Macromolecules 1985, *18*, 869-871

Poly(acetylene-*co*-ethylene) via Isomerization of Poly(1,3-butadiene)

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ABSTRACT: The potassium *tert*-butoxide catalyzed isomerization of poly(1,3-butadiene) in THF/Me_2SO is reported. UV–vis, infrared, and NMR spectra indicate positional isomerization of double bonds leading to conjugated segments of ~10 double bonds. The length of conjugation is independent of the reaction temperature but is affected by the strength of the base employed. A sample isomerized for 7 days exhibited a conductivity of $5 \times 10^{-7}\ \Omega^{-1}\ cm^{-1}$ upon iodine doping.

Introduction

Significant effort has recently been directed toward syntheses of soluble polymers containing a conjugated polyene structure with the objective of preparing processable organic polymers exhibiting electronic conductivity. This research includes the preparation of graft copolymers[1-3] and substituted poly(diacetylenes)[4-6] as well as the modification of preformed soluble polymers.[7-13] From this vantage we have viewed poly(1,3-butadiene) (1) as an alternating copolymer of acetylene and ethylene and report herein our efforts toward its modification to a soluble conducting polymer.

$$\left(CH_2{-}CH_2{-}CH{=}CH\right)_n$$

1

$$\left[\left(CH_2{-}CH_2\right)_x\left(CH{=}CH\right)_y\right]_n$$

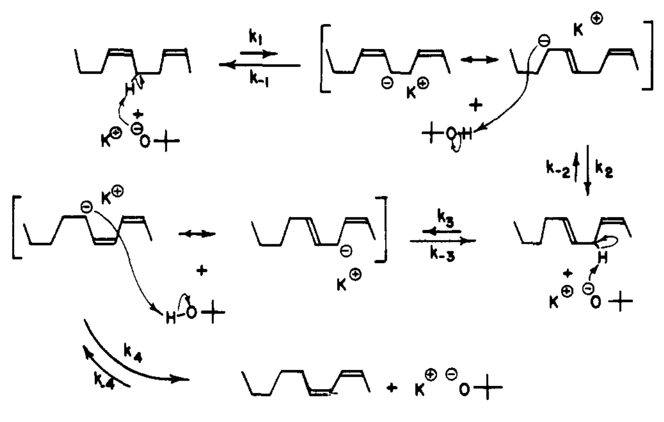
2

Poly(1,3-butadiene) (1) is enthalpically the least stable isomer of poly(acetylene-*co*-ethylene) (2), and if a reaction coordinate were available via which positional isomerization of double bonds could occur, 1 would isomerize to a more blocky poly(acetylene-*co*-ethylene). The resonance energy for conjugated dienes obtained from combustion data and heats of hydrogenation is 3–4 kcal/mol.[14] Entropic factors should tend to randomize double bonds along the chain; thus the blockiness of the copolymer should be dependent on the temperature of isomerization. Recently the alkaline-catalyzed isomerization of poly(butadiene) and its copolymers has been reported to yield polymers containing conjugation lengths of two and three units, thereby producing materials with superior drying characteristics.[15-18]

Experimental Section

Materials. Polybutadiene (random cis–trans mixture, MW = 100 000) was obtained from Scientific Polymer Products and dried by swelling with benzene and then removing the solvent at reduced pressure. Dimethyl sulfoxide (Aldrich Gold Label) and dimethyl-d_6 sulfoxide (Aldrich Gold Label) were distilled from calcium hydride at 70 °C (7 mm) and stored under nitrogen. Benzene and tetrahydrofuran (Fisher HPLC grade) were distilled from sodium benzophenone dianion and stored under nitrogen. Benzene-d_6 (Aldrich Gold Label) and acetonitrile (Aldrich HPLC grade) were distilled from calcium hydride trap to trap on a vacuum manifold and stored under nitrogen. Calcium hydride, potassium *tert*-butoxide, and potassium hydride (35 wt % dispersion in mineral oil) were obtained from Aldrich and used without further purification. Methanol (Fisher reagent grade) was degassed by three consecutive freeze–pump–thaw cycles in a Teflon flask prior to use. Cyclopentadiene was prepared by cracking dicyclopentadiene (Aldrich) prior to use.

