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Synthesis of Narrow-Distribution “Perfect” Polyethylene and Its Block Copolymers by Polymerization of Cyclopentene

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ABSTRACT: Polycyclopentene with controllable molecular weight and polydispersity below 1.1 was obtained by ring-opening metathesis polymerization (ROMP) of cyclopentene at room temperature using a commercial Mo-based ROMP initiator in the presence of trimethylphosphine. Polydispersities were kept low by limiting the degree of cyclopentene conversion. These narrow-distribution polycyclopentenes were catalytically hydrogenated to narrow-distribution linear polyethylenes, providing a facile route to model polyethylenes free from both short- and long-chain branching. The “living” nature of ROMP also permits the synthesis of well-defined diblock copolymers containing polycyclopentene, including poly(ethylidenenorbornene)−polycyclopentene diblocks. The hydrogenated derivatives of these diblocks represent a new type of crystalline−amorphous diblock, possessing much higher levels of crystallinity than when block copolymers containing anionically polymerized high-1,4-polybutadiene are hydrogenated.

Introduction

Block copolymers containing linear (high-density) polyethylene blocks have been of interest for at least 40 years,[1] and many investigators have pursued this elusive goal. Because of the efficiency with which Ziegler catalysts polymerize ethylene, most researchers have used such catalysts to synthesize the polyethylene, obtaining the block architecture either through an anionic-to-Ziegler transformation[2] or through the use of a tubular flow reactor with a judicious choice of catalyst and feed points.[3] However, the polyethylene blocks in these materials retain the broad molecular weight distributions characteristic of Ziegler catalyst products, complicating the elucidation of structure−property relationships and obscuring the connection between molecular architecture and microdomain morphology. A more “living” catalyst system would enable the synthesis not only of well-defined block copolymers but also of narrow-distribution polyethylene homopolymers for detailed studies of the physics of polyethylene (e.g., ref 4), for use as calibration standards, etc.

Classically, anionic polymerization has been used to synthesize near-monodisperse polymers and well-defined block copolymers from suitable monomers.[5] However, ethylene does not polymerize readily in the presence of typical carbanions. The reactivity of alkyllithiums toward ethylene can be greatly increased in the presence of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA), and in the 1960s butyllithium−TMEDA complexes were shown to oligomerize[6] and polymerize[7] ethylene. This system has been used to prepare both narrow-distribution polyethylene[8] and polyethylene-containing block copolymers;[9] however, the slow rate of ethylene polymerization and the room-temperature insolubility of polyethylene at high molecular weights made it possible to achieve narrow-distribution materials (PDI $\approx$ 1.1, where PDI = polydispersity index = M_w/M_n) only at very low polyethylene molecular weights (<2000 g/mol).

An alternative route to near-monodisperse polyethylene-like homopolymers and block copolymers is to use anionic polymerization to prepare a high-1,4-polybutadiene block, which is subsequently saturated. While this approach has been extensively and profitably employed in the study of polyethylene block copolymers,[10−12] the minor but unavoidable content of 1,2-additions in the polybutadiene block produces a saturated product which is essentially a random copolymer of ethylene with a minor amount of 1-butene. These butene units greatly reduce the melting point (to 100−115 °C) and degree of crystallinity (30−45 wt %, depending on exact polymerization conditions) of the “polyethylene” relative to the values for truly linear polyethylene (typically 130−135 °C and 70−80% crystallinity).[13]

The most successful routes to the preparation of narrow-distribution linear polyethylene and its block copolymers employ ring-opening metathesis polymerization (ROMP)[14−16] of monocyclic alkenes, followed by hydrogenation. Grubbs and co-workers[17,18] showed that polycyclobutene, which is structurally equivalent to all-1,4-polybutadiene, can be prepared with PDI < 1.1 via ROMP of cyclobutene, using well-defined tungsten and molybdenum alkylidene initiators in the presence of trimethylphosphine (PMe_3). Polycyclobutene prepared by this method was hydrogenated to give polyethylene with a peak melting point of 126 °C.[18] Furthermore, well-defined block copolymers of cyclobutene and norbornene were prepared via sequential monomer addition.[18] However, this method has not been widely adopted, largely because of technical challenges associated with the cyclobutene monomer, which is a gas at room temperature and is not commercially available.

Monocyclic alkenes or polyenes with carbon numbers above four are liquids or solids at room temperature, and a variety are commercially available; in principle, polymers of any of these could serve as suitable precursors to linear polyethylene. However, polymerization of such monomers with various well-defined tungsten and molybdenum catalysts[19] yielded products with polydispersities generally greater than 1.4 and often with number-average degrees of polymerization far in excess of the monomer:initiator ratio. A notable exception is

