in the work reported here we sought to develop a synthetic protocol using *trans*-3-hexene (bp 67 °C), (Scheme 2). The trans isomer is more readily available and is significantly cheaper than the cis isomer. Three additions of 5 equiv of *trans*-3-hexene were required to drive the reaction to completion. Approximately 90% conversion was observed after the first addition. This was determined by comparison of the ^1H NMR resonance of the alkylidene proton from the ruthenium benzylidene initiator at 20.62 ppm in C_6D_6 and that of propylidene at 19.61 ppm. After two further additions, no residual signal from the starting material at 20.62 ppm was observed by ^1H NMR (Figure 2).

Using the ruthenium propylidene complex (**II**) for the macroinitiator synthesis, the byproduct of the forward reaction is 1-butene, a gas at room temperature and atmospheric pressure, which can be easily removed from the reaction mixture by bubbling a steady flow of an inert gas (e.g., argon) through the reaction mixture thereby driving the exchange to completion. ^1H NMR (Figure 3) shows the complete loss of the signal for the alkylidene proton of the ruthenium propylidene (**II**), a triplet at 19.61 ppm in solution in C_6D_6 and the emergence of the new alkylidene proton signal for PEO−Ru macroinitiator (**III**), a singlet at 20.56 ppm, (Figure 3). The ^1H NMR spectrum also contains a small peak at 20.64 ppm (c in Figure 3), which we believe is due to macroinitiator in which the PEO is in a *meta* position relative to the alkylidene proton. The 4-VBC used in this research contains a trace of 3-VBC. This will also react with the living PEO during the end functionalization reaction and will eventually result in a trace of PEO ruthenium macroinitiator with the meta PEO substitution on the benzylidene moiety. A series of PEO macroinitiators were synthesized with the number-average molecular weight (M_n) of PEO (DMF SEC) ranging from 2400 to 38800 g mol^{-1}, and narrow PDI (1.04−1.06).

The PEO ruthenium macroinitiators were used to initiate the polymerization of three norbornene derivatives (Figure 4) to give a series of well-defined block

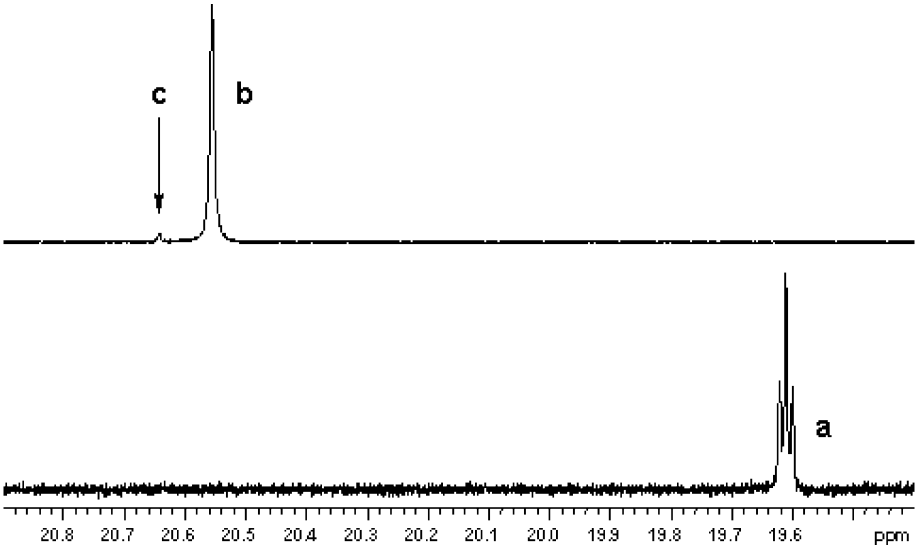


Figure 3. Comparison of the ^{1}H NMR analysis of the ruthenium propylidene initiator and the PEO macroinitiator formed as a product of the alkylidene exchange reaction between the propylidene initiator and PEO macromonomer. Spectra recorded in C_6D_6 referenced against TMS: (a) ruthenium propylidene initiator; (b) ruthenium PEO macroinitiator from 4-VBC functionalized PEO macromonomer; (c) ruthenium PEO macroinitiator from 3-VBC functionalized PEO macromonomer.

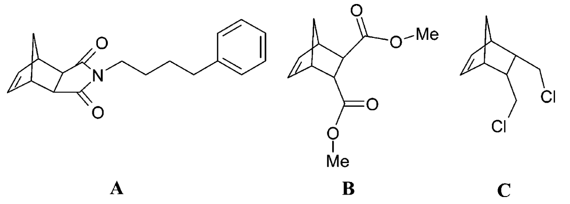


Figure 4. Norbornene derivatives used as monomers in block copolymer synthesis.

copolymers of varying molecular weights and compositions (Table 1). A range of molar ratios of PEO macroinitiator [MI] to monomer [M] were used, [M]/[MI] = 100, 200, and 500. In all cases the consumption of monomer was quantitative and in almost all cases the block copolymers have a narrow molecular weight distribution (1.1−1.2), consistent with a living polymerization technique. This suggests that the PEO macroinitiators are efficient initiators for ROMP of the norbornene derivatives used in this study. The value of the PDI reported for the block copolymers includes the presence of a small peak (less than 2% of the main peak) at lower elution volumes (b in Figure 5), which appears to be approximately double the molecular weight of the first peak and may result from some polymer−polymer coupling after the completion of polymerization. We have observed polymer−polymer coupling in some cases involving the ROMP of fluorinated norbornenes using Schrock's molybdenum initiators, which was attributed to reaction of the living chain end with molecular oxygen.[32] The decomposition mechanism for the Grubbs ruthenium initiators is reported to involve dissociation of a phosphine ligand followed by coupling of the two monophosphine species.[33] Then the biruthenium complex rearranges to give the dimer of the organic fragment of the alkylidene ligand. A similar decomposition pathway could presumably take place on a very small scale (less than 2%) in our system, after the polymerization is complete, resulting in the polymer−polymer coupling. The identity of the small peak will however be the subject of further studies.

