J. Am. Chem. Soc. 1989, 111, 4413–4422

on silica gel (elution with 1% triethylamine in petroleum ether) provided 0.177 g (86%) of furan **26** as a colorless oil: IR (film) 3080, 3060, 3020, 2960, 2920, 1945, 1800, 1700, 1580, 1500, 1455, 1425, 1385, 1330, 1260, 1235, 1190, 1160, 1105, 1075, 1040, 1000, 980, 920, 885, 800, 750, and 705 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16–7.30 (m, 5 H), 5.84 (s, 1 H), 3.88 (s, 2 H), 2.34 (q, J = 7 Hz, 2 H), 2.20 (s, 3 H), and 1.11 (t, J = 7 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.9, 146.5, 139.4, 128.4, 128.3, 126.1, 122.5, 107.0, 32.2, 18.1, 15.1, and 13.5; HRMS *m/e* calcd for $C_{14}H_{16}O$ 200.1201, found 200.1201.

Acknowledgment. We thank the National Science Foundation for generous financial support. We are also pleased to thank Dr. David A. Becker for his contributions to the development of the [3 + 2] heteroaromatic annulation strategy. Brian R. Dixon developed the procedure for the purification of allene **6**.

New Morphologies of Polyacetylene from the Precursor Polymer Polybenzvalene

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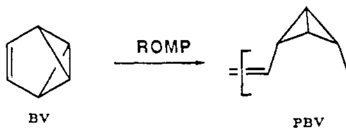
Abstract: The synthesis and properties of the polymer polybenzvalene and its conversion to polyacetylene are presented. This conversion is performed by treating polybenzvalene with Lewis acidic catalysts. The highest quality material was obtained from the isomerization with $HgCl_2$. The polyacetylene (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 Ω^{-1} cm^{-1} with I_2 doping. Materials stretched to elongations of $l/l_0 = 2.3$ and $l/l_0 = 6$ displayed conductivities of 13 Ω^{-1} cm^{-1} and 49 Ω^{-1} cm^{-1}, respectively. Block copolymers of polynorbornene and polybenzvalene were produced. These copolymers exhibited no phase separation as determined by DSC. The isomerization of these materials produced a polyacetylene–polynorbornene 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 polynorbornene.

The field of conductive polymers has seen considerable study in the last 10 years.[1] Polyacetylene (PA) has received the most extensive investigation[1,2] 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.[4a] 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.

Scheme I



A strategy based on intramolecular, electrocyclic rearrangements may successfully meet the nonextrusive criterion.[6] In this scheme, olefins are masked by incorporating them into ring systems. 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.

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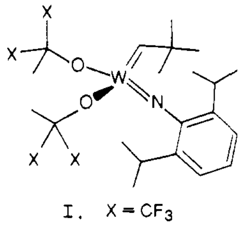
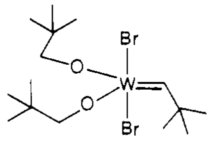
Recent advances in well-defined, active, organometallic catalysts[8] for ring-opening olefin metathesis polymerization (ROMP) have enabled the polymerization of monomers that were previously incompatible with the highly Lewis acidic ROMP catalysts. In addition, these catalysts provide living polymerizations in some cases.[9] The living nature of the polymerization allows the synthesis of block copolymers which allow for a greater variation in the morphology 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 in the production of polyacetylene[4a,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)[8a,b] and Osborn (III)[8c–i] 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 bicyclobutane 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 (≥20 °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.