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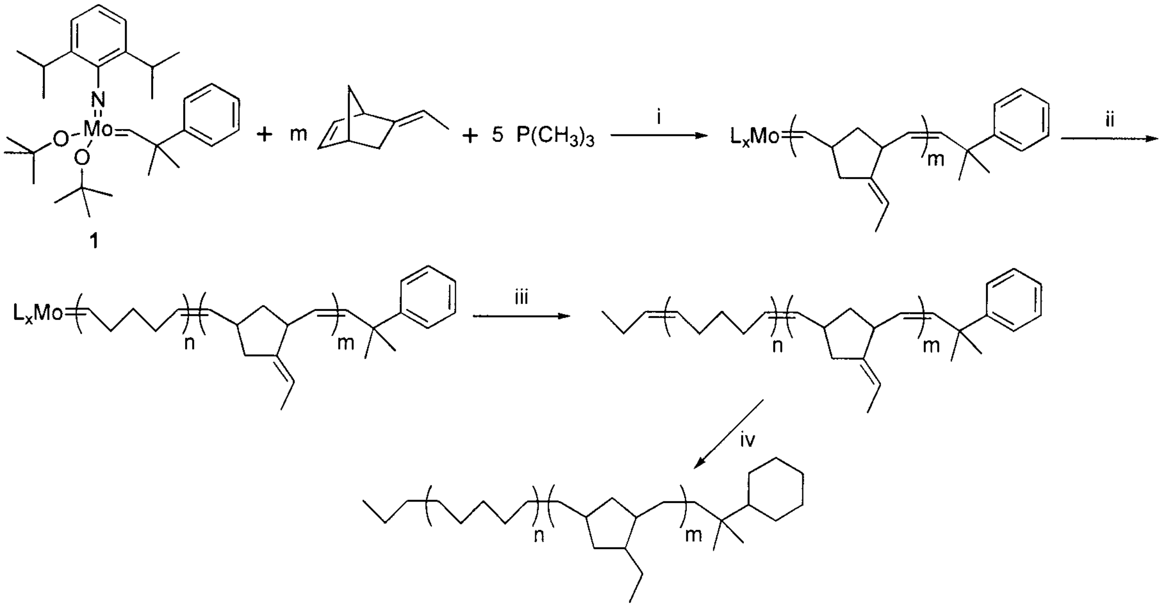
Scheme 1. Synthesis of Hydrogenated Polyethylidenenorbornene/Hydrogenated Polycyclopentene (HPEN/HPCP) Diblocks[a]



[a] (i) Toluene, room temperature, 1 h. (ii) Cyclopentene, room temperature, 1 h. (iii) Propionaldehyde, room temperature, 30 min. (iv) 500 psig of H_2, 100 °C, 80/20 v/v mixture of cyclohexane and THF, approximately 200 h. All other polymers described herein are prepared via subsets of this scheme.

cyclopentene polymerized with a well-defined tungsten initiator, which Schrock et al. had previously[20] shown to yield a “largely living” polymerization at −40 °C, producing narrow-distribution polymer (PDI < 1.1) with controllable molecular weights. Hydrogenation of polycyclopentene prepared by this process[21] yielded polyethylene with a melting point of 130 °C. This approach would also seem conducive to block copolymer synthesis, and it avoids the need to work with cyclobutene monomer. However, it has not been widely adopted either, as it requires the synthesis of the air- and moisture-sensitive tungsten alkylidene initiator; molybdenum alkylidene initiators with structures similar to those commercially available did not yield narrow-distribution polycyclopentene, even at −45 °C.[19] Furthermore, the need to run the reaction at such low temperatures (but above dry ice temperatures) complicates the synthesis of sizable batches of material.

Herein, we report the ROMP of cyclopentene using a commercially available molybdenum alkylidene initiator at room temperature in the presence of trimethylphosphine to yield near-monodisperse polycyclopentene, which was hydrogenated to give “perfect” polyethylene. The living nature of ROMP also permitted the synthesis of block copolymers with near-monodisperse polycyclopentene blocks, which were hydrogenated to yield block copolymers with “perfect” polyethylene blocks, as illustrated in Scheme 1.

Experimental Section

Materials. Toluene used as the solvent for polymerizations was dried over sodium benzophenone ketyl, degassed by freeze−pump−thaw cycles, and vacuum-transferred prior to use. Cyclopentene (96%) and trimethylphosphine were dried over sodium, degassed by freeze−pump−thaw cycles, and vacuum-transferred prior to use. 5-Ethylidene-2-norbornene (99%, mixture of endo and exo, denoted simply as ethylidenenorbornene throughout) was dried over sodium, distilled under reduced pressure, and degassed by freeze−pump−thaw cycles. Propionaldehyde was dried over magnesium sulfate, degassed by freeze−pump−thaw cycles, and vacuum-transferred. Benzaldehyde was dried over magnesium sulfate, distilled under reduced pressure, and degassed by freeze−pump−thaw cycles. Reduced palladium (5%) on calcium carbonate and 2,6-diisopropylphenylimidoneophylidenemolybdenum(VI) bis(*tert*-butoxide) (**1**) were purchased from Strem Chemicals, Inc., and used as received. Other solvents were obtained from commercial sources and used as received.

Methods and Procedures. Polymerizations were performed in flame-dried glassware under a nitrogen atmosphere in a drybox from Innovative Technology, Inc. ^{1}H NMR spectra were recorded on a General Electric QE 300. All signals were broad singlets or multiplets, and chemical shifts are reported in ppm relative to residual $CHCl_3$ ($\delta = 7.24$). Block copolymer compositions were determined from the ^{1}H NMR spectra by comparison with spectra of blends of the two homopolymers prepared at known weight ratios. Infrared spectra were recorded using a Nicolet 730 FTIR, and band intensities (at wavenumbers, cm^{-1}) are reported as strong (s), medium (m), or weak (w). Molecular weights and polydispersity indices were determined by gel permeation chromatography (GPC); except for the high-temperature GPC results explicitly noted, GPC analyses were run at room temperature using a Waters 515 HPLC pump, Waters model 410 differential refractometer detector, and two 30 cm Polymer Laboratories PLgel Mixed-C columns calibrated with high 1,4-polybutadiene standards that were obtained from Goodyear Chemicals, Polymer Laboratories, and American Polymer Standards. Molecular weights of polycyclopentene are reported versus these 1,4-polybutadiene standards due to their close structural similarity.[22] Block copolymer molecular weights[23] were determined from the change in polybutadiene-equivalent M_n between the first block and diblock (corresponding to the true polycyclopentene block molecular weight) and the diblock composition, typically as determined from ^{1}H NMR. Early work determined the compositions directly from GPC,[23] dividing the polybutadiene-equivalent molecular weights obtained for the polyethylidenenorbornene first block by 1.065. All hydrogenations were done in a 2 L Parr batch reactor. Thermal transition temperatures and heats of fusion were determined by differential scanning calorimetry at a scan rate of 10 °C min^{-1}, using a Perkin-Elmer DSC 7 calibrated with indium and mercury.

