New Morphologies of Polyacetylene from the Precursor Polymer Polybenzvalene

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Abstract. The synthesis and properties of the polymer polybenzvalene and its conversion to polyacetylene are presented. This conversion is performed by treating polybenzvalene with Lewis acidic catalysts. The highest quality material was obtained from the isomerization with HgCl₂. The polyacetylene (PA) produced by this precursor route has a morphology that is considerably more amorphous than other forms of polyacetylene that have been previously reported. Orientation of the precursor polymer by stretching induced crystallinity and chain alignment as determined by X-ray diffraction. The unoriented PA exhibited a conductivity of 1 10⁻³ cm⁻¹ with I₂ doping. Materials stretched to elongations of 1/λ₀ = 2.3 and 1/λ₀ = 6 displayed conductivities of 13 10⁻⁴ cm⁻¹ and 49 10⁻⁴ cm⁻¹, respectively. Block copolymers of polyborborene and polybenzvalene were produced. These copolymers exhibited no phase separation as determined by DSC. The isomerization of these materials produced a polyacetylene–polyborborene copolymer which exhibits a dominant X-ray diffraction peak with a d spacing of 4.7 Å. These results indicate that the interchain spacing of the block copolymer is significantly greater than that of the polyacetylene homopolymer due to the intimate mixing of the polyacetylene with the polyborborene.

The field of conductive polymers has seen considerable study in the last 10 years. Polyacetylene (PA) has received the most extensive investigation¹ and has been shown to display conductivities that rival copper.³ This deceptively simple material is a fundamental cornerstone upon which the field of conductive polymers has been based. Hence, new synthetic routes which can generate new morphologies of PA should be pursued. Conductive polymers including PA are often insoluble and infusible materials with low tensile strength. Thus, the manipulation of these materials into useful shapes and morphologies is limited. The morphology of many conductive polymers is fixed in the polymerization and is not easily modified.¹ One solution to the problems encountered in processing conductive polymers has been to use a processable precursor polymer which can be transformed into a conductive polymer. Precursor routes to conductive polymers have successfully produced high molecular weight materials with high conductivities and oriented morphologies.⁴ The most relevant precursor method here is the synthesis of PA by Feast.⁶ PA synthesized by Feast’s method has been called “Durham PA” and has seen considerable study.⁵ However, known precursor methods have been limited to processes which involve the extrusion of molecular fragments. In some cases, this extrusion involves over half the mass of the precursor polymer. Extrusions such as these restrict the processing of these materials into large shapes and prohibit processing by methods such as mold injection. In addition, materials produced by extrusion processes often have a porous structure which is undesirable for some applications. Thus, the development of nonextrusive precursor methodologies for the synthesis of conductive polymers is worth pursuing.

A strategy based on intramolecular, electrocyclic rearrangements may successfully meet the nonextrusive criterion.⁵ In this scheme, olefins are masked by incorporating them into ring structures. The resulting saturated centers of the ring act to make the polymer backbone nonplanar and more flexible, thus imparting greater solubility to the polymer. Demonstrating this idea, we recently reported preliminary results regarding a new synthesis of PA from the precursor polymer polybenzvalene (PBV).⁷ We report herein a more detailed account of this process and the production of new morphologies of PA using this precursor method.

Scheme 1

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Recent advances in well-defined, active, organometallic catalysts\(^8\) for ring-opening olefin metathesis polymerization (ROMP) have enabled the polymerization of monomers that were previously incompatible with the highly Lewis acidic ROMP catalysts. In addition, these catalysts provide living polymerizations in some cases.\(^9\) The living nature of the polymerization allows the synthesis of block copolymers which allow for a greater variation in the morphologies and properties of the resulting materials.\(^10\) ROMP is an effective method for conductive polymer synthesis since double bonds are not sacrificed in the polymerization, as is the case for most polymerizations. The utility of ROMP in conductive-polymer synthesis has been previously demonstrated by Schrock and Osborn (III)\(^11\) and a cross-conjugated, conductive-polymer precursor.\(^12\)

Results and Discussion

Synthesis and Properties of PBV. The ROMP catalysts recently reported by Schrock (I and II)\(^{13,14}\) and Osborn (III)\(^{15}\) were effective in the polymerization of BV as shown in Scheme I. PBV is a soluble polymer, which may be precipitated as a powder by slowly adding the polymerization mixture to acetone. These powders were off-white to tan and would not redissolve after precipitation. As a result of this irreversible dissolution, PBV must be handled in solution, and film casting was performed directly from the polymerization reaction mixture. PBV films are initially soft, swellable, and display viscoelastic properties. After a few days, the films are noticeably more brittle and not swellable. As a result of the high strain energy associated with the bicyclobutene ring system,\(^13\) PBV is a sensitive material that will undergo spontaneous exothermic decomposition (detonation) with application of severe mechanical stress (stretching or compression) or with rapid heating (\(\geq 20^\circ C/min\)). Solid samples of PBV must be handled carefully and, for safety, quantities of this material were usually kept below 1 g. However, on the numerous occasions that the material was detonated (accidentally and intentionally) it seldom produced explosions that were violent enough to pose a threat on the prescribed scales. The spontaneous decomposition of freshly prepared samples is extremely exothermic and the heat liberated is substantial.\(^14\) Powders were found to be particularly prone to detonation. Fresh samples produced orange smoke and an orange-brown, oily residue when detonated. Older samples (2 months old) detonated with heating, but not with mechanical stress, and produced black smoke and ash.

PBV gelled when polymerizations were run at too high a concentration. Solutions of PBV also gel upon standing or with partial evaporation of the solvent. Gels that were washed with a nonsolvent such as methanol, acetone, or acetonitrile could be partially recovered by repeated precipitations of freshly prepared samples is extremely exothermic and the heat liberated is substantial.\(^14\) Powders were found to be particularly prone to detonation. Fresh samples produced orange smoke and an orange-brown, oily residue when detonated. Older samples (2 months old) detonated with heating, but not with mechanical stress, and produced black smoke and ash.