Scheme I



Infrared spectra of films cast on sodium chloride plates were recorded on a Perkin-Elmer 283. UV–vis spectra were obtained on polymer solutions using anaerobic cells and a Perkin-Elmer Lambda 3A spectrometer. Proton NMR spectra of samples prepared in sealed tubes were recorded at 90 MHz using a Perkin-Elmer R32 spectrometer. Conductivity of films cast from the reaction solution, washed with methanol, and mounted on two platinum electrodes was measured at room temperature and 0.05 mm with a Fluka multimeter. Iodine doping entailed exposing the electrode-mounted film to dry solid iodine for 4 h at room temperature (initial pressure 0.05 mm).

Isomerization of Polybutadiene. Poly(butadiene) (1.0 g) was weighed into a clean, dry, degassed, and tared Schlenk tube containing a Teflon-coated stirring bar. The flask was capped, evacuated, and then flushed with nitrogen before 90 mL of THF was introduced via syringe. The mixture was stirred to dissolve the polymer. Potassium *tert*-butoxide (2.24 g) in 10 mL of Me_2SO was added dropwise via syringe to the stirred polymer solution. The reaction was followed in the early stages by UV–vis spectrophotometry of this reaction mixture in sealed cuvettes. Later stages were characterized both by this method and by analysis of the polymer obtained by precipitation with methanol. This procedure was followed at 0, 25, and 80 °C. Isomerization reactions using other bases were carried out in similar fashion: Potassium acetonitrilide was prepared from 2 M potassium dimsyl and excess acetonitrile. Potassium dimsyl was prepared from potassium hydride and Me_2SO.[19] Potassium cyclopentadienide was prepared by adding 5 mL (excess) of cyclopentadiene to an isomerization reaction initiated with potassium *tert*-butoxide.

Results and Discussion

Addition of potassium *tert*-butoxide in Me_2SO to THF solutions of poly(1,3-butadiene) induces positional isomerization of the double bonds and formation of conjugated structures. The most obvious indication of conjugation is the visual change from a colorless to a blue-black solution; changes in proton NMR, infrared, and UV–vis spectra

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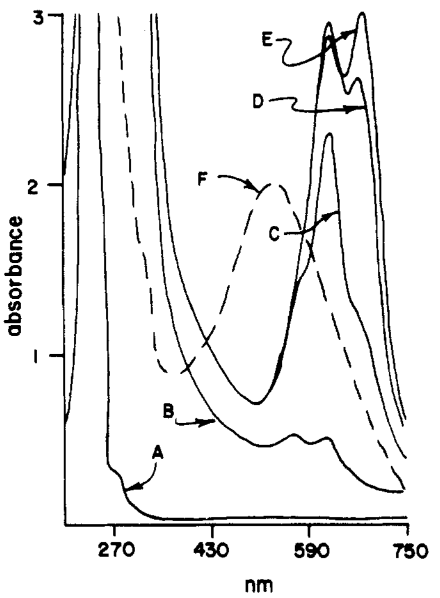


Figure 1. UV–vis spectra of isomerization solutions (potassium *tert*-butoxide in Me$_2$SO used as a base): (A) t = 0 min; (B) t = 5 min; (C) t = 30 min; (D) t = 120 min; (E) t = 210 min; (F) 72 h and then quenched with methanol.

are consistent. Scheme I depicts the mechanism for this base-catalyzed isomerization. The vinyl groups present (8% by NMR) are not represented in this scheme; they undergo analogous isomerizations and do not interfere with the depicted process.

An important requirement for this isomerization is the presence of Me$_2$SO.[20] When the base was added as a solution in *tert*-butyl alcohol, no change in color or the UV–vis spectrum was observed after 24 h. With Me$_2$SO as the base solvent, a rapid coloration ensues. Figure 1 exhibits UV–vis spectra of isomerization solutions. These spectra do not resemble the typical finger pattern of low molecular weight polyenes,[21] although they do exhibit shifts to longer wavelengths and increasing intensity as the conjugation length increases. The majority of the absorbance is due to the polyanion. If the solution is exposed to oxygen, the blue color instantly discharges, leaving an orange solution and precipitated cross-linked polymer. If the solution is quenched with methanol, the color becomes violet (Figure 1F). After isomerization for 72 h, the UV–vis spectrum of the methanol-treated sample has a maximum absorbance at 230 nm, indicating that most of the conjugation is in the form of dienes and trienes, and a broad peak centered at 512 nm with an experimental extinction coefficient of 260 M^{-1} cm^{-1}.[22] This indicates that the polymer contains a range of conjugation lengths centered at 10 double bonds and approximately 0.2% have a length of 10 double bonds.[21,22] After 72 h, a further shift to longer wavelengths is not observed, but the intensity at 512 nm increases. The isomerized polymer is isolable as a violet air-sensitive solid.

