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Synthesis and characterization of poly[(2-trimethylsilyl-2-cyclopentene-1,4-diyl)vinylene]

Derek A. Stonich and William P. Weber*

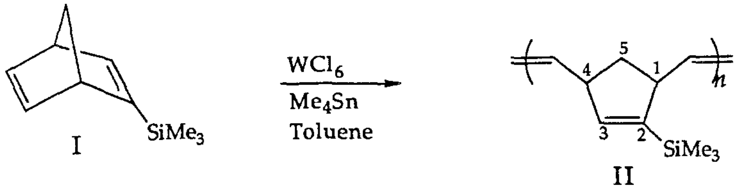
D. P. and K. B. Loker Hydrocarbon Research Institute, Department of Chemistry, University of Southern California, Los Angeles, CA 90089-1661, USA

SUMMARY

Ring opening metathesis polymerization (ROMP) of 2-trimethylsilylbicyclo [2.2.1]-hept-2,5-diene (I) with a tungsten hexachloride/tetramethyltin co-catalyst system yields poly[(2-trimethylsilyl-2- cyclopentene-1,4-diyl) vinylene] (II). The product polymer (II) has been characterized by ^{1}H, ^{13}C, ^{29}Si, IR and UV-VIS spectroscopy. Its molecular weight distribution has been determined by gel permeation chromatography (GPC), its thermal stability by thermogravimetric analysis (TGA) and its glass transition temperature (T_g) by differential scanning calorimetry (DSC).

INTRODUCTION

Ring opening metathesis polymerization (ROMP) of cyclic olefins to yield unsaturated hydrocarbon polymers has been extensively studied. (1) More recently, examples of ROMP of functionalized cyclic olefins to give functionalized unsaturated hydrocarbon polymers have been reported. (2-4) As part of our effort to synthesize polymers which are capable of facile chemical modification as well as to develop polymeric coupling agents, (5) we should like to report our results on the ROMP of I. Vinyl silanes are well known to undergo regiospecific electrophilic desilation reactions. (6) Application of this concept to the chemical modification of polymeric vinyl silanes has been reported. (7,8) In this regard, II may have considerable utility.



Equation 1

EXPERIMENTAL

^{1}H, ^{13}C and ^{29}Si NMR spectra were obtained using a Bruker AM-360 MHz FT NMR spectrometer. ^{13}C NMR spectra were acquired with broad band proton decoupling. One percent solutions in chloroform-*d* were used to obtain all NMR spectra. ^{1}H and ^{13}C NMR spectra were internally referenced to chloroform. ^{29}Si NMR spectra were externally referenced to tetramethylsilane in chloroform-*d* and acquired using an inverse gated heteronuclear decoupling sequence (NONOE). (9) IR spectra of neat films were recorded on a Perkin-Elmer PE-281 spectrometer on NaCl plates.

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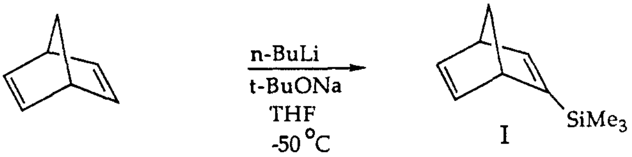
*To whom offprint requests should be sent

GPC analysis of the polymer molecular weight distribution was performed on a Waters system comprised of a U6K injector, a 510 pump, a R401 differential refractometer and an 820 Maxima Control system. A Waters 7.8 mm x 30 cm, 10 µm, cross-linked polystyrene gel column was used. HPLC grade THF at a flow rate of 0.6 mL/min was used as the elution solvent. Retention times were calibrated against monodisperse polystyrene standards of molecular weight 612,000, 114,200, 47,500, 18,700 and 5,120 having M_w/M_n of less than 1.09.

Thermal stability of the polymer was determined by TGA. A Perkin-Elmer TGS-2 with nitrogen flow rate of 40 cm^3/min was used. The temperature profile used was; 50°C for 10 min followed by heating at a rate of 4°C/min to 750 °C. The glass transition temperature(Tg) was determined using a Perkin-Elmer DSC-7 differential scanning spectrometer. The temperature profile began at -100°C and increased at a rate of 20°C/min to 150°C.