Polycyclopentene (PCP). A typical synthetic procedure for PCP is described below. In various runs, the monomer concentration, reaction time, monomer:initiator ratio, and PMe_3:initiator ratio were varied independently to investigate their effects. Toluene (25 mL), PMe_3 (13.2 μL, 0.127 mmol), and **1** (14 mg, 0.025 mmol) were combined in a 250 mL flask. Cyclopentene (9.0 mL, 100 mmol) was added to the reaction, the flask was sealed with a greased ground glass stopper, and the reaction was stirred for 1 h. Propionaldehyde (0.184 mL, 2.55 mmol) was then added to the solution, and the flask was sealed again with a greased ground glass stopper and stirred for 30 min. The solution was then concentrated under a stream of nitrogen and dripped into stirring acetone to give a white precipitate. The polymer product was redissolved in tetrahydrofuran (THF), reprecipitated into stirring acetone, and dried under vacuum to give 0.489 g of product with M_n = 28 100 g/mol and PDI = 1.05. ^{1}H NMR ($CDCl_3$): 5.36, 1.96, 1.37. IR (thin film): 3005 w, 2923 s, 2852 m, 2840 m, 1454 w, 1437 w, 965 s, 710 w.

Hydrogenation of PCP. PCP (1.71 g, M_n = 19 600 g/mol, PDI = 1.07) was dissolved in 750 mL of cyclohexane with 0.2 wt % (based on polymer) of butylated hydroxytoluene (BHT) routinely added to guard against decomposition. $Pd^0/CaCO_3$ (8.54 g, catalyst plus support) was added to the solution. Hydrogenation conditions were set at 400 psig of H_2 and 80 °C. The polymer was completely saturated after 22 h, as determined by FTIR using the trans stretch at 965 cm^{-1} (detection limit 1 double bond per 4000 carbons). The catalyst was subsequently separated from the polymer solution by hot filtration. The polymer was isolated by precipitation into methanol and dried in a vacuum oven to give 1.0 g of polyethylene (57% yield). M_n = 20 400 g/mol; PDI = 1.12 by high-temperature GPC.[22,24] IR (thin film): 2918 s, 2849 m, 1473 w, 1463 w, 730 w, 719 w.

Polyethylidenenorbornene (PEN). Toluene (124 mL) and **1** (34 mg, 0.062 mmol) were combined in a 250 mL flask. Ethylidenenorbornene (2.80 mL, 20.8 mmol) was added to the reaction, the flask was sealed with a greased ground glass stopper, and the reaction was stirred for 2 h. Propionaldehyde (0.446 mL, 6.18 mmol) was then added to the solution, and the flask was sealed again with a greased ground glass stopper and stirred for 30 min. The solution was then concentrated under a nitrogen stream and dripped into stirring acetone to give a white precipitate. The polymer product was redissolved in THF, reprecipitated into stirring acetone twice, and dried under vacuum to give 2.48 g of product (99% yield). M_n = 52 500 g/mol (vs polybutadiene standards); PDI = 1.08. ^{1}H NMR ($CDCl_3$): 5.42−5.10, 3.28, 3.15, 2.90, 2.48, 2.28, 2.09, 1.92, 1.55, 1.18. IR (thin film): 3030 w, 2945 s, 2920 s, 2880 m, 2854 s, 2830 w, 1449 m, 1420 w, 1378 w, 965 s, 827 w, 738 w.

Hydrogenation of Polyethylidenenorbornene (PEN). PEN (1.50 g, M_n = 46 900 g/mol vs polybutadiene standards, PDI = 1.04) was dissolved in 700 mL of an 80/20 v/v mix of cyclohexane and THF with 0.2 wt % BHT (based on polymer). $Pd^0/CaCO_3$ (5.07 g) was added to the solution. Hydrogenation conditions were set at 500 psig of H_2 and 100 °C. $Pd^0/CaCO_3$ (5.10 g) was added to the reactor after 48 h for a total catalyst addition of 10.17 g. The progress of hydrogenation was monitored by observing the disappearance of the stretches at 826 cm^{-1} (exocyclic double bond) and 965 cm^{-1} (backbone trans double bond) in the infrared spectrum. The polymer showed complete saturation from FTIR and ^{1}H NMR after 89 h (detection limit approximately 3% residual unsaturation by both techniques). The catalyst was subsequently separated from the polymer solution by hot filtration. The polymer was isolated by precipitation into methanol and dried under vacuum to give 0.80 g of product (53% yield). M_n = 39 800 g/mol vs polybutadiene standards; PDI = 1.04. ^{1}H NMR ($CDCl_3$): 1.96−0.68. IR (thin film): 2956 m, 2920 s, 2872 m, 2852 m, 1458 w, 1376 w.