PBV gelled when polymerizations were run at too high a concentration. Solutions of PBV also gel upon standing or with partial evaporation of the solvent. Gels that were washed with a nonsolvent such as methanol, acetone, or acetonitrile could be stretched more than 30 times their original length. However, these materials often detonated at such high elongations. Due to its sensitive nature, BV is synthesized, isolated, and handled in solution.\(^15\) This leads to the presence of other solvents


in the polymerization mixture which complicate the NMR spectrum. Thus, to obtain solution NMR spectra of PBV, polymerization solutions were subjected to cycles of partial evaporation and addition of CD$_2$Cl$_2$ to remove residual solvents. Catalyst II has been found to exhibit a high selectivity for producing cis double bonds in the polymerization of norbornene and other monomers. The solution $^{13}$C NMR spectrum of PBV produced with II exhibits only three resonances indicating that only one olefin isomer is produced (Figure 1). The assignment of the double-bond stereochemistry is unclear from infrared spectroscopy. As shown in Figure 2, PBV synthesized with II displays bands at 750 and 1000 cm$^{-1}$, which are the regions where cis and trans olefins respectively exhibit C-H out-of-plane bending modes. Nevertheless, there is no reason to believe that the general cis preference of II should not be exhibited in the ROMP of BV. Hence, we assign an all cis structure to PBV produced with II. The $^{13}$C NMR chemical shifts of cis-PBV can be compared with those of bicylobutane, the saturated analogue of BV. In the IR spectrum, as shown in Figure 2, the allylic carbon of PBV in the vinylene content may be the result of the relatively conformational rigidity of the backbone. However, the polyolefin signal observed in the $^{13}$C NMR signals exhibited by PBV produced with II and III are the result of decomposition cannot be ruled out.

Infrared spectroscopy, as shown in Figure 2, supports the contention that the polymers obtained with catalysts I–III differ only in the isomeric ratios of the olefins. A strong mixing of the vibrational modes is observed for BV. PBV also exhibits considerable mixing in its vibrational modes, which precludes a detailed assignment of all the bands in the spectra of Figure 2. All three materials exhibit two distinct C–H stretching bands at approximately 3025 and 2920 cm$^{-1}$, which correspond to saturated and unsaturated centers, respectively. In addition each material displays a distinctly similar and unusual pattern in the C=C stretching region. There are similar strong bands at approximately 1450, 1370, 1000, and 750 cm$^{-1}$ for each of these materials. The infrared spectrum of PBV synthesized with III is slightly broader than that produced with I and II. This broadness may be the result of some chemical degradation and/or a more disordered structure as a result of the cis to trans ratio. Due to the selectivity of catalysts I and II for cis olefins, we used these catalysts to produce PBV for additional investigations. These catalysts gave essentially indistinguishable material in all of our subsequent studies. The majority of PBV studied was produced with I, as this catalyst polymerizes BV smoothly at room temperature. Polymerizations with I are therefore conveniently performed in a glovebox, while II must be used at lower temperature in order to prevent catalyst decomposition.

As seen in these compounds, the bridgehead carbon of the bicylobutane moiety shows considerable chemical shift dispersion and is shifted downfield with increasing ring strain. Thus, the signal upfield at 12.8 ppm in the $^{13}$C NMR spectrum of PBV is most likely the bridgehead carbon of the bicylobutane group, which has been shifted upfield from the 48.3 ppm chemical shift exhibited by this carbon in BV. The 47.8 ppm signal in Figure 1 corresponds to the allylic carbon of PBV. The $^1$H NMR spectrum of PBV synthesized with II is complicated by residual hexane as shown in Figure 1. The $^1$H NMR spectra of cis-PBV is very similar to that of BV, which has $^1$H NMR peaks at 5.95, 3.53, and 1.84 ppm in benzene.

Both vinyl and divinyl polymerize norbornene to produce poly-norbornene (PN) with high trans double-bond content. NMR spectra reveal that catalyst I produces mainly cis-PBV as obtained with II. However, there are minor peaks which may be the result of a small amount of trans-PBV. PBV produced with III has very similar physical properties to polymer produced with I and II. However, as shown in Figure 3, the $^{13}$C NMR spectrum of PBV produced with III is quite different. The chemical shifts of the dominant signals of PBV produced with III are identical with those of most of the minor $^{13}$C NMR signals in PBV produced with II. The $^{13}$C NMR spectrum of PBV produced with III exhibits an additional olefin signal at 12.9 ppm which may arise from trans double bonds. Examination of the $^1$H NMR spectrum also shows the same correlation of signals between the materials produced with catalysts I and II. The complexity of the NMR spectra may result from the polymer's conformational microstructure, which varies with cis and trans double-bond content. Other polymers produced by ROMP also exhibit numerous $^{13}$C NMR peaks as a consequence of cis/trans-vinylene distribution, however, the chemical shift dispersion and number of signals is usually lower. This large variation of the $^{13}$C NMR spectra with cis/trans-vinylene content may be the result of the relatively conformational rigidity of the backbone and the sensitivity of the bicylobutane resonances to their environment. As discussed previously, the bridgehead carbon of the bicylobutane moiety may display chemical shifts ranging from -3 to 48 ppm depending on ring strain. The -2.2 ppm $^{13}$C NMR signal in Figure 2 would thus correspond to a bicylobutane moiety which contains little extra strain due to the polymer conformation. To account for all the $^{13}$C NMR signals in Figure 3, it must be assumed that the bicylobutane resonances are sensitive to the configuration of olefins not directly connected to each bicylobutane. This is not unreasonable considering the conformational rigidity of the polymer backbone. However, the polyolefin signal observed in the $^{13}$C NMR signals exhibited by PBV produced with I and III is the result of decomposition cannot be ruled out.

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As discussed previously, PBV is relatively unstable and cannot be redissolved after precipitation or casting into a film. The nature of the decomposition was investigated with solid-state $^{13}$C NMR spectroscopy with cross-polarization and magic angle spinning (CPMAS). The spectra consisted of broad peaks (w$_{1/2}$ = 1.5–2.5 kHz) at 137, 56, and 39 ppm. In addition, integration of the CPMAS $^{13}$C NMR spectra of material that had been stored at ambient temperature for 2 weeks revealed the olefinic region was approximately 40–45% of the total carbon signal, which is larger than the 33% that would be expected for the structure of PBV.

