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Synthesis of Narrow Dispersed Linear Polyethylene and Block Copolymers from Polycyclobutene†

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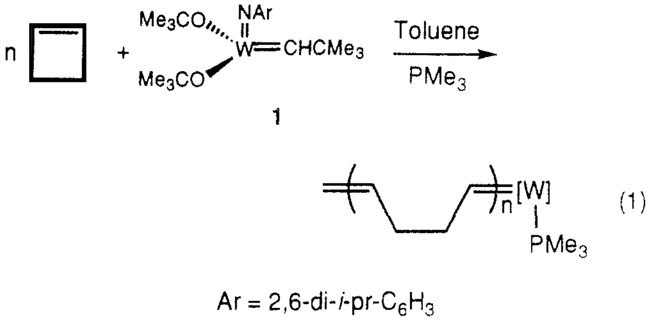
ABSTRACT: Near monodispersed linear polyethylene can be synthesized y hydrogenation of polybutadiene prepared by the living ring-opening metathesis polymerization (ROMP) of cyclobutene. The polyethylene is highly crystalline, as determined by powder X-ray diffraction, and defect free, as shown by spectroscopic data. Living polycyclobutene can also react with anthracene dialdehyde to give a labeled polymer and with norbornene to produce a block copolymer.

Introduction

Polyethylene is an important commercial material and monodispersed linear polyethylene has long been both a synthetic challenge and theoretical interest.[1] Low polydispersity polyethylene has been synthesized by hydrogenation of 1,4-polybutadiene prepared by anionic polymerization of 1,3-butadiene. This approach results in branched polyethylene, since the polybutadiene produced by this technique contains C_2 branches as a result of the low level of 1,2-polymerization of 1,3-butadiene.[1]

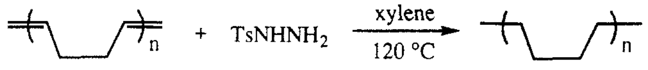
Recently, we reported the development of a new living polymerization system based on the ROMP[2] of cyclobutene (eq 1), which has resulted in the synthesis of polybutadiene with narrow dispersity.[3]



This paper reports the synthesis and characterization of the first linear near monodispersed ($M_w/M_n < 1.1$) polyethylene as well as the formation of narrow dispersed block copolymers from the reaction of the intermediates of the "living" polycyclobutene with an aldehyde or norbornene.

Results and Discussion

Synthesis and Characterization of Near Monodispersed Polyethylene from the Hydrogenation of Polycyclobutene. Near monodispersed polybutadiene can be prepared by ROMP of cyclobutene in the presence of PMe_3.[3] The polymer was characterized by ^1H and ^{13}C NMR and IR spectroscopy. The spectroscopy data are consistent with a perfectly linear polybutadiene.[4] The polybutadiene can be readily hydrogenated to saturated linear polyethylene using tosyl hydrazide in xylene at 120 °C (eq 2). Analysis of the ^1H (δ 1.56 ppm) and ^{13}C (δ 29.82 ppm) NMR spectroscopy data (in C_6D_5Cl, 100 °C) of the resulting hydrogenated polymer is consistent with a perfectly linear polyethylene.[5] The absence of a C—H stretch at 3002.1 cm^{-1} in the IR spectrum shows that the hydrogenation is complete. The resulting polyethylene exhibits a melting point at 126 °C measured by differential scanning calorimetry (DSC) (Figure 1).[6a] Analysis of the powder X-ray diffraction pattern (Figure 2) of the polyethylene sample indicates that the polymer is highly crystalline and the crystallinity is greater than 95%.[6b-d]