PEN−PCP Block Copolymer. Toluene (66 mL), PMe_3 (65.0 μL, 0.628 mmol), and **1** (69 mg, 0.126 mmol) were combined in a 250 mL flask. Ethylidenenorbornene (2.81 mL, 20.9 mmol) was added to the reaction, the flask was sealed with a greased ground glass stopper, and the reaction was stirred for 1 h. A small aliquot of the reaction mixture was then removed for GPC analysis of the PEN block. Cyclopentene (22.10 mL, 251 mmol) was then added to the stirring reaction, and the flask was sealed again with a greased ground glass stopper. The aliquot containing the first block was then quenched with a few drops of benzaldehyde. After allowing the cyclopentene to polymerize for 1 h, propionaldehyde (0.906 mL, 12.6 mmol) was then added to the solution, and the flask was sealed again with a greased ground glass stopper and stirred for 30 min. The solution was then concentrated under a stream of nitrogen and dripped into stirring acetone to give a white precipitate. The polymer product was redissolved in THF, reprecipitated into stirring acetone twice, and dried under vacuum to give 4.91 g of product. First block M_n = 20 600 g/mol (vs polybutadiene standards); PDI < 1.03. Block copolymer M_n = 41 200 g/mol (vs polybutadiene standards); PDI = 1.07. Weight fraction of cyclopentene estimated by GPC = 0.52, yielding a true diblock M_n = 39 800 g/mol. ^{1}H NMR ($CDCl_3$): 5.42−5.10, 3.27, 3.15, 2.90, 2.47, 2.28, 2.09, 1.96, 1.55, 1.37, 1.19. IR (thin film): 3010 w, 3005 w, 2922 s, 2853 m, 1452 w, 1437 w, 1377 w, 965 s, 827 w, 738 w.

Hydrogenation of PEN−PCP Block Copolymer. The PEN−PCP diblock described above (4.91 g) was dissolved in 1000 mL of an 80/20 v/v mix of cyclohexane and THF with 0.2 wt % BHT (based on polymer). $Pd^0/CaCO_3$ (10.44 g) was added to the solution. Hydrogenation conditions were set at 500 psig of H_2 and 100 °C. Additional $Pd^0/CaCO_3$ was charged to the reactor after 67 h (19.64 g) and 116 h (7.43 g). FTIR showed complete saturation after 212 h. The catalyst was subsequently separated from the polymer solution by hot filtration. The polymer was isolated by precipitation into methanol and dried under vacuum to give 3.95 g of product (80% yield). M_n = 34 200 g/mol (vs linear polyethylene standards); PDI = 1.15 by high-temperature GPC.[24] IR (thin film): 2955 w, 2849 s, 2918 s, 1473 w, 1462 w, 1376 w, 730 w, 720 w.

Results and Discussion

Synthesis of Near Monodisperse Polycyclopentene. We found that cyclopentene could be polymerized by $Mo(NAr)(CHCMe_2Ph)(O\text{-}t\text{-}Bu)_2$ (**1**) (Ar = 2,6-diisopropylphenyl) in the presence of PMe_3 at room temperature to yield polycyclopentene with narrow molecular weight distributions (PDI < 1.1). As previously reported with a similar tungsten alkylidene initiator,[20] we found that polycyclopentenes with broader molecular weight distributions (PDI typically 1.8) were obtained when the polymerizations were performed under identical reaction conditions but omitting PMe_3. Polymerization in the absence of PMe_3 also proceeded much more rapidly, as gauged by viscosity buildup of the solutions.

In studies of the polymerization of cyclobutene with a tungsten alkylidene initiator, Grubbs and co-workers[17] showed that PMe_3 binds reversibly to the propagating species far more strongly than it does to the initiating species, due to the bulk neophylidene ligand on the initiator (which is replaced by the growing polymer chain after initiation). The catalyst sites bound by PMe_3 are less active (or inactive) for polymerization, so propagation is slowed considerably relative to initiation, and polycyclobutene with well-controlled molecular weight and narrow molecular weight distribution was obtained.[17,18] Grubbs and co-workers[17] also reported a similar effect of PMe_3 in yielding narrow-distribution polycyclobutene when polymerization was initiated with a molybdenum initiator closely similar to that employed here. We thus infer that PMe_3 is operating in a similar manner in our cyclopentene polymerizations initiated by **1**, slowing the rate of propagation and producing narrow-distribution polycyclopentene.

However, a major difference between cyclobutene and cyclopentene polymerizations is that the smaller ring strain present in the cyclopentene monomer leads to a significant monomer concentration at equilibrium[16] and hence to facile depropagation events. Indeed, Schrock and co-workers showed that "living" polycyclopentene can depolymerize under reduced pressure to regenerate the original metal alkylidene initiator in high yields.[20] Consequently, cyclopentene polymerizations must be run above the equilibrium monomer concentration to yield *any* polymer, and polymerizations should be restricted to conversions well below the equilibrium value to avoid broadening of the molecular weight distribution through propagation−depropagation equilibration. These two factors motivated the systematic study of reaction conditions and the kinetic modeling described below, so that narrow-distribution polycyclopentene (PCP) of precisely targeted molecular weight could be obtained. All polymerizations were run at room temperature (approximately 23 °C). Standard polymerization conditions were as follows: initial cyclopentene concentration 3.0 M; monomer:initiator molar ratio 2000:1; PMe_3:initiator molar ratio 5:1; 1 h polymerization (≈15% conversion). Each of these reaction parameters was systematically altered to probe its effect on the M_n and PDI of the resultant polymer.