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(20) The infrared spectra of PBV films produced with the other catalysts also became broadened in time as a result of partial decomposition.
(21) PA with cis olefin has been found to exhibit superior mechanical properties and generally produces materials with higher conductivities when doped than trans-PA.
(22) Catalyst II reacts with BV at room temperature to give a bright red solution and a low yield of polymer ~20%.
Scheme II

PBV: Hence, it appears that the decomposition leads to additional unsaturation. However, the broad lines indicate that this chemistry is rather unselective.

As mentioned earlier, interesting properties result from the high strain energy of PBV. High-energy materials may have applications in propulsion technologies. The amount of strain energy can be measured experimentally by determining the heat of formation of a material. The strain energy is defined as the difference in the heat of formation of the material of interest and that expected for a hypothetical strainless molecule with the same atoms and chemical bonds. By the use of Franklin's constants, the heat of formation of the strainless repeating unit is calculated to be 14.5 kcal/mol. The heat of formation was experimentally determined to be 65 kcal/mol for a sample of PBV stored for approximately 1 week at room temperature. Hence, the measured strain energy per repeating unit is calculated to be ~51 kcal/mol. This measurement is compared with the strain energy of bicyclobutene which is 64 kcal/mol. The lower than expected heat of formation is the result of partial decomposition of the sample before the measurement could be made.

Catalyst I has been demonstrated to provide a living polymerization of norbornene. The living polymer IV was prepared and BV was added to the mixture and polymerized to give the PBV:PN block copolymer as shown in Scheme III. 1H NMR spectroscopy confirms the presence of both PBV and PN. The ratio of the two polymers is readily determined by integration of the 1H NMR olefinic signals. The block copolymers showed less of a tendency to gel and were more soluble than the PBV homopolymer.

Films of the block copolymer exhibited a soft, rubbery nature which was retained after a month of storage at room temperature. Thus, it appears that the block copolymers have an improved stability over the PBV homopolymer.

Isomerization of PBV to PA. Bicyclobutanes are known to rearrange to 1,3 dienes thermally, photochemically, and with transition-metal catalysts. The analogous transformation for PBV produces PA as shown in Scheme III.

The thermal transformation of PBV into PA is an attractive goal. Bicyclobutanes rearrange to 1,3-dienes at approximately 150–200 °C. Differential scanning calorimetry (DSC) of PBV reveals major exothermic processes at 153 and 308 °C as shown in Figure 4. Reheating of the same sample after scanning to 440 °C shows no exotherms and indicates the approximate position of the base line. Integration of freshly prepared PBV from 50 to 420 °C reveals the liberation of 59 kcal/mol per repeating unit. The exotherm at 153 °C is in the right thermal range and may be due to the desired chemistry. Samples that had been stored for 2 months at room temperature displayed a similar DSC trace with a decrease in the liberated heat due to partial decomposition.

Thermogravimetric analysis of PBV indicates that minor weight loss begins with the second exotherm and that onset of the major weight loss occurs at approximately 400 °C. Thermomechanical analysis revealed that an abrupt expansion of the material (2%) occurs with the 153 °C exotherm. The proposed ring-opening of the bicyclobutanes is consistent with an expansion of the material since it will produce an increase in the length of the polymer backbone. Thermomechanical analysis shows a contraction of the sample with the 308 °C exotherm. Thus, the thermal analysis results suggest that the desired chemistry may be occurring to some degree in the 153 °C exotherm, but the 308 °C exotherm corresponds to other undesirable decomposition pathways.

Thermal treatment of PBV at a variety of temperatures between 150 and 300 °C produced dark brown materials which were insulators even after prolonged exposure to I2 vapor. It was noticed that a small amount of oxygen present in the thermolysis resulted in the formation of black and shiny materials. However, these materials could not be made conductive with I2 or AsF5 treatment.

Figure 4. DSC thermogram of PBV at 10°/min. The solid line is for the first scan and the broken line is for the reheated sample. Integration from 50 to 420 °C reveals the liberation of 59 kcal/mol for the first scan.

Scheme IV

(24) Wardle, R. B. Personal communication.
(25) The heat of formation was determined experimentally by bomb calorimetry and was performed by Mortor, Thiokol, Inc.
Solid-state CP MAS $^{13}$C NMR spectra of the heated samples revealed extremely broad signals ($\omega_{1/2} \approx 10-13$ kHz). These spectra displayed a major peak at 150 ppm and a smaller peak at 30 ppm. The broad nature of the $^{13}$C NMR signals indicate that the thermal chemistry is unselective and results in an inhomogeneous environment around the carbon centers.

Attempts at photochemically promoting the isomerization of PBV to PA were unsuccessful. PBV was photolyzed with a mercury-arc lamp (350 W) in a quartz tube with and without triplet sensitizers with no observable change. Illumination with a 193-nm laser light (ArF excimer laser) with peak powers up to 30 MW was also investigated and produced no visible change. Hence, photochemical methods do not appear to be efficient at opening the bicyclobutane rings in this system.

Chemical opening of the bicyclobutane rings was pursued in light of the thermal and photochemical results. Gassman has reported the isomerization of tricyclo[4.1.0.0²,7]heptane (V) by a variety of Lewis acidic catalysts. In this investigation it was reported that isomerization of V with AgBF₄, ZnI₂, and HgCl₂ gave predominantly VI and a minor product VII (Scheme IV). The ring-opening of V to VI is analogous to the desired transformation for PBV shown in Scheme III. Thus, the isomerization of PBV by a similar group of catalysts was investigated. These isomerizations were performed by soaking freshly cast films of PBV in a THF solution of the catalyst and then washing the catalyst from the films. In analogy to Gassman's results, we expected two products from the isomerization of PBV, PA and the cross-conjugated polymer VIII (Scheme V).