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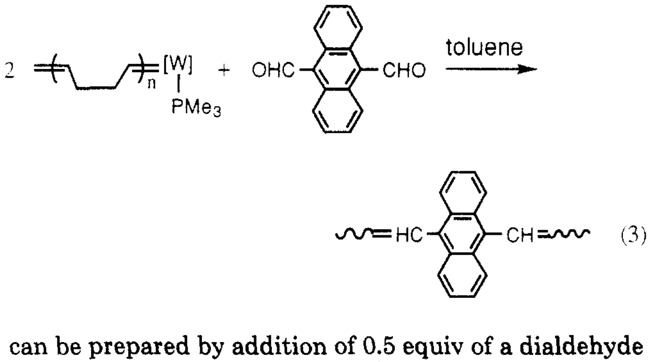
Reaction of Living Polycyclobutene with Aldehyde or Ketone. The reaction of living polycyclobutene with aldehydes and ketones was also investigated. The preparation of monodispersed polybutadiene or polyethylene with a fluorescence moiety in the center of the polymer chain is of interest since this type of material may serve as a luminescence probe to study the local mobility of the polymer chain.[7] As a demonstration of this possibility, anthracenedialdehyde is used to couple living polycyclobutene in a Wittig-like reaction (eq 3). The polymer can be prepared by addition of 0.5 equiv of a dialdehyde to a solution of living polybutadiene prepared by polymerizing cyclobutene in the presence of PMe_3. The GPC trace shows two peaks corresponding to a major coupled polymer peak and a minor homopolymer peak. The molecular weight of the coupled polymer is twice that of the homopolymer and exhibits a narrower polydispersity. The homopolymer that resulted from the incomplete coupling can be separated from the coupled polymer by fractional precipitation.[8] The living polycyclobutene can also react with acetone. The reaction, however, is extremely slow and requires extended reaction time to reach completion even in the presence of a large excess of acetone.



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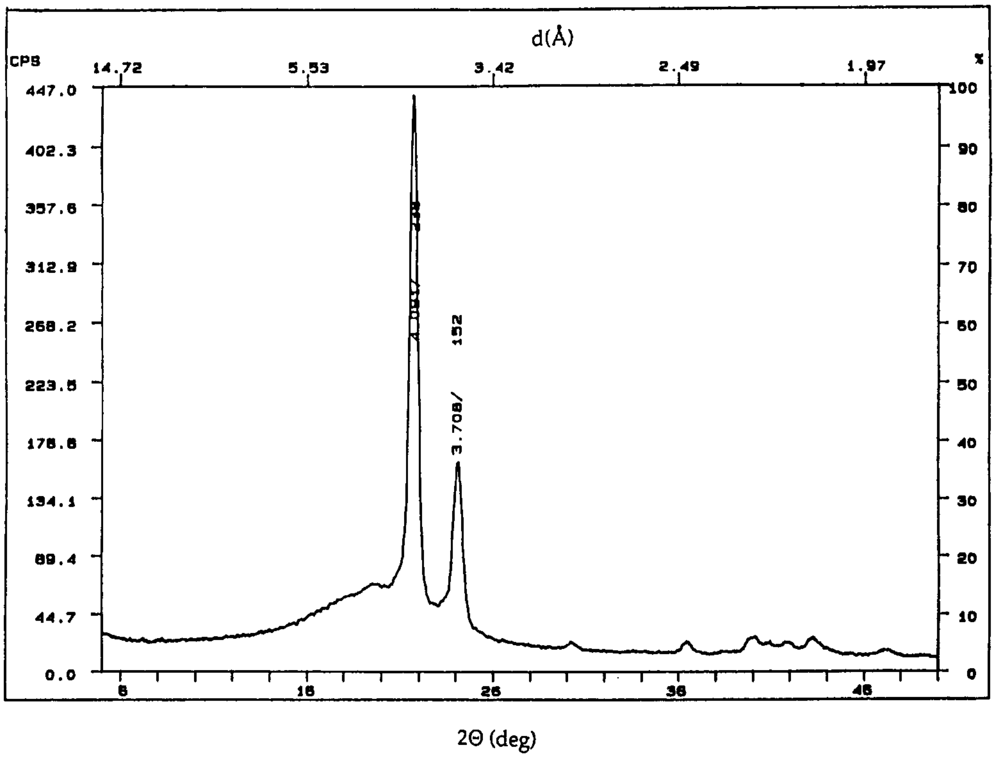


Figure 1. Powder X-ray diffraction data of polyethylene prepared by hydrogenation of polycyclobutene.