The block copolymers were precipitated into hexane, a nonsolvent for PEO, and the corresponding polynorbornene homopolymers. In most cases SEC analysis showed a single well-defined peak corresponding to the block copolymer but in a couple of cases the SEC trace showed a small peak at the same elution volume as the PEO block (a in Figure 5). This PEO homopolymer is only present in 1−2% and probably results from the introduction of traces of impurities, possibly with the 4-VBC resulting in PEO that has not been end-functionalized.

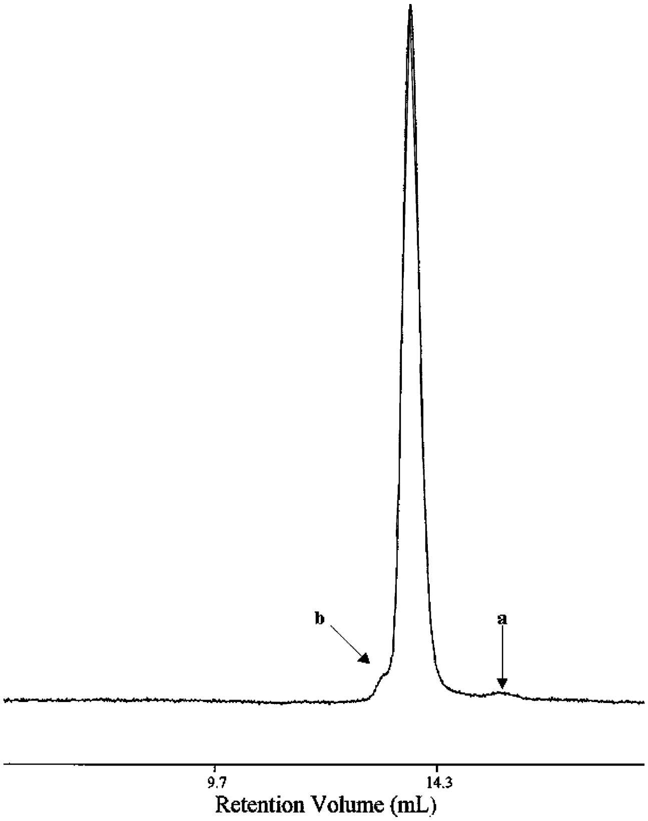


Figure 5. SEC chromatogram of a block copolymer prepared from PEO and monomer **B**. M_n (SEC) = 14 400 g mol^{-1}, PDI = 1.1 contaminated with a trace of PEO homopolymer M_n = 2400 g mol^{-1}, PDI = 1.06 (a). Peak b is at approximately double the molecular weight of the block copolymer and may result from polymer−polymer coupling.

The number-average molecular weights (M_n) of the block copolymers were calculated both by SEC and ^{1}H NMR. The values calculated by SEC are much smaller than the predicted molecular weights, the reason for this being that the copolymers were analyzed using a calibration curve generated from PEO/PEG standards. SEC columns separate the eluting polymers by molecular size (hydrodynamic volume) rather than molecular weight and since the block copolymers undoubtedly have different hydrodynamic properties to the standards we would not expect the data to be correct.[34] The three norbornene derivative monomers (**A**−**C**) were polymerized by ROMP initiated by Grubbs benzylidene initiator $RuCl_2(=CHPh)(PCy_3)_2$, in stoichiometries designed to produce homopolymers with degrees of polymerization (DP) of 100 for comparison with the block copolymers. All three polymers possessed good solubility in DMF and as expected DMF SEC produced molecular weight values significantly below the predicted in all cases. For instance, a homopolymer of monomer **A** produced a value for M_n of 17600 (PDI = 1.11) substantially lower than its theoretical value, $M_n = 29\,500$. Despite this, the SEC data from the block copolymers is useful for qualitative analysis and determination of polydispersity. To obtain a quantative measure of the molecular weights of the block copolymers we also calculated the M_n by ^{1}H NMR, by comparing the intensity of the methylene PEO (of known molecular weight) protons at 3.4 ppm to the olefinic protons of the polynorbornene backbone, which fall between 5 and 6 ppm. The values obtained for M_n agree well with the predicted values (Table 1).

The methodology used here is expected to open up the possibility of producing entirely novel materials with new and potentially interesting properties from combinations of monomers not previously possible. We are currently extending the range of block copolymers to include other monomers that maybe polymerized by anionic polymerization, e.g., styrene, dienes, and methacrylates.

Conclusions

In this study, we have shown for the first time that it is possible to synthesize block copolymers by transformation of living anionic polymerization into ROMP. ^{1}H NMR shows conclusively that the alkylidene exchange reaction to form the PEO macroinitiator is quantitative. Furthermore, upon addition of a series of norbornene derivatives to the PEO macroinitiator, block copolymers were synthesized with low polydispersity and molecular weights in good agreement with those predicted by the stoichiometry.

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