The results of the catalytic isomerization of PBV are summarized in Table I along with the results reported by Gassman. Materials produced from the isomerization of PBV with AgBF₄, HgBr₂, HgCl₂, and ZnI₂ display similar spectra. A small infrared band at 895 cm⁻¹ is present in materials produced with HgBr₂ and ZnI₂. This band is indicative of the vinylidene moiety and indicates that some VII is likely to have been produced in the isomerization. The absorption bands of PPA are wide in comparison with those of Shirakawa PA₂ as a result of a more disordered structure. Infrared spectra of PPA after thermal isomerization to trans-PPA show a slight sharpening of the spectral bands and a decrease of the modes at 740 and 1395 cm⁻¹. The band at 1395 cm⁻¹ is expected to rise due to the cis olefinic in-plane bending. The infrared spectra also reveal the presence of residual saturation as evidenced by the C-H stretching band at 2800 cm⁻¹. Materials produced with HgBr₂ and ZnI₂ display similar spectra. A small infrared band at 895 cm⁻¹ is present in materials produced with HgBr₂, HgCl₂, and ZnI₂. This isomerization with HgCl₂ in addition to yielding materials exhibiting the highest conductivity with I₂ doping (1 $\Omega^{-1} \text{cm}^{-1}$), gave materials with excellent mechanical properties. This material is extremely durable and has a qualitatively high tensile strength. Hence, the remainder of this paper will focus on this material.

Table I. Results of the Catalytic Isomerizations

<table>
<thead>
<tr>
<th>catalyst</th>
<th>appearance</th>
<th>conductivity, $\Omega^{-1} \text{cm}^{-1}$</th>
<th>isomerization of PA</th>
<th>% yield of products</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgBF₄</td>
<td>silvery-black, dull</td>
<td>10⁻⁴</td>
<td>VI</td>
<td>100</td>
</tr>
<tr>
<td>ZnI₂</td>
<td>black, shiny</td>
<td>10⁻⁶</td>
<td>VI</td>
<td>88 11</td>
</tr>
<tr>
<td>HgBr₂</td>
<td>black, shiny</td>
<td>10⁻⁷</td>
<td>VI</td>
<td>85 8</td>
</tr>
<tr>
<td>HgCl₂</td>
<td>silvery-black, shiny</td>
<td>10⁻⁵</td>
<td>VI</td>
<td>100</td>
</tr>
<tr>
<td>[Rh(COD)Cl]₂</td>
<td>burgundy-red</td>
<td>10⁻⁴</td>
<td>VI</td>
<td>0 98</td>
</tr>
</tbody>
</table>

*From ref 28b. [Rh(COD)Cl]₂ was used in ref 28b.

Infrared spectroscopy of PPA reveals broad, major absorptions for cis and trans olefins at 740 and 1005 cm⁻¹, respectively. The infrared spectra also reveal the presence of residual saturation as evidenced by the C-H stretching band at 2800 cm⁻¹. Materials produced with HgBr₂ and ZnI₂ display similar spectra. A small infrared band at 895 cm⁻¹ is present in materials produced with HgBr₂, HgCl₂, and ZnI₂. This band is indicative of the vinylidene moiety and indicates that some VII is likely to have been produced in the isomerization. The absorption bands of PPA are wide in comparison with those of Shirakawa PA₂ as a result of a more disordered structure. Infrared spectra of PPA after thermal isomerization to trans-PPA show a slight sharpening of the spectral bands and a decrease of the modes at 740 and 1395 cm⁻¹. The band at 1395 cm⁻¹ may be due to the cis olefinic in-plane bending. The broad nature of the infrared spectra of PPA precludes a quantitative determination of the cis to trans content. However, (32) cis-PA synthesized by the Shirakawa procedure exhibits a C-H in-plane bending mode at 1329 cm⁻¹ which we do not observe. However, a peak at 1395 cm⁻¹ is observed which is in the region that isolated olefins exhibit this mode. Hence, the 1395 cm⁻¹ band may be due to the cis-PA C-H in-plane bending mode.
the cis:trans ratio is estimated to be approximately 40:60. As described earlier, PBV is nearly exclusively cis before isomerization to PPA. Therefore, the bicyclobutane ring-opening must mainly produce trans olefins. A trans preference is also observed for the catalytic ring-opening of other bicyclobutanes to acyclic dienes.\textsuperscript{28a} PPA as produced was too ductile to be ground into a homogeneous, tightly-packed sample necessary to achieve the spinning rates required by the CPMAS \textsuperscript{13}C NMR experiment.\textsuperscript{31} Trans-PPA is considerably more brittle than cis-PPA,\textsuperscript{2} and thus \textsuperscript{13}C NMR samples were first isomerized to trans-PPA at 150 °C for 6 h and then ground. Thus, the CPMAS \textsuperscript{13}C NMR spectrum shown in Figure 5 is of trans-PPA. The CPMAS \textsuperscript{13}C NMR spectrum also exhibits an additional peak at 40 ppm which is the result of sp\textsuperscript{3} carbon centers. At longer cross-polarization contact times this peak is diminished, and with a contact time of 10 ms, only the 135 ppm peak is observed. This relaxation behavior indicates that the carbons responsible for the 40 ppm resonance are in a more rigid environment, and hence have a shorter $T_2$ relaxation time than the 135.5 ppm signal.\textsuperscript{24} A more rigid environment is consistent with these sp\textsuperscript{3} carbon centers resulting from cross-linking. Quantitative measurements of the amount of sp\textsuperscript{3} carbons in PPA were performed at a cross-polarization contact time of 2 ms. Integration determined the PPA to contain \textasciitilde 15-19% of saturated material.

The cross-linking in PPA is also manifested in the fact that the thermal isomerization to trans-PPA requires a higher temperature than observed for other forms of PA. DSC analysis of PPA displays an exotherm for the cis to trans isomerization with a peak at 205 °C. Other forms of PA exhibit DSC peaks for this isomerization at lower temperatures (\textasciitilde 150 °C).\textsuperscript{2,4a,11} A crankshaft mechanism for the isomerization of cis- to trans-PA has recently been proposed.\textsuperscript{36} Cross-linking would inhibit the crankshaft motion, thus resulting in the higher isomerization temperature. The product of RH\textsuperscript{1}-catalyzed isomerization of PBV exhibited an extremely broad infrared spectrum. Infrared bands which may be assigned to cis, trans, and vinylidene olefins are observed. However, a strong C–H stretching band at 2900 cm\textsuperscript{-1} indicates there is considerable saturated material present. DSC reveals the absence of the 153 °C exotherm exhibited by PBV. This suggests

\textsuperscript{33} Spinning rates of 3.5-5 kHz are required to reduce the sidebands in the CPMAS \textsuperscript{13}C NMR experiment at a carbon frequency of 50.36 MHz.
\textsuperscript{34} Eckert, H.; Yesinowski, J. P.; Sandman, D. J.; Velazquez, C. S. J. Am. Chem. Soc. 1987, 109, 761.
\textsuperscript{37} We have investigated the ROMP of 3,4-dimethylenecyclobutene and found the resulting polymer to be highly susceptible to cross-linking reactions.