Toluene was distilled from sodium benzophenone ketyl immediately prior to use. WCl_6 and Me_4Sn were used as received from Aldrich. All reactions were carried out under a nitrogen atmosphere in flame dried glassware.

2-Trimethylsilylbicyclo[2.2.1]hepta-2,5-diene (I) was prepared according to a literature method. (10) It had spectral properties in agreement with literature values. (11) ^{13}C NMR δ: 155.73, 153.26 143.18 142.34 74.08, 53.28, 51.93, -2.10. ^{29}Si NMR δ: -9.6.



Equation 2

ROMP of 2-Trimethylsilylbicyclo[2.2.1]hepta-2,5-diene (I)

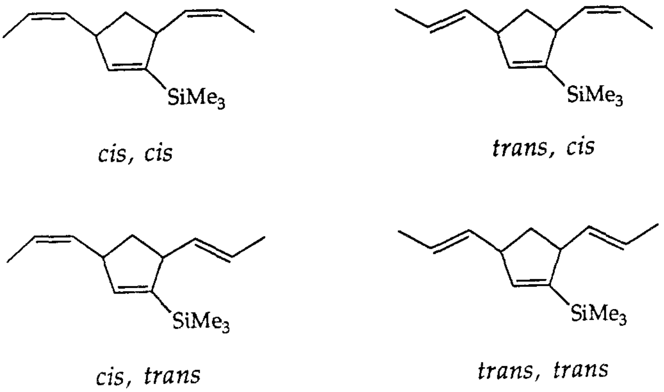
The reaction was carried out in a dry 50 mL round bottom flask which contained a Teflon-covered magnetic stirring bar and was sealed with a rubber septum. The WCl_6 (30 mg) was weighted into a round bottom flask in a Vacuum Atmospheres dry box. Toluene (10 mL) and 40 µL of Me_4Sn were added by syringe. Initially, the solution is a deep burgundy or red-black color. The mixture was stirred for approximately 3 minutes, before addition of I (370 mg) via syringe. Almost instantly, the solution changes to a yellow-gold color and its viscosity increases. Within 1 h the mixture is completely gelled. The reaction was allowed to stand for 4 h at room temperature, prior to quenching it by addition of 50 mL of methanol. The solvents were removed by evaporation under reduced pressure. The residue was dissolved in CCl_4 and filtered to remove insoluble material. Most of the solvent was removed by evaporation under reduced pressure. The polymer was then precipitated by addition of methanol. A light yellow solid (170 mg, 46%) was recovered. It had the following properties: ^{1}H δ: 5.82(br.m, 1H), 5.25(br.m,2H), 3.67(br.s,1H), 3.25(br.s,1H), 2.30(br.s,1H), 1.24(br.s,1H), 0.04(br.s,9H). ^{13}C NMR δ: 148.18, 145.53, 134.66, 134.20, 133.13, 132.11, 53.84, 50.69, 48.02, 45.90, 40.58, -0.77. ^{29}Si NMR δ: -9.03. IR γ: 2959, 1725, 1250, 1039, 1600, 835 and 750 cm^{-1}. UV-VIS: 239.2 nm, ε = 136. GPC: Mw/Mn = 86,166/25,903. T_g = 108°C. Elemental analysis: Calc: C, 73.09; H, 9.81; Si, 17.10. Found: C, 71.80; H, 9.68.