Proton NMR and infrared spectra also indicate isomerization. The ratio of benzene (proton impurities in NMR solvent—used as an internal standard) to allylic protons (centered at δ 1.87) decreases from 13.1 to 9.5 after 72 h at 80 °C (the temperature was increased to increase the isomerization rate; see below). Four allylic hydrogens are lost for each conjugation (see Scheme I). The infrared spectra show the development of a broad asymmetric shoulder to the long-wavelength side of the carbon–carbon double-double absorbance at 1630 cm^{-1}. This is indicative of conjugated double bonds.

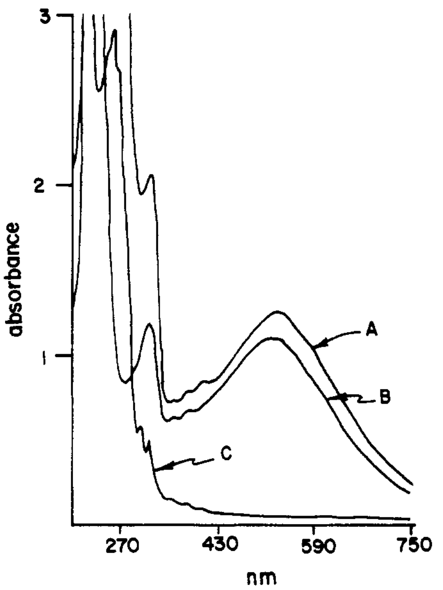
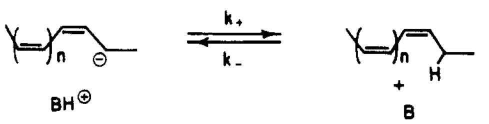


Figure 2. UV–vis spectra of isomerized (24 h) samples after reaction with methanol: (A) potassium cyclopentadienide; (B) potassium *tert*-butoxide; (C) potassium acetonitrilide.

The reaction temperature was varied to test whether the conjugation length could be affected thermodynamically. UV–vis spectra of reactions run at 0, 25, and 80 °C exhibit identical absorbance positions; thus conjugation length is unaffected.

The equilibria depicted in Scheme I suggest that the length of conjugation should be affected by the strength of the base: isomerization should occur until the pK_b of the polyanion is equal to the pK_b of the base catalyst (eq 1); thus a weaker base should render a longer length of conjugation. Figure 2 shows UV–vis spectra of samples isomerized using potassium acetonitrilide (stronger base), potassium *tert*-butoxide, and potassium cyclopentadienide (weaker base). The relative basicities have not been studied for this solvent system so the exact differences in basicity are not known. Potassium cyclopentadienide causes a 14-nm shift to longer wavelengths, and potassium acetonitrilide causes a >100-nm shift to shorter wavelengths.



(1)

Conductivity was measured on films cast directly from the isomerization solutions under a nitrogen atmosphere. The resulting blue films were washed with methanol until all of the base was removed (phenolphthalein indicator). The resulting red films were dried at 80 °C (0.05 mm) for 24 h before they were mounted on electrodes. The films were from samples that were isomerized with potassium *tert*-butoxide for various times, the longest being 7 days. Only this sample showed measurable electronic conductivity, 5 × 10^{-7} Ω^{-1} cm^{-1} after 4 h of iodine doping (10^{-9} before doping). The value increases gradually and levels at this point.

Conclusions

Poly(1,3-butadiene) can be isomerized to blocky poly(acetylene-*co*-ethylene) using base catalysis in THF/Me$_2$SO solution. The materials formed with potassium *tert*-butoxide contain lengths of conjugation of ~10 double bonds. The conjugation length is not a function of the temperature of the isomerization but is a function of the strength of the base used.