Scanning electron microscopy (SEM) revealed that films of PBV have a smooth, featureless surface. After isomerization to PPA, the surface exhibits some texture but is devoid of the pronounced fibrilar morphology observed in Shirakawa PA. The bulk density of PPA is 0.87 g/cm³, which is higher than that of Shirakawa PA, but lower than Durham PA (p > 1). As shown in Figure 6, SEM shows lines on the surface of PPA, indicating that films are stressed with isomerization. X-ray diffraction indicates a low level of crystallinity in PPA. This low crystallinity is in part due to the morphology of the precursor polymer PBV which is amorphous. A plot of X-ray (Cu Kα) diffraction intensity of PPA as produced and after thermal annealing is shown in Figure 7. PPA exhibits a diffraction peak at 2θ = 23° with a d spacing of 3.80 Å, which is the dominant peak observed in other forms of PA. The full width at half height (w1/2) of this peak is 2θ = 9.8°. This is considerably broader than PA produced by other methods. For example, Shirakawa cis-PA has a w1/2 of 2θ = 1.5°, and unoriented, Durham cis-PA has a w1/2 of 2θ = 4°. There is no noticeable change in PPA upon annealing at 120 °C whereas the 2θ peak of Durham PA was observed to narrow with thermal annealing to widths of 2θ = 20°. The 2θ = 23.4° peak of PPA is noticeably asymmetric with a shoulder at lower angles. This shoulder at high d spacing may be the result of cross-links which cause the chains to distort from tight, crystalline packing. In contrast, Durham PA exhibits a nearly symmetric 2θ peak. The tail of an intense amorphous halo is also observed in Figure 6 and results in a sloping baseline under the 2θ = 23.4° peak. At larger angles there is a hint of the 2θ = 43° diffraction peak observed in other forms of PA.

Low crystallinity also results in a decrease in conjugation length due to twisting of the PA backbone from planarity. UV–vis spectroscopy of trans-PPA shows an absorption onset at ~1.9 eV and an absorption maximum at 2.8 eV. The absorption onset yields a band gap of 1.9 eV for this material. In comparison Shirakawa trans-PA has a band gap of 1.4 eV2 and unoriented Durham trans-PA has a band gap of 1.5 eV and an absorption maximum of 2.3 eV. The higher energy band gap and absorption maxima indicate that the conjugation lengths are shorter in PPA than in Shirakawa and Durham PA. This is likely in part due to the amorphous nature of unoriented PPA but is also the result of the cross-linking. As discussed earlier, PBV is a soft, rubbery material which is readily stretched. PBV was oriented by casting films on a polyethylene sheet and then stretching. The PBV was held in an extended form by the polyethylene support and isomerized to PPA. The oriented PBV was then removed from the polyethylene backing as a strong, flexible ribbon. Two different polyethylene sources were used which allowed the PBV to be homogeneously stretched to 2.3 or 6.0 times its initial length. As expected, the conductivity of oriented PPA is higher than that of the unoriented material. The elongated PPA /l/l0 = 2.3 and /l/l0 = 6.0 displayed conductivities of 13 and 49 Ω⁻¹ cm⁻¹, respectively, when doped to saturation with I₂ vapor.

The SEM photograph of oriented PPA shown in Figure 6 reveals that this material has a highly textured appearance. Oriented PPA displays small troughs that are ~0.5 µm apart and a fibrillar morphology similar to that exhibited for Shirakawa PA. The fibrils of the oriented material are ~200 Å in diameter. Stretching polymers is known to induce crystallinity, and thus X-ray diffraction of the oriented PPA was investigated. The X-ray diffraction intensity of oriented PPA (/l/l0 = 6) at two different orientations with respect to the X-ray detection is shown in Figure 8. The interchain diffraction is most intense when the X-ray intensity is monitored perpendicular to the direction of orientation. The reduction of the X-ray diffraction intensity in the parallel direction confirms that the chains are aligned in the stretching direction. The 2θ = 23.4° peak shape is qualitatively the same as a fibrillation with a birefringence and hence an amorphous material. The X-ray diffraction of PBV exhibits a peak at 2θ = 17° (d = 5.2) and a very broad asymmetric peak from ~2-20°.

Morphology of Block Copolymers. Binary polymer blends usually phase separate, even when the two materials are very similar in structure. This is a consequence of the fact that polymers exhibit a small entropy of mixing, the thermodynamic driving force responsible for the mixing of simple fluids. Block copolymers are well-known to make compatible polymers which would otherwise phase separate as a blend.19 The PBV:PN block copolymers were shown to exist as a single phase, as DSC showed no detectable glass transition (Tg) for PN. Phase separated PN should have a Tg in the range of 30-40 °C. However, the DSC thermogram displayed no phase transitions over the region of 20-50 °C. The molecular weights of the block copolymers were kept low and were approximately 35 and 50 repeating units for PBV and PN, respectively. Short segments such as these will have less of a tendency to phase separate than higher molecular weight materials.19 In addition, the similarity in the structure of PN and PBV aids in producing a single phase. By isomerizing the PBV to PPA in the block copolymer we sought to produce a unique morphology in which the PPA is intimately dispersed with the PN. Isomerization of the PBV to PPA in the block copolymer resulted in some phase separation as determined by DSC which revealed a PN Tg at 38 °C.