RESULTS AND DISCUSSION

ROMP of I proceeds regioselectively with opening of the disubstituted carbon-carbon double bond in preference to the trimethylsilyl substituted carbon-carbon double bond. This result was anticipated since ROMP of cycloalkenes is generally sensitive to steric effects, such that disubstituted carbon-carbon double bonds undergo ring opening in preference to trisubstituted ones. Nevertheless, the only reported example of ROMP of a silyl substituted cycloalkene involves opening of a trimethylsilyl substituted carbon-carbon double bond. Specifically, Katz et al. have reported the ROMP of 1-trimethylsilylcyclobutene catalyzed by $[Ph_2C{=}W(CO)_5]$ yields E-poly(2-trimethylsilyl-2-butene). (12)

ROMP of I yields a polymers whose ^1H, ^{13}C and ^{29}Si NMR spectra can be analyzed in terms of four microstructures (Figure 1). The variable feature of these microstructures is the stereochemistry of the vinylene units bonded at C_1 and C_4. These can be *cis,cis; cis,trans; trans,cis* and *trans,trans*. Four groups of resonances (45.7, 47.8, 50.6, and 53.9 ppm) assigned to methine carbons are

These are distinguished by the stereochemistry of the adjacent vinylene group and their proximatity to the trimethylsilyl group. Each of these four groups is further split. This undoubtedly results from the orientation (head to head, head to tail, tail to head or tail to tail) of adjacent 2-trimethylsilylcyclopent-2-ene groups as well as other factors. The relative intensity of these methine signals is approximately 1:1:1:1. This is consistent with a *cis/trans* ratio of approximately 50/50. This is in agreement with the results reported by Feast and Wilson for the ROMP of various fluorinated bicyclo[2.2.1]hepta-2,5-diene monomers using a WCl_6/Ph_4Sn catalyst system. (2) Two signals for the methine hydrogens are observed in the ^1H NMR (3.67 and 3.25 ppm). The high field resonance is assigned to the methine hydrogen which is proximate to the trimethylsilyl group.



cis, cis

trans, cis

cis, trans

trans, trans

Figure 1. Polymer (II) microstructures.

A group of peaks centered at 40.2 ppm is assigned to the methylene units C_5 of II. Apparently, these are less sensitive to the differences in stereochemistry of the vinylene groups. Two signals of equal intensity are observed for the methylene hydrogens in the ^1H NMR (2.30

and 1.24 ppm). Two distinct environments for the methylene hydrognes result from the *syn* orientation of the vinylene groups bonded to C$_1$ and C$_4$ of the cyclopentene ring (Figure 2). Single resonances are observed in the ^{1}H (0.04 ppm), observed in the ^{13}C NMR.

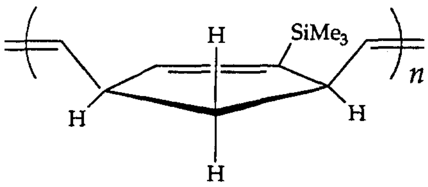
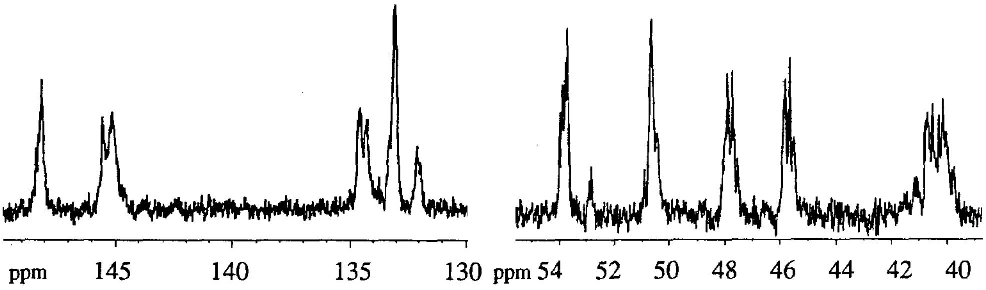
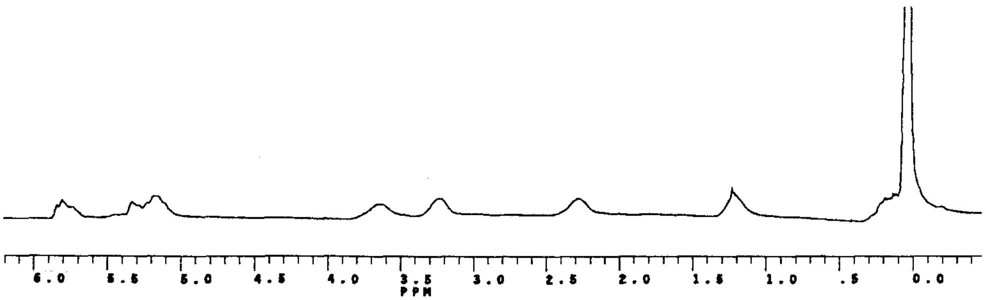