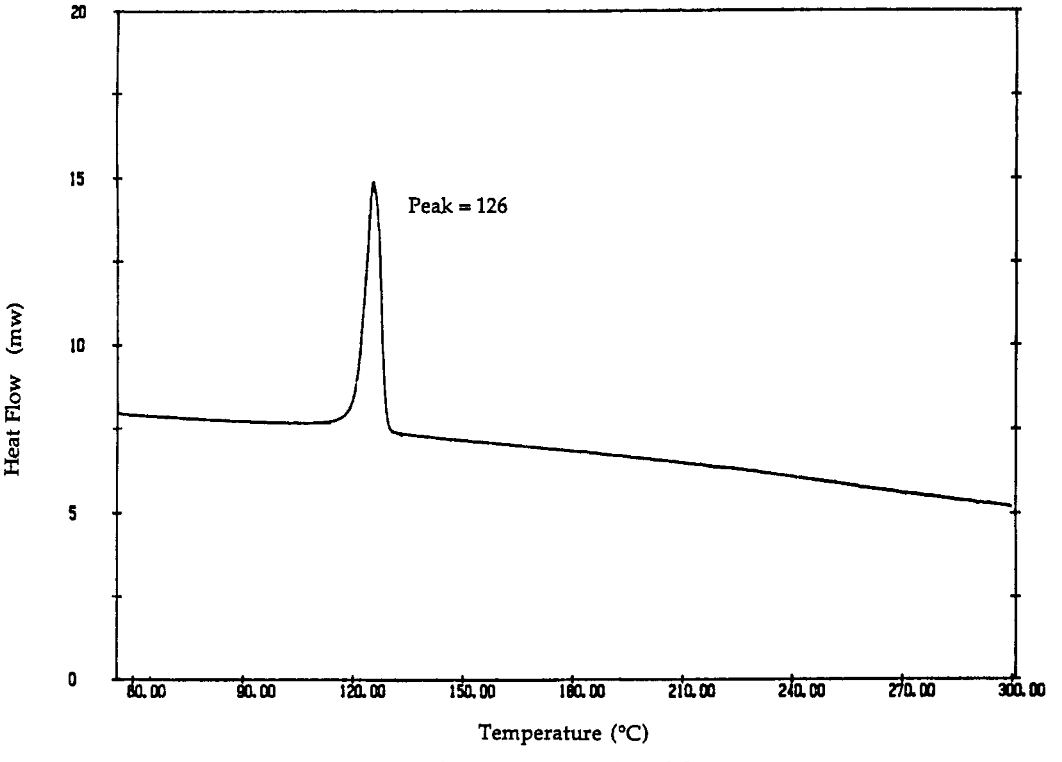
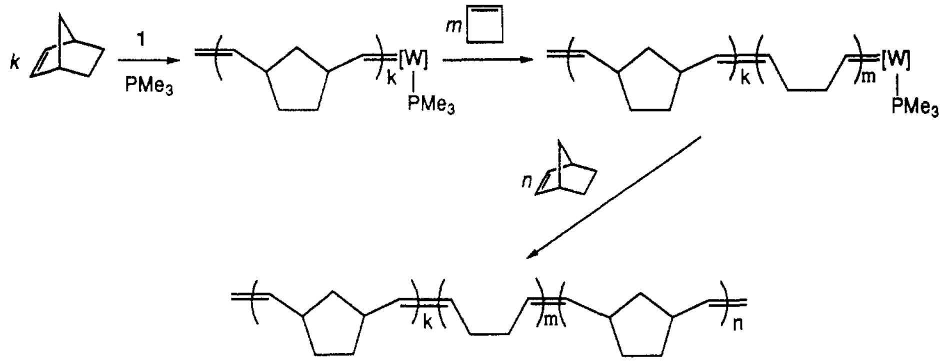


Figure 2. DSC profile of polyethylene prepared via hydrogenation of polycyclobutene.

Reaction of Living Polycyclobutene with Norbornene. The most convenient way to prepare a block copolymer of the A–B or A–B–A type is the sequential addition of monomers to a living polymerization system.[9] The block copolymer formed by hydrogenation of polynorbornene-*block*-polybutadiene is a potential thermoplastic and the narrow dispersed copolymer should exhibit phase separation into microdomains.[10] The formation of block copolymers employing the living polycyclobutene and polynorbornene systems was investigated. As shown in Scheme 1, when 5 equiv of PMe_3 was added to a toluene solution of polynorbornene prepared by polymerizing 26 equiv of norbornene with 1 (0.008 M), two alkylidene species were observed at 11.21 and 10.29 ppm corresponding to the two (*anti* and *syn*) PMe_3-bound propagating alkylidenes of polynorbornene.[3] When 32 equiv of cyclobutene was added to the above solution, all the resonances corresponding to the propagating species of polynorbornene were displaced by two new resonances at 11.30 and 10.38 ppm corresponding to the propagating species of polycyclobutene. When the polymerization was complete, another 35.5 equiv of norbornene was added to the mixture, the two propagating species corresponding to polycyclobutene disappeared, and resonances corresponding to the propagating species of polynorbornene reappeared. This observation indicates the formation of