The conductivity of the PPA:PN block copolymer (1:1.2) was found to be 7 × 10⁻² Ω⁻¹ cm⁻¹ when saturated with I₂. Orientation (/l/l0) of the block copolymers resulted in an increase of the conductivity to 0.37 Ω⁻¹ cm⁻¹ when saturated with I₂. The decrease in the conductivity of the oriented copolymer from that of the oriented PPA homopolymer (/l/l0 = 6) is greater than a factor of 100. This decrease of conductivity is more than a dilution effect. As shown in Figure 6, SEM reveals that the block copolymer has a much smoother appearance than the PPA homopolymer. Also, it appears that the PN allows the material to relax or to flow, relieving some of the stress encountered with orientation. There is only a hint of fibrillation in this material when viewed at high magnification. X-ray diffraction of the oriented PPA:PN block copolymer as shown in Figure 9, is dominated by a large intensity 2θ = 19.6° peak (d = 4.67 Å). The 19.6° diffraction is isotropic in the oriented material since it displays approximately the same intensity at both orientations. The isotropic nature of this peak indicates that the material responsible for this peak is randomly oriented even after stretching. The X-ray diffraction perpendicular to the orientation displays a shoulder at the 23° interchain polyacetylene diffraction. There is also a shoulder at...
that the 23° shoulder displays a stronger diffraction with the data at hand the exact nature of the morphology of the slight shoulder at 23°. In the oriented material, diffraction parallel to the orientation indicating that the phase-separated PPA is aligned in the polymer with a major diffraction at a spacing of the PPA chains. 

produce olefins. This polymerization has only been made possible by this method is of lower crystallinity than other forms of PA separated PPA is aligned with stretching. Prior to this study Bates and Baker reported polystyrene:PA block copolymers and found the PA portion to exhibit microcrystalline domains. These materials exhibited a crystal different from that of the PA homopolymer with a major diffraction at a spacing of 4.43 Å. Hence, with the data at hand the exact nature of the morphology of the PPA:PN homopolymer is not clear. However, the larger d spacing is consistent with the PN block serving to increase the interchain spacing of the PPA chains.

23° in the unoriented material, however, it is not as pronounced. The 23° peak is a result of PPA which has phase separated from the PN. There is only a hint of the 23° shoulder in the X-ray diffraction parallel to the orientation indicating that the phase-separated PPA is aligned with stretching. Prior to this study Bates and Baker reported polystyrene:PA block copolymers and found the PA portion to exhibit microcrystalline domains. These materials exhibited a crystal different from that of the PA homopolymer with a major diffraction at a spacing of 4.43 Å. Hence, with the data at hand the exact nature of the morphology of the PPA:PN homopolymer is not clear. However, the larger d spacing is consistent with the PN block serving to increase the interchain spacing of the PPA chains.

Conclusion
We have developed a new precursor route to PA from PBV by the ring-opening isomerization of the bicyclobutane rings to produce olefins. This polymerization has only been made possible by use of non-Lewis acidic metathesis catalysts.

PA produced by this method is of lower crystallinity than other forms of PA and has residual saturation due to cross-linking. The crystallinity and conductivity of the PA are increased by stretching the precursor polymer before conversion to PA. New block copolymer morphologies of PA can be produced with this method by transforming a precursor block copolymer which exists as a single phase into a PA block copolymer. The PA block copolymer has a larger d spacing than the PA homopolymer. The concept of "masking" unsaturation by the use of nonextrusive ring opening may find future utility in conductive polymer synthesis.

Experimental Section
General Procedures. All manipulations of air- and/or moisture-sensitive compounds were carried out using standard Schlenk or vacuum-line techniques. All the polymers and catalysts were treated as air-sensitive materials. The flush gas (argon) was purified by passage through columns of activated BASF RS-11 (Chemalog) oxygen scavenger and Linde 4-Å molecular sieves. Manipulation of solids and film casting was performed in a Vacuum Atmospheres glovebox equipped with a MO-40-1 purification train. The purification train was charged with activated Ridox oxygen scavenger and Linde 11-Å molecular sieves. When dealing with moisture-sensitive materials, all glassware was rinsed with base, dried in a 140 °C oven, and subjected to vacuum while hot. H and 13C NMR spectra were recorded on a JEOL FX-90Q spectrometer (90.6 MHz for H, 23.53 MHz for 13C). Chemical shifts were referenced to the solvent (13C NMR) or to residual protons in the solvent (H NMR). Infrared spectra were acquired on a Shimadzu IR-435 spectrometer. Infrared samples were films of the polymers. UV–vis spectra were obtained on a HP-8451A diode array spectrometer. Samples for UV analysis were films 0.1-μm thick. The conductivity measurements were made with the four-point method on a home-built probe (four-wire with Electrodag attachments) similar to that described in ref 2 and/or on a commercial Sigmatone sheet-resistivity probe. In the conductivity measurements current was supplied by a Power Designs 605 precision power source (0.1–6 V), current was measured with a Keithley 181A digital multimeter (0.1–10–10 A), and the voltage was measured with a Fluke 895A differential voltmeter. Gel permeation chromatographic (GPC) analyses were performed utilizing a low-resolution Altech TSKgel GMH6 column with solvone as a solvent. High-resolution columns were not used as a result of residual catalyst in the polymer solution and the tendency of the polymer to gel. GPC analysis was performed on polymer solutions taken directly from the reaction mixtures, diluted to a 2% by weight solution, and then injected. Hence, residual solvents were also present and the GPC data was only used as a qualitative indication of the molecular weight. The polymer was detected with a Spectroflow 757 variable wavelength absorbance detector and a Knauer differential refractometer. Injection volumes of 0.10 mL were used with a flow rate of 1.5 mL/min. Molecular weights were referenced to narrow dispersity polystyrene samples (Polysciences) ranging from MW = 3550 to 1300000. CPMAS 13C NMR spectra were obtained on a home-built spectrometer at a carbon frequency of 50.36 MHz. A commercial Bruker Scientific CPMAS probe was used and spinning speeds of 2–5 KHz were obtained. The samples were ground with Na2SO4 into a homogeneous mixture and packed tightly in a 7-mm o.d. sapphire rotor (Doty Scientific) with Kel-F end caps. Sample sizes were 100–200 mg and the balance was Na2SO4. Data collection was performed with a Nicolet 1200 commercial and Nicolet NMR software. Chemical shifts were referenced to an external adamantane standard. The adamantane standard was used for setting the Hartmann–Hahn matching condition and the 90° H pulse which was typically ~5 μs. Cross-polarization contact times were 2 or 3 ms. A "rolling baseline" in some samples was eliminated by left-shifting the free-induction decay by 0–100 μs, or by using a baseline-fit routine in the software. X-ray diffraction was measured with a LKB Bromma Ultrascan XL laser densitometer. X-ray photographs of the oriented films at different orientations were of the same samples and of identical exposure time. The X-ray film from these experiments were developed simultaneously to further insure the correct relative intensities. Thermal analysis was performed on Perkin Elmer DSC-7, TGS-2 thermogravimetric analyzer, TMS-2 thermomechanical analyzer, and a 3600 data station. Scanning rates of less than 20 °C/min were used to avoid decomposition of the PBV samples. SEM photographs were obtained on an ETEC autoscanning electron microscope. Samples were prepared by coating the materials with 100 Å of Au-Pd (80:20) with a Technics Hummer 5 sputter coater. The photographs shown were taken at an angle of 65° to the surface. Thermolysis of PBV was conducted in a tube furnace under dynamic vacuum. The temperature was monitored on a thermocouple which was put in the furnace wire to the tube. Materials. Solvents were dried and deoxygenated. Ether, THF, benzene, toluene, and pentane were dried with sodium benzophenone ketyl. Pentane was purified prior to drying and deoxygenation by treatment with H2S04 for 3 weeks. CH2Cl2 and chlorobenzene were dried with P2O5. Catalysts I and II were made by the published procedure and purified by recrystallization from pentane (20–50 °C). Catalyst III was made by the method of Kress and Osborn. The methanol or acetone used to precipitate the polymer was not dried but was deoxygenated by pumping on the solvent multiple times and then building argon through the solvent for half an hour or more. HCl (Baker) was purified by sublimation under dynamic vacuum. ZnI2 (Alrich) was purified by heating at 100 °C under vacuum for 12 h. AgBF4 (Alfa), HgBr2 (Allied Chemical), and (RhCl(COD))2 (Strem) were used without purification. Polyethylene was used as a substrate for... 