I. X = CF_3
II. X = CH_3



III

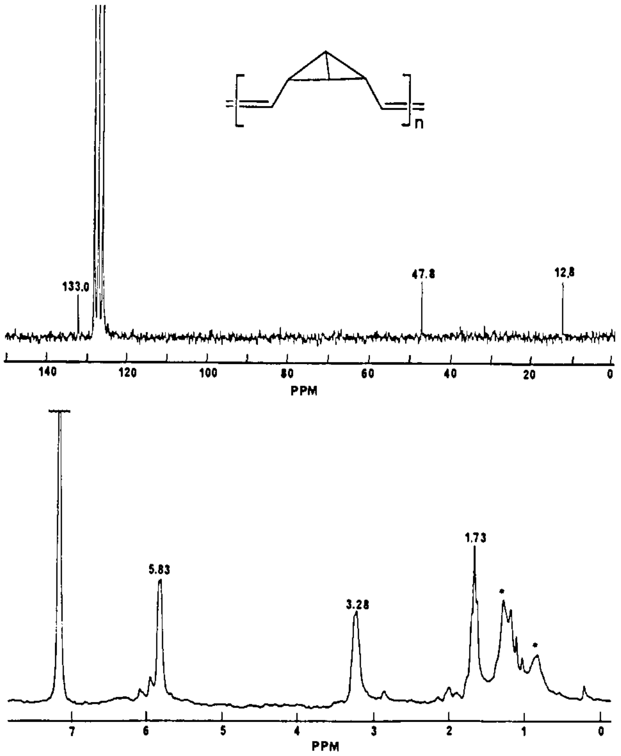


Figure 1. (a) ^{13}C NMR and (b) ^{1}H NMR spectra of *cis*-PBV produced with II in C_6D_6. The asterisks indicate peaks due to residual hexane.

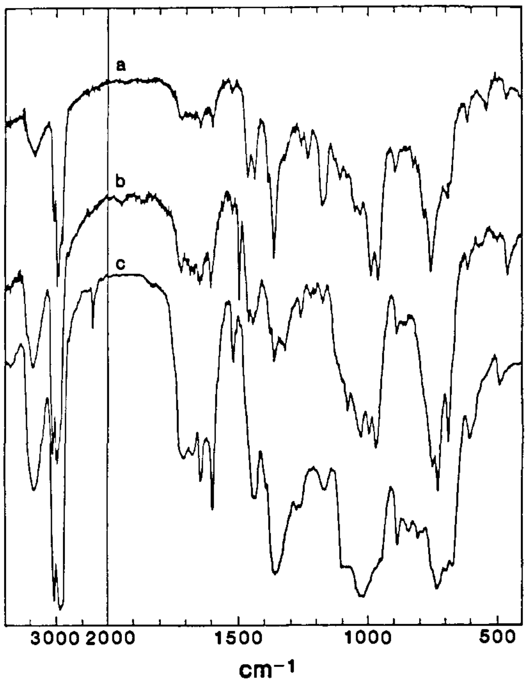


Figure 2. Infrared spectra (films on KBr plates) of PBV produced with I (a), II (b), and III (c). These materials all have distinctively similar spectra.

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

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[14] The heat liberated from the detonation of 100–200 mg samples was sufficient to melt the latex gloves with which the author was handling the sample.

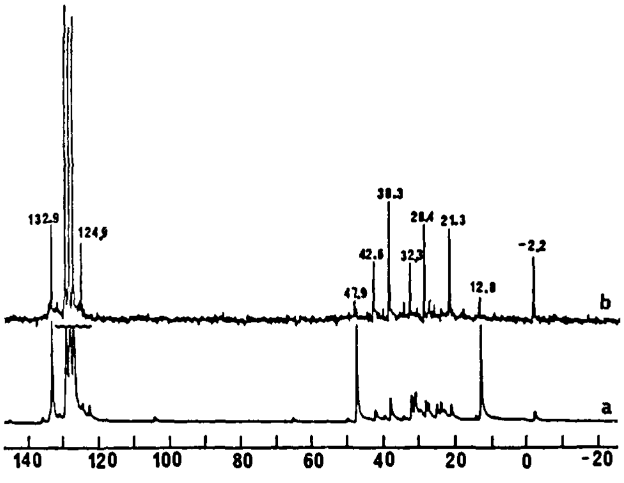
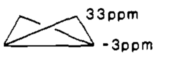
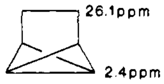
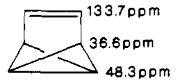


Figure 3. ^{13}C NMR (C_6D_6) spectra of PBV produced with I (a) and III (b). Note the correlation of signals between the two materials.