Effect of Monomer Concentration. To estimate the value of the equilibrium monomer concentration $[M]_{eq}$, we initially ran a series of experiments following the cyclopentene synthesis described above, but with the polymerization time shortened to 30 min and at variable cyclopentene concentrations. No polymer was detectable by GPC when the starting monomer concentration was 1.27 M or below, but a distinct quantity of low molecular weight polymer was formed when the starting monomer concentration was 1.41 M; adding additional monomer charges to this reaction mixture and measuring after 30 min increments showed a steady increase in molecular weight. Therefore, we estimate $[M]_{eq}$ as 1.3 M. As the synthesis of substantial quantities of narrow-distribution PCP mandates that syntheses be carried out well away from $[M]_{eq}$, all further polymerizations were run at 2.8−9.0 M (bulk cyclopentene is 11.4 M at room temperature).

Increasing the starting monomer concentration from 2.8 to 9.0 M increased the polymer molecular weight only modestly and did not significantly increase the polydispersity, as shown in the first block in Table 1. Since polymerizations were run for a fixed time and to low conversion, one might expect the conversion and hence the molecular weight of the polymer to increase roughly linearly as monomer concentration is increased at a fixed starting monomer:initiator ratio ($[M]_0/[I]$). However, since the PMe_3:initiator ratio ($[P]_0/[I]$) is also held fixed, an increase in monomer concentration is accompanied by an increase in PMe_3 concentration, which slows propagation. This effect is captured in the kinetic model described below.

Reaction Time. Preliminary experiments clearly showed that both M_n and PDI increased with reaction time. Since conversion must be kept low to limit depropagation events and ensure low PDI, a standard reaction time of 1 h was adopted early in this work. The second block in Table 1 shows a representative example of the effect of reaction time; the sublinear increase in M_n with time is expected for a reaction that is first-order in monomer. With $[M]_{eq} = 1.3$ M, the M_n at equilibrium conversion in the 3 h experiment ($[M]_0 = 3.2$ M) would be 86 000 g/mol, so the reaction reached only 40% of the equilibrium conversion; the PDI (1.09) for the polymer produced in this reaction is still low but significantly higher than the PDI = 1.04 obtained after only 1 h of polymerization.

Table 1. Effect of Reaction Conditions on Polycyclopentene M_n and PDI

run	$[M]_0$ (mol/L)[a]	$[M]_0/[I]$[b]	$[P]_0/[I]$[c]	t_p (h)[d]	M_n (g/mol)	PDI
1	2.8	2000	5.0	1.0	19 600	1.07
2	6.0	2000	5.0	1.0	22 900	1.05
3	9.0	2000	5.0	1.0	25 100	1.06
4	3.5	2050	5.9	1.0	17 500	1.04
5	3.2	1770	6.0	3.0	35 100	1.09
6	2.9	2000	2.0	1.0	29 800	1.23
7	3.0	2000	3.0	1.0	25 000	1.11
8	3.0	2000	4.0	1.0	21 500	1.09
1	2.8	2000	5.0	1.0	19 600	1.07
4	3.5	2050	5.9	1.0	17 500	1.04
9	3.0	980	4.9	1.0	14 200	1.07
1	2.8	2000	5.0	1.0	19 600	1.07
10	3.0	4010	5.0	1.0	28 100	1.05
11	3.0	6000	5.0	1.0	42 200	1.05
12	3.0	8100	5.0	1.0	53 400	1.08
13	3.0	10000	5.0	1.0	67 800	1.08

[a] Starting monomer (cyclopentene) concentration. [b] Starting monomer:initiator (**1**) molar ratio. [c] PMe_3:initiator (**1**) molar ratio. [d] Polymerization time prior to quenching with propionaldehyde.

PMe_3:Initiator Ratio. The number of equivalents of PMe_3 present in the reaction (PMe_3:initiator molar ratio, $[P]_0/[I]$, varied from 2 to 5.9) had a significant impact on the M_n and PDI values of the resulting polymers, as shown in the third block in Table 1. Increasing the PMe_3 concentration slows the overall rate of propagation by decreasing the fraction of "free" catalyst centers, thus reducing the conversion and M_n. With $[M]_{eq} = 1.3$ M, the M_n at equilibrium conversion for $[M]_0 = 3.0$ M and $[M]_0/[I] = 2000$ would be 77 000 g/mol; the highest M_n observed is less than 40% of this maximum value, so all polymerizations were indeed terminated well short of the equilibrium conversion. More dramatically, increasing the PMe_3:initiator ratio greatly decreased the polymer PDI to <1.1 for ratios of 4 and above. Since increased PMe_3 also leads to a reduction in M_n for a fixed polymerization time, a compromise of 5 equiv of PMe_3 was adopted for most of this work.

Monomer:Initiator Ratio. As expected, M_n increased strongly with the initial cyclopentene:initiator ratio, $[M]_0/[I]$. PCP with M_n ranging from 14 000 to 68 000 g/mol was synthesized, as shown in the bottom block of Table 1. Figure 1 illustrates the essentially linear relationship between M_n and $[M]_0/[I]$ when all other reaction conditions are held constant. This simple correlation permits the straightforward synthesis of PCP with a specific molecular weight using these reaction conditions.