the stretching of films. One source of polyethylene was Handi Wrap which could be stretched to 2.3 times its length. The other source of polyethylene was obtained from the strapping bands which hold six-packs gassed, placed under inert atmosphere, and stored over 4-A molecular and was determined by NMR integration diethyl ether of approximately 1 M with no residual dimethyl ether. Both were determined by weighing precipitated powders. As a result of the decomposition when scraped away from the walls of glassware. Films should be gently cut with a razor blade since tearing may also cause decomposition. As a result of the Tendency for PBV to undergo spontaneous exothermic decomposition, it is Isomerization procedures presented below are based on a concentration of diylium ether of approximately 1 M with no residual dimethyl ether. Both PBV and PB are potentially dangerous materials and should be handled with caution.

**General Synthesis of PBV.** The polymerization of PBV is described below for catalysts I-III. Films of PBV were cast directly from the reaction mixture onto glass slides. PBV may also be precipitated as white, slightly yellow powdery by slow crystallization of the polymer mixture to a 10-fold or greater volume of a nonsolvent such as acetone or methanol. Approximate polymerization yields in the procedures below were determined by weighing precipitated powders. As a result of the tendency for PBV to undergo spontaneous exothermic decomposition, it is recommended that solid samples be limited to 1 g or less. Powders of PBV even at concentrations below 1 g were observed to decompose as soon as they were exposed to the walls of glassware. Films should be handled with caution. The concentration of BV was determined by NMR integration of a 1.0–1.5 M solution in hexanes (other residual solvents are also present). The concentration of BV may be as high as 1.0 M, with no residual dimethyl ether. Both PBV and PB are potentially dangerous materials and should be handled with caution.

**Synthesis of PBV with I.** Catalyst I is most conveniently used since the reaction proceeds smoothly at room temperature and is best accomplished in a glovebox. Polymerization reaction conditions were 0.5 M in benzene, a 60:1 monomer to catalyst ratio, and a reaction time of 2.5 h. For example: 0.75 mL of a 1.5 M solution of BV (1.13 mmol) is added to a 1.75 mL benzene solution of C6D6. Samples were evaporated to approximately one-third the original volume with each cycle. As this procedure is repeated, a greater portion of the polymer begins to gel. Hence, the best results were obtained by subjecting the sample to approximately 7–10 cycles and samples contained a small amount of residual hexane.

**Synthesis of PBV with II.** Catalyst II is most conveniently used since the reaction proceeds smoothly at room temperature and is best accomplished in a glovebox. Polymerization reaction conditions were 0.5 M in benzene, a 60:1 monomer to catalyst ratio, and a reaction time of 2.5 h. For example: 0.75 mL of a 1.5 M solution of BV (1.13 mmol) is added to a 1.75 mL benzene solution of C6D6. Samples were evaporated to approximately one-third the original volume with each cycle. As this procedure is repeated, a greater portion of the polymer begins to gel. Hence, the best results were obtained by subjecting the sample to approximately 7–10 cycles and samples contained a small amount of residual hexane.

**Synthesis of PBV with III.** Catalyst III is most conveniently used since the reaction proceeds smoothly at room temperature and is best accomplished in a glovebox. Polymerization reaction conditions were 0.5 M in benzene, a 60:1 monomer to catalyst ratio, and a reaction time of 2.5 h. For example: 0.75 mL of a 1.5 M solution of BV (1.13 mmol) is added to a 1.75 mL benzene solution of C6D6. Samples were evaporated to approximately one-third the original volume with each cycle. As this procedure is repeated, a greater portion of the polymer begins to gel. Hence, the best results were obtained by subjecting the sample to approximately 7–10 cycles and samples contained a small amount of residual hexane.

**General Isomerization of PBV.** In general, due to the instability of PBV, efforts were made to isomerize the materials as soon as possible. Hence, as soon as the films were evaporated to a level at which they were tacky, the solution of the polymer was poured onto glass microscope slides in a glovebox. Polymerization reaction conditions were 0.5 M in benzene was added to 30 mg (0.052 mmol) of I in 2 mL of benzene. This reaction was stirred for 1 h at room temperature. At this time, the reaction was diluted with 10 times the volume of benzene and the solvent with THF for 48 h resulted in the disappearance of these peaks. However, if the films were not evaporated enough the resulting materials had poor mechanical properties and were not as smooth in appearance. The isomerization of the PBV homopolymer was performed in a glovebox. As a result of the solvent used for the isomerization of the block copolymers (see below), the isomerization of these materials was performed by Schlenk techniques.