Figure 2. Orientation of methylene hydrogens in II.

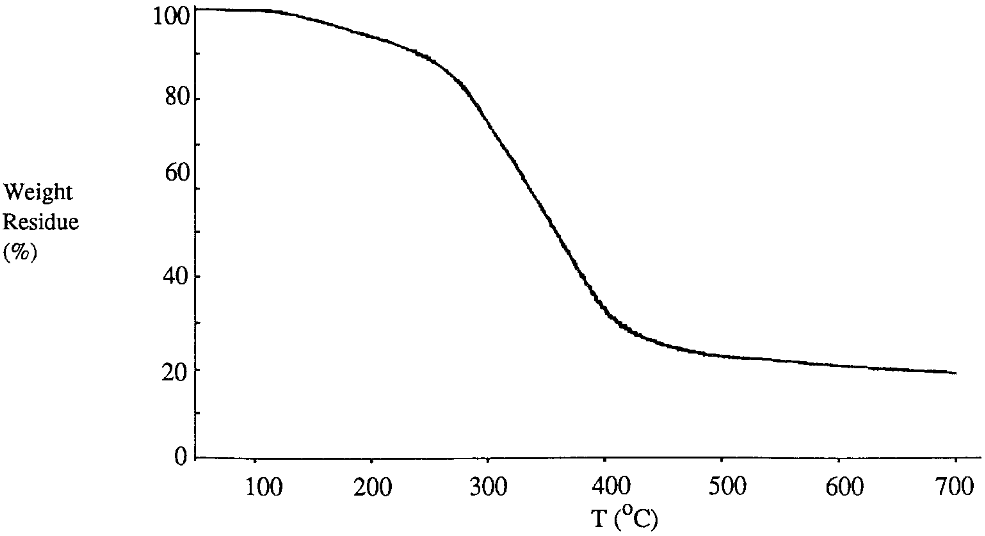
^{13}C (-0.77 ppm) and ^{29}Si (-9.03 ppm) NMR for the trimethylsilyl group. Presumably, the trimethylsilyl group is insensitive to microstructure. The vinyl carbons give rise to two sets of resonances. The first are due to cis and trans- vinylene carbons (134.7, 134.2, 133.1, and 132.1 ppm), while the latter are due to the vinyl carbons of the 2-trimethylsilylcyclopent-2-ene ring (148.3, 145.5, and 141.2 ppm). Presumably the trimethylsilyl substituted vinyl carbons only give rise to a single signal (148.1 ppm) due to a lack of sensitive to the stereochemical differences of neighboring vinyl groups. This assignment is consistent with the ^{13}C chemical shift for the trimethylsilyl substituted vinyl carbon in I. (11) Two broad resonances are observed for the vinyl hydrogens in the ^{1}H NMR (5.82 and 5.25 ppm, 1:2). The low field resonances is assigned to the C$_3$-hydrogen.



Vinyl region ^{13}C spectra of II *(above, left)*; Aliphatic region ^{13}C spectra of II *(above, right)*; ^{1}H spectra of II *(below)*.



The thermal stability of II has been determined by TGA. II is only stable to 125°C. Between 125 and 275°C the polymer slowly loses fifteen percent of its initial weight. Between 275 and 400°C more rapid decomposition occurs. Twenty-five percent of the initial weight remains at 400°C. Above 700°C there is a black residue accounting for 19% of the initial weight.



Residual weight versus temperature

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