Kinetic Model. The polymerization data given in Table 1 can be quantitatively understood through a simple kinetic model. The rate of disappearance of monomer M is assumed to be first-order in monomer concentration and first-order in "active" (uncomplexed) initiator concentration, and reversibility of the reaction leads to a significant equilibrium monomer concentration $[M]_{eq}$:

$$-\frac{d[M]}{dt} = f\,k_1[I]([M] - [M]_{eq}) \tag{1}$$

where k_1 is the polymerization rate constant and f is the fraction of "active" catalyst sites C, namely those

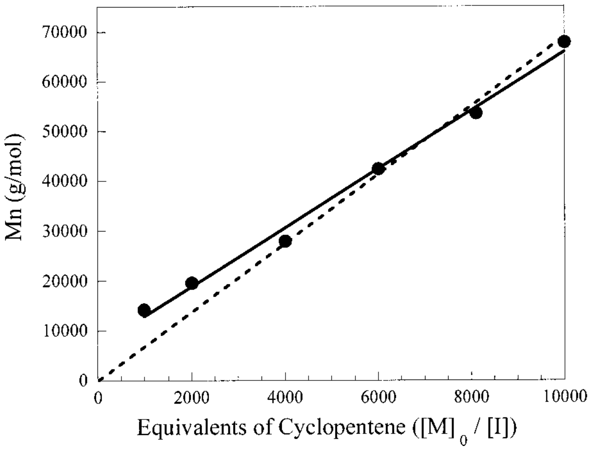


Figure 1. Effect of starting monomer:initiator ratio ([M]$_0$/[I]) on number-average molecular weight of polycyclopentene; data corresponding to bottom block of Table 1. Reaction conditions: room temperature, $[M]_0 = 2.8-3.0$ M, $[P]_0/[I] = 4.9-5.0$, $t_p = 1$ h. Solid line shows least-squares fit to the data; dashed line shows prediction of eq 3 with $k_1/K_{eq} = 0.72$ h^{-1}.

that are uncomplexed through reaction with phosphine P ($C + P \rightleftarrows C{\cdot}P$, equilibrium constant K_{eq}, complex C·P assumed inactive for polymerization):

$$K_{eq} = \frac{[C{\cdot}P]}{[C][P]} \approx \frac{1}{f([P]_0 - [I])} \tag{2}$$

where the total concentration of initiator $[I] = [C] + [C{\cdot}P]$, the total concentration of phosphine $[P]_0 = [P] + [C{\cdot}P]$, and the approximation employed in the right equality is valid for small values of f, consistent with the large value of K_{eq} measured by Wu et al.[17] for a related tungsten alkylidene active center. Since the polymerizations are taken to low conversion, we may roughly approximate [M] in eq 1 by its initial value [M]$_0$, leading to the following result for M_n:

$$M_n = m_0\left(\frac{k_1 t_p}{K_{eq}}\right)\left(\frac{1}{\left(\frac{[P]_0}{[I]} - 1\right)}\right)\left(\frac{[M]_0 - [M]_{eq}}{[M]_0}\right)\left(\frac{[M]_0}{[I]}\right) \tag{3}$$

where t_p is the polymerization time and m_0 the monomer molecular weight. Equation 3 qualitatively captures all the features observed in our experiments: weak increase in M_n with [M]$_0$ (at fixed [M]$_0$/[I] and [P]$_0$/[I], block 1 of Table 1); strong decrease in M_n with increasing [P]$_0$ (at fixed [M]$_0$ and [I], block 3 of Table 1); and strong increase in M_n with increasing [M]$_0$/[I] (at fixed [M]$_0$ and [P]$_0$/[I], block 4 of Table 1). In particular, eq 3 predicts that the data points plotted in Figure 1 should describe a straight line passing through the origin; for comparison, a dashed line (corresponding to $k_1/K_{eq} = 0.72$ h^{-1} in eq 3) is shown.

Though eq 3 makes the effects of various reaction parameters clear, for quantitative evaluation, the integrated form of eq 1 should be used, rather than setting $[M] = [M]_0$. The full result is

$$M_n = m_0\left(\frac{[M]_0 - [M]_{eq}}{[M]_0}\right)\left(\frac{[M]_0}{[I]}\right)(1 - e^{-k_1 t_p/K_{eq}[([P]_0/[I])-1]}) \tag{4}$$

The data in Table 1 are adequately described by eq 4 with $k_1/K_{eq} = 0.9$ h^{-1}. This parameter value yields calculated M_n values within 25% of experimental for all but two cases, which represent extrema in the series: run 6 (calculated M_n exceeds experimental by 50%), which showed the highest PDI (>1.2), and run 9 (calculated M_n low by 45%), which had the lowest M_n value (<15 000 g/mol). The parameter whose effect is least-well described by the model is the PMe$_3$:initiator ratio (block 3 of Table 1); the experimental variation of M_n with [P]$_0$/[I], though substantial, is smaller than predicted. While further investigation may reveal subtleties not captured in this simple kinetic model, eq 4 with $k_1/K_{eq} = 0.9$ h^{-1} at room temperature provides a working description of the reaction kinetics, especially for the cases of principal interest (narrow PDI, $M_n > 15\,000$ g/mol).