**Isomerization of PBV with HgCl2 and HgBr2.** A 5% solution of HgCl2 was prepared in THF. Freshly cast films of PBV on glass slides were immersed in this solution in a glovebox at room temperature. The films turned red within seconds, blue-green over the next 30 s, and finally to a dark brown color within 3 min. Films were washed with THF for at least 1 h and then removed from the glass slide. The resulting, free-standing films of PPA were washed with THF and further purified by Soxhlet extraction with THF. A similar procedure was carried out for PBV with HgBr2 with similar results. With HgBr2 the rate of color change was ~10 times slower and the films were not quite as silver as those obtained with HgCl2. The residual HgCl2 was difficult to remove from the films. X-ray diffraction of films that were washed with THF multiple times displayed many sharp diffraction peaks indicating residual HgCl2. It is interesting to note that these peaks did not index with any of the HgCl2 with or without exposure to THF. Soxhlet extraction with THF removed all traces of HgCl2. However, elemental analysis (Spang Microanalytical Laboratories) revealed the films to be 89.2% carbon and hydrogen (C/H = 1.09). Further Soxhlet extraction with acetone (24 h) and then methanol (24 h) gave analyses (Caltex Microanalytical Facility) with a carbon and hydrogen content of 91.55 (C/H = 0.955). CPMAS 13C NMR: 135.5 (s) and 40 ppm. Infrared: 3450 (s, br), 930 (s, br), 900 (s, br), 890 (s, br), 735 (s, br), 615 (w, br) cm−1. UV–vis (film isomerized at 150 °C in 6 b) λmax 420. The PBV-polynorbornene block copolymer is isomerized in much the same fashion except acetone was used instead of THF. This was necessary because the PBV homopolymer was soluble in THF and hence produces poor-quality films.

**Isomerization of PBV with AgBF4.** The isomerization with AgBF4 was much slower than was observed with HgCl2. Films soaked in a 2% solution of AgBF4 solution in THF turned red over the course of 5 min. The isomerization appeared at times to initiate in small areas of the film and then spread throughout the film. The films turned to a dark, silvery,
null material over the course of 30 min. CPMAS $^{13}$C NMR: 135, 127 ppm. Metallic silver deposited in the film precluded infrared analysis. Isomerization of PBV with ZnI$_2$. ZnI$_2$ has a limited solubility in THF, and hence a saturated solution was used with excess solid ZnI$_2$. This isomerization is slow and after 2 h the PBV films were red. After soaking in the ZnI$_2$ solution for 24 h, the films were black and shiny. These films were then rinsed multiple times with THF and were strong and flexible. Infrared: 3090 (s, sh), 2900 (s, br), 1715 (s, br), 1650 (s, br), 1430 (s, sh), 995 (s, br), 970 (s, br), 866 (s, br), 745 (s, br), 685 (sh, cm$^{-1}$).

Isomerization of PBV with (RhCl(COD))$_2$. PBV films were soaked in a 1% solution of (RhCl(COD))$_2$ in THF for 5 days. The films became red over this period and were brittle. These films were rinsed multiple times with THF and were strong and flexible. Infrared: 3090 (s, sh), 2900 (s, br), 1715 (s, br), 1650 (s, br), 1430 (m, sh), 995 (s, br), 970 (s, br), 866 (s, br), 745 (s, br), 685 (s, sh) cm$^{-1}$.

Abstract: Diatomic carbon, C$_2$, reacts with propylene and (E)- and (Z)-2-butene in the condensed phase at 77 K. Products can be rationalized by a mechanism involving initial addition of C$_2$ to the alkene to generate a 1,4-diradical. This diradical may then either abstract hydrogens or add another alkene molecule to give a 1,6-diradical which disproportionate to an enyne. Thus, reaction of C$_2$ with propylene gives 1-pentene, 3-methyl-1-butyne, 4-methylhex-6-en-1-yn, 6-methylhept-1-en-4-yne, and oct-1-en-4-yne. Ab initio calculations at the HF/3-21G level predict that both C$_2$ and C$_4$ will add to ethylene without barrier. At the MP2/6-31G$^*$/3-21G level, the triplet adduct is calculated to be more stable than C$_2$ and ethylene by 46.0 kcal/mol. The reactions of C$_2$ and 'C$_2$ with methane and hydrogen have also been investigated theoretically.

Diatomic carbon has been the subject of theoretical, spectroscopic, and kinetic studies, but little is known of the mechanisms and products of its reactions. Ballik and Ramsay have demonstrated that there are two low-lying electronic states of C$_2$, the singlet ($^1$C) and the triplet ($^3$C$_2$), the triplet being only slightly above the ground state. Thus any thermal generation of C$_2$ will inevitably produce triplet-singlet mixtures. A theoretical calculation indicates the structure -C=C- for the ground state singlet and

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\begin{align*}
\text{C} & \equiv \text{C} \\
\text{C} & \equiv \text{C}
\end{align*}
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for the triplet. With fluorescence spectroscopic methods, it has proved possible to follow the decay of both the lowest singlet and triplet states of C$_2$ in the presence of various substrates and to obtain kinetic information.

Skell and co-workers have reported the products in the reaction of diatomic carbon at low temperature, in condensed phase, with alcohols, carboxylic compounds, alkenes, alkynes, and ethers. The known reactions of C$_2$ with C-H bonds include abstraction to generate acetylene, in which the hydrogens can come from the same carbon or from different carbons, and formation of cumulenes in what is formally a double C-H insertion. One of us has previously reported that C$_2$ reacts with C=C double bonds to generate vinylidene intermediates which subsequently add another molecule of alkene to produce alkylidene cyclopropanes. In the present study, the reaction of C$_2$ with alkenes has been reinvestigated since the original structures of the addition products were based on primitive methods (by current standards) and were

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Some Reactions and Properties of Molecular C$_2$. An Experimental and Theoretical Treatment

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Supplementary Material Available: Figures showing $^1$H NMR of PBV produced with 1 and III and of PBV-PN block copolymer, thermogavimetric and thermomechanical analysis of PBV, CPMAS $^{13}$C NMR of PBV after storage, and IR spectra of PPA (5 pages). Ordering information is given on any current masthead page.