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(22) ϵ at 512 nm was obtained from the slope of a Beer's law plot using samples that were quenched with methanol and serial diluted. The concentration of these solutions was obtained by evaporating 5 mL in a tared beaker. The resulting residue was then washed with methanol until the base was removed and then dried 24 h at 50 °C (0.05 mm) before reweighing. The value 0.2% is based on monomer units, or in other words, 0.2% of the double bonds are present in 10 double-bond conjugated units.

Syntheses and Properties of Tertiary Peptide Bond Containing Polypeptides. 6.[1] Conformational Studies of Oligopeptides Containing the Pro-Pro Sequence by ^{13}C and ^{1}H NMR

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Received May 7, 1984

ABSTRACT: The conformation of Boc-Leu$_3$-Pro$_2$-Gly-OBzl (**1**) in Me$_2$SO-d_6 and CDCl$_3$ has been studied by ^{13}C and ^{1}H NMR spectroscopies. The related oligopeptides Boc-Pro$_2$-Gly-OBzl (**2**), Boc-Leu-Pro$_2$-Gly-OBzl (**3**), Boc-Leu$_2$-Pro$_2$-Gly-OBzl (**4**), Boc-Leu$_3$-Pro-OBzl (**5**), Boc-Leu$_3$-OBzl (**6**), and Boc-Leu$_3$-Pro$_2$-Gly-OH (**7**) have also been studied by NMR spectroscopy. The content of cis isomers about the Pro-Pro bonds was determined from peaks of α carbons of Pro in the ^{13}C NMR spectra and was ca. 15% for the peptides **1**, **3**, and **4** in Me$_2$SO-d_6. From the temperature dependencies of the NH chemical shifts in Me$_2$SO-d_6, the amide protons of **1**–**6** were shown to be almost fully exposed to the solvent. Only the NH protons of Leu(2) of **1** and **5** and the NH proton of Gly(6) of **1** in the cis configuration about the Pro-Pro bond are slightly shielded from the solvent. The NH chemical shifts of **1** show no concentration dependence, indicating that **1** is not intermolecularly hydrogen bonded among the solutes in Me$_2$SO-d_6. In the CDCl$_3$ solution of **1**, the content of the cis isomer about the Pro-Pro bond was determined as 43% and the NH protons of the Leu$_3$ sequence are intermolecularly hydrogen bonded. In addition, the NH proton of Gly(6) is shielded from the solvent. This is probably due to hydrogen-bond formation between the NH proton of Gly(6) and the carbonyl of Leu(3) (type VI β-turn) in the cis conformation about the Pro-Pro bond in CDCl$_3$.

Introduction

One of the serious problems encountered in achieving smooth couplings in protein syntheses is the decreasing solubility and reactivity of large peptides as the peptide chain length increases.[2,3] The decrease in solubility and reactivity has so far been attributed to the appearance of higher structures of large peptides.[2,3] As a means to solve this solubility problem of large peptides, we have proposed the concept of "peptide segment separation" and have shown that the insertion of tertiary peptide bonds such as X-Pro and X-(Z)Y bonds into central positions of peptide chains could achieve remarkable improvement in solubility.[4,5] X and Y in the above X-Pro and X-(Z)Y bonds are arbitrary amino acids and Z is a suitable protecting group for the X-Y peptide bond. The improvement in solubility of the peptides having tertiary peptide bonds has been attributed to their randomly coiled structure in solution.[6,7]

In order to ascertain the relationship among the conformation, solubility, and reactivity of large peptides, sequential polypeptides, Boc-(Leu$_3$-Pro$_2$-Gly)$_n$-OX (X = H or Bzl, n = 1, 2, 4, 6, 8, 10, and 12) have been prepared previously.[5] These peptides have excellent solubility in polar solvents and their N-deprotected derivatives, H-(Leu$_3$-Pro$_2$-Gly)$_n$-OBzl (n = 2, 4, 6, 8, and 10), have high reactivity to give Boc-(Leu$_3$-Pro$_2$-Gly)$_{n+2}$-OBzl in high yields. The conformational study of these peptides by molar rotation measurement in various polar solvents and CD measurement in methanol also indicated that their predominant structure was that of a random coil in polar solvents.[7]

This paper studies in detail the conformational properties of Boc-Leu$_3$-Pro$_2$-Gly-OBzl (**1**) and the related peptides by ^{13}C and ^{1}H NMR measurements. In the following paper, we will report on the sequential polypeptides.[8] The information to be obtained from the studies

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