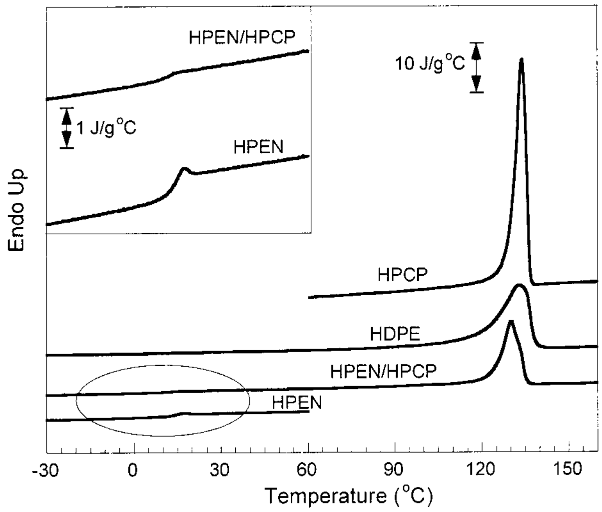


Figure 2. DSC traces, top to bottom: HPCP ($M_n = 20\,200$ g/mol); commercial HDPE (UCC-6097); HPEN/HPCP diblock (total $M_n = 39\,800$ g/mol, 52 wt % HPCP); HPEN homopolymer (PEN precursor $M_n = 46\,900$ g/mol vs polybutadiene standards). Inset shows the HPEN glass transition region for both the HPEN homopolymer and HPEN/HPCP diblock.

Synthesis of Near-Monodisperse Linear Polyethylene from PCP. Near-monodisperse PCP was completely hydrogenated to yield near-monodisperse linear polyethylene. Pd^0 on CaCO$_3$ was chosen as the hydrogenation catalyst because it cleanly hydrogenates high-1,4-polybutadiene to an ethylene/butene copolymer without causing any cross-linking or chain scission.[25] Figure 2 shows the differential scanning calorimetry (DSC) trace for polyethylene prepared by hydrogenating PCP ($M_n = 19\,600$ g/mol, PDI = 1.07). The HPCP exhibits a peak melting temperature $T_m = 133$ °C and an 82% crystallinity (taking 277 J/g as the value for 100% crystalline polyethylene[26]). These values are comparable to those for linear polyethylene obtained, for example, by hydrogenation of poly(octenylene) prepared by acyclic diene metathesis polymerization.[27] For comparison, Figure 2 also includes the DSC trace of a commercial high-density polyethylene (Union Carbide UCC-6097), which shows a broader endotherm with a peak $T_m = 133$ °C (identical to the hydrogenated polycyclopentene, HPCP) and a slightly lower crystallinity of 70%. We attribute the narrower endotherm and higher crystallinity of the HPCP to its narrower molecular weight distribution; more detailed morphological characterization is underway.

ROMP of Ethylidenenorbornene and Hydrogenation of Polyethylidenenorbornene (PEN). ROMP of ethylidenenorbornene using a ruthenium complex has

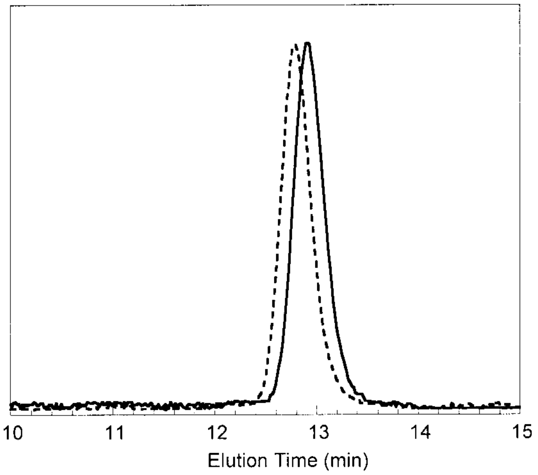


Figure 3. GPC traces of PEN homopolymer (M_n = 46 900 g/mol vs polybutadiene, dashed curve) and its hydrogenated product (HPEN, solid curve). Curves are superimposable with a simple shift in elution time, due to the change in hydrodynamic volume upon hydrogenation.

been reported in the literature,[28] though no characterization of the product was reported. Ethylidenenorbornene was polymerized with **1** in this study to give polymers with PDI < 1.1; unlike cyclopentene, the higher ring strain in the bicyclic ethylidenenorbornene permits it to be polymerized to essentially complete conversion. Comparison experiments run under identical conditions but with PMe_3 added ($[P]_0/[I] = 5$) showed no effect of PMe_3 on the molecular weight distribution of the resultant polymer and no obvious effect on rate (as gauged by solution viscosity increase). These observations suggest that the greater chain cross section of polyethylidenenorbornene (as compared with that of polycyclopentene) inhibits binding of PMe_3 to the catalyst site when ethylidenenorbornene is being polymerized; hence, PMe_3 plays no significant role.

The hydrogenated polyethylidenenorbornene, HPEN, is amorphous with a glass transition temperature of 15 °C, as shown by DSC in Figure 2. Since HPEN is easily soluble at room temperature, analysis by GPC was straightforward; as shown in Figure 3, the elution time trace of the hydrogenated product can be fully superimposed on that of the unhydrogenated precursor with a simple shift in elution time to account for the differences in hydrodynamic volume. This is an important point to note, given the longer times required for hydrogenation of polyethylidenenorbornene (see Experimental Section) compared with polycyclopentene and other polydienes hydrogenated previously in our laboratory.