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 C_6D_6 to remove residual solvents. Catalyst II has been found to exhibit a high selectivity for producing cis double bonds in the polymerization of norbornene[9a] and other monomers.[16] 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 bicyclobutane, the saturated analogue of BV, and BV.







As seen in these compounds, the bridgehead carbon of the bicyclobutane moiety shows considerable chemical shift dispersion and is shifted downfield with increasing ring strain.[17] Thus, the signal upfield at 12.8 ppm in the ^{13}C NMR spectrum of PBV is most likely the bridgehead carbon of the bicyclobutane 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 ^1H NMR spectrum of PBV synthesized with II is complicated by residual hexane as shown in Figure 1. The ^1H NMR spectra of *cis*-PBV is very similar to that of BV, which has ^1H NMR peaks at 5.95, 3.53, and 1.84 ppm in benzene.

Both I[9a] and III[8g,h] polymerize norbornene to produce polynorbornene (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 124.9 ppm which may arise from trans double bonds. Examination of the ^1H 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,[18] 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 conformationally rigid PBV backbone and the sensitivity of the bicyclobutane resonances to their environment. As discussed previously, the bridgehead carbon of the bicyclobutane 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 bicyclobutane 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 bicyclobutane resonances are sensitive to the configuration of olefins not directly connected to each bicyclobutane. This is not unreasonable considering the conformational rigidity of the polymer backbone. However, the possibility that some of the ^{13}C NMR signals exhibited by PBV produced with I 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.[19] 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[20] 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,[21] 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.[22]

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).[23] The spectra consisted of broad peaks ($w_{1/2} \approx$ 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

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(19) Griffith, D. W. T.; Kent, J. E.; Dwyer, F. O. *Aust. J. Chem.* **1975**, *28*, 1397.

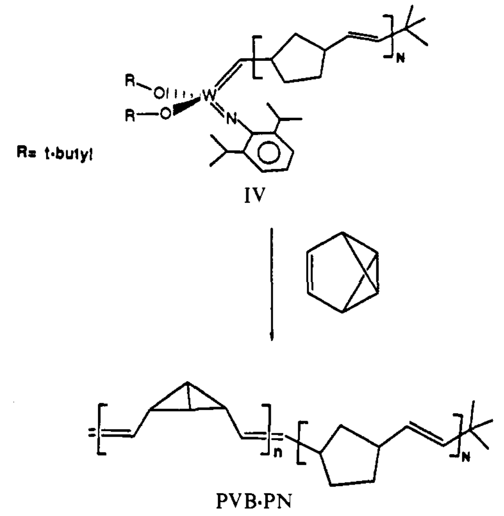
(20) The infrared spectra of PBV films produced with the other catalysts also became broadened in time as a result of partial decomposition.

(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.

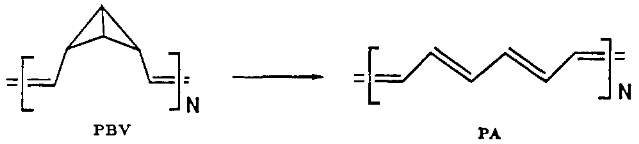
(22) Catalyst II reacts with BV at room temperature to give a bright red solution and a low yield of polymer ~20%.

(23) Yannoni, C. S. *Acc. Chem. Res.* **1982**, *15*, 201–208.

Scheme II



Scheme III



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.[24] 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.[13] By the use of Franklin's constants, the heat of formation of the strainless repeating unit is calculated to be 14.5 kcal/mol.[13] 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.[25] Hence, the measured strain energy per repeating unit is calculated to be ~51 kcal/mol. This measurement is compared with the strain energy of bicyclobutane 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.[9b] 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 II. ^{1}H NMR spectroscopy confirms