Scheme 1



a polynorbornene–polycyclobutene–polynorbornene triblock copolymer. The preparation of diblock copolymers of polynorbornene and polycyclobutene was also investigated by either adding cyclobutene to a living polynorbornene in the presence of PMe_3 or in the reverse sequence. For example, 48 equiv of norbornene was polymerized in toluene followed by sequential addition of 9 equiv of PMe_3 and 18 equiv of cyclobutene. The diblock polymer obtained has a molecular weight of 17 200 and a PDI of 1.04. Reversing the order of addition, after 16 equiv of cyclobutene had been polymerized in the presence of 10 equiv of PMe_3, we added 48 equiv of norbornene to produce a diblock copolymer with M_n = 23 700 and PDI = 1.08.

On the basis of these diblock experiments, the preferred order of addition is to add cyclobutene to the living polynorbornene solution in the presence of PMe_3. Since PMe_3 binds more strongly to the less bulky propagating carbene of the polycyclobutene than to the propagating carbene of polynorbornene, the rate of the first insertion of cyclobutene, k_i, into the living polynorbornene will be faster than the rate of the subsequent propagation, k_p, to form the polycyclobutene block. The diblock prepared in this manner will be expected to have a narrower polydispersity and a better-defined molecular structure. In the formation of both diblock copolymers, small peaks (less than 2%) resulting from high molecular weight polymers were also observed in the GPC. In most cases reported in the past where this type of catalyst was employed in the ROMP of strained olefins, such high molecular weight fractions have been observed.[11]

Conclusion

We have demonstrated the synthesis of the first linear near monodispersed polyethylene through the hydrogenation of near monodispersed polycyclobutene. The polyethylene was characterized by spectroscopic and thermal techniques and powder X-ray diffraction. The polymer exhibits a high degree of crystallinity due to the absence of defects. The living polycyclobutene can also react with anthracenedialdehyde to form a narrow dispersed polymer and react with norbornene to give diblock or triblock copolymers. The ROMP technique provides an excellent route to the synthesis of model polymer systems.

Experimental Section

General Procedures. All manipulations of air- and/or moisture-sensitive compounds were carried out using standard Schlenk or vacuum-line techniques or in a N_2-filled drybox. Argon was purified by passage through a column of BASF RS-11 (Chemlog) and Linde 4 Å molecular sieves. ^1H NMR spectra were recorded on a JEOL GX-400 MHz (399.65 MHz ^1H; 100.4 MHz ^{13}C; 61.25 MHz ^2H) or a QE-Plus 300 MHz (300.1 MHz ^1H; 75 MHz ^{13}C) spectrometer. Gel permeation chromatography (GPC) utilized Shodex KF-803, KF-804, and KF-805 columns and a Knauer differential refractometer or a Waters-ALC-150C GPC. Calibration was based on narrow dispersity polystyrene standards (Polyscience) ranging from M_n = 3 550 to 600 000. Powder X-ray diffraction was performed on a Scintag/USA PAD V powder X-ray diffractometer using Cu Kα radiation. Infrared spectra were recorded using a Perkin-Elmer 1600 series FT-IR spectrometer. Differential scanning calorimetries were performed on a Perkin-Elmer PC Series DSC-7 at a heating rate of 10 °C/min.

Materials. $W(CH\text{-}t\text{-}Bu)(O\text{-}t\text{-}Bu)_2(NAr)$ (1) (Ar = 2,6-diisopropylphenyl) was prepared according to literature procedures.[11a] Toluene was distilled from sodium benzophenone ketyl. Norbornene was distilled from Na. Acetone-d_6 was dried over B_2O_3. Benzaldehyde was washed with 10% Na_2CO_3 and saturated Na_2SO_3, then dried over $MgSO_4$, and distilled under reduced pressure. Xylene was dried over 4 Å molecular sieves. All the purified solvents were stored under Ar or N_2.