Interestingly, the high-M component commonly observed in ROMP polymerizations[18,29] was not observed in any of the syntheses described here, with or without PMe_3, though our GPC system is easily capable of revealing broad minor peaks at the commonly quoted level of 2 wt %. Narrow minor peaks (<10% of total) at twice the molecular weight of the primary peak were occasionally observed in the ethylidenenorbornene polymerizations and in the first-block samples from the diblock polymerizations described below and are attributed to end coupling of two polymer chains through bimolecular termination with trace oxygen.[30,31] (Though such coupling peaks are absent from Figure 3, they are evident in Figure 4, described in the following section.) These coupling peaks were not included in calculating polymer PDI values. Similarly, small shoulders were occasionally observed on the high-molecular-weight end of the PCP or diblock GPC traces. These shoulders were not easily resolved from the main peak and hence were included in PDI calculations. The difference in appearance (resolved peak vs shoulder) results from the time variation of the polymerization rate in the two cases. As the ethylidenenorbornene polymerization rate decays exponentially with time as full conversion is approached, most coupling occurs when the chains have grown to nearly their full length, producing material having twice the main product molecular weight. Since the cyclopentene polymerization rate is nearly constant with time up to the limited conversions employed, coupled material with a range of molecular weights (with an upper limit of twice the main product molecular weight) is obtained.

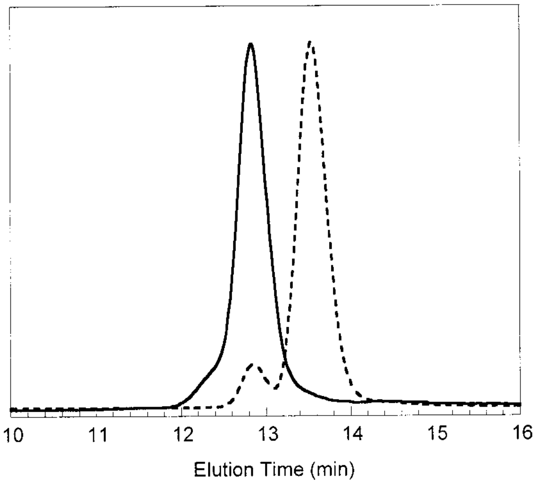


Figure 4. GPC traces of PEN/PCP block copolymer (solid curve; 52 wt % PCP, diblock M_n = 39 800 g/mol) and its first (PEN) block (dashed curve). Minor peak/shoulder eluting just prior to the main peak in each trace is attributed to coupling.[30,31]

Synthesis of Block Copolymers with Perfect Polyethylene Blocks. Block copolymers with perfect polyethylene blocks were synthesized by hydrogenating PEN/PCP block copolymers synthesized through the sequential addition of monomer charges. Because the cyclopentene is not polymerized to complete conversion, it is important that it be the last monomer added. Ethylidenenorbornene was first polymerized by **1** in the presence of PMe_3. Cyclopentene was then added to the solution once all of the ethylidenenorbornene monomer was consumed. Finally, the polymerization was terminated with propionaldehyde in a Wittig-like reaction to give PEN/PCP block copolymers with PDI < 1.1. Specific end groups can be placed on ROMP-synthesized polymers through the choice of aldehyde used to quench the polymerization.[32] Propionaldehyde was chosen so as to cap the polycyclopentene block with a linear propyl group; upon hydrogenation, this yields polyethylene blocks that are defect-free from end to end. Figure 4 shows GPC traces of a sample of the PEN first block taken during a diblock synthesis, as well as the trace of the PEN/PCP diblock. Small coupling peaks are evident in both traces, as discussed above; however, the peak corresponding to the main product is narrow in both cases, and negligible terminated first block is seen, demonstrating the formation of well-defined block copolymers.

Figure 2 shows the DSC trace of this HPEN/HPCP diblock, which exhibits an HPEN glass transition at 13 °C and an HPCP (polyethylene) peak melting temperature of 130 °C. The degree of crystallinity of the HPCP, normalized for its content in the diblock, is 77 wt %, consistent with the 82 wt % crystallinity measured for the HPCP homopolymer to within the combined uncertainty. These DSC results for the HPCP/HPEN diblock indicate that it is cleanly microphase separated, though it is unclear at present whether this reflects incompatibility of the blocks in the melt or simply crystallization of the polyethylene block from a single-phase melt.[33] This question and other aspects of the morphology of these materials will be the subject of further reports.

Conclusions

Cyclopentene was polymerized at room temperature using a commercially available ROMP initiator in the presence of PMe$_3$ to give polycyclopentene with a polydispersity index below 1.1. Though cyclopentene cannot be polymerized to complete conversion, narrow-distribution polycyclopentene of targeted molecular weight can be obtained through proper control of reaction conditions (monomer:initiator ratio, PMe$_3$:initiator ratio, monomer concentration, reaction time). The effects of these reaction parameters on M_n are adequately described through a simple kinetic model. Hydrogenation of polycyclopentene yields a narrow-distribution linear polyethylene, with a melting point and degree of crystallinity at least equal to conventional high-density polyethylene. Well-defined polyethylidenenorbornene/polycyclopentene diblocks were also synthesized by sequential monomer addition and hydrogenated to yield polymers containing defect-free polyethylene blocks. The hydrogenated diblocks are cleanly microphase-separated at room temperature. These rubbery−crystalline diblocks should prove useful as model crystalline−amorphous block copolymers containing high-crystallinity blocks and may be compared with previously studied diblocks where the "polyethylene" block (hydrogenated high-1,4-polybutadiene) exhibits a significantly lower crystallinity and melting point.[10−12,33]

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