Hydrogenation of Polycyclobutene. In a typical experiment, 68 mg of polycyclobutene was dissolved in 3.0 mL of xylene in a small Schlenk tube. To the above solution was added 1.5 g (6.4 equiv relative to the repeating unit) of tosyl hydrazide and a trace amount of BHT. The mixture was then degassed twice via a freeze–pump–thaw cycle and a reflux condenser was assembled under Ar. The Schlenk tube was heated to 110 °C. At 98 °C, a homogeneous solution resulted and nitrogen started to evolve. The solution was stirred at 110–120 °C for 3 h until the evolution of nitrogen stopped. The solution was cooled to room temperature and precipitated into methanol. The polymer collected was washed with dilute HCl and several times with hot water. The white cottonlike material was further purified by dissolving in hot cyclohexane and reprecipitating into methanol. The polymer was dried in vacuo overnight, yield 60 mg (85%; M_n = 85 000, PDI < 1.1). ^1H NMR (400 MHz, C_6D_5Cl): δ 1.56. ^{13}C NMR (100.4 MHz, C_6D_5Cl): δ 29.82. Anal. Calcd for $(CH_2)_n$: C, 85.7; H, 14.3. Found: C, 85.6; H, 13.94.

Reaction of Polycyclobutene with Aldehyde and Ketone. (A) Reaction with 9,10-Anthracenedialdehyde. In the drybox, 0.0031 g of catalyst 1 was dissolved in 0.8 mL of toluene in a small flask equipped with a Teflon valve. After the addition of 5.6 μL of PMe_3 (10 equiv), the flask was brought out of the drybox and 53.4 mg (183 equiv) of cyclobutene was added. The mixture was then stirred at room temperature for 1.5 h before 57.46 μL (0.0469 M) of 9,10-anthracenedialdehyde in pyridine was added using a gastight syringe. The color of the solution gradually became red. The resulting solution was stirred at room temperature for 3 h before it was added to methanol and the polymer collected was analyzed by GPC, which showed two peaks corresponding to the coupled polymer (M_n = 54 000, PDI = 1.05) and homopolymer (M_n = 27 000, PDI = 1.06).

(B) Reaction with Acetone. In the drybox, 0.0027 g of catalyst 1, 0.4 mL of toluene, and 4.0 μL of PMe_3 (8.3 equiv) were weighed into an NMR tube. The tube was brought out of the drybox and 0.15 mL of 1.6 M cyclobutene solution was added using a gastight syringe at −78 °C. The reaction was then monitored by ^1H NMR spectroscopy. When the reaction was nearly complete (99%), 10 μL of acetone-d_6 was added to the tube. After 7 h, the polymer was isolated by precipitation in methanol. The end group was observed by ^2H NMR spectroscopy. ^2H NMR (61.25 MHz, C_6H_6): δ 1.57, 1.65. Integration against an internal standard showed that 83% of the polymer was end-capped by acetone.

Formation of Triblock Copolymers. Inside the drybox, 0.0023 g of catalyst 1 was weighed into an NMR tube and dissolved with 0.5 mL of toluene-d_8. Then 2 μL of PMe_3 and 25 mg of norbornene were added into the tube sequentially. The tube was brought out of the drybox, and the reaction was monitored by ^{1}H NMR spectroscopy. When the polymerization was complete in 0.5 h, 1.3 mL of 1.6 M cyclobutene in toluene-d_8 was added using a syringe. Upon completion of this reaction, 13 mg of norbornene was added into the NMR tube. After the reaction was complete, the solution was added to methanol. The GPC of the precipitated polymer showed two peaks. The minor higher molecular weight peak was for M_n = 184 000, PDI = 1.05, and the main lower molecular weight peak (triblock copolymer) corresponded to M_n = 8300, PDI = 1.08.

Preparation of Diblock Copolymers. Inside the drybox, a small flask equipped with a Teflon valve was charged with 0.003 g of catalyst 1 and 0.4 mL of toluene. To the above solution was added using a syringe 23.6 mg of norbornene dissolved in 0.3 mL of toluene. After the mixture was stirred at room temperature for 0.5 h, 40 μL of toluene containing 1.2 M PMe_3 was added by syringe followed by 48.3 mg of cyclobutene via vacuum transfer. The resulting mixture was stirred at room temperature for 0.5 h and then 10 μL of benzaldehyde was added. The content of the flask was added dropwise to rapidly stirring methanol. The polymer was collected, dried in vacuo overnight (70%), and analyzed by GPC (M_n = 17 200, PDI = 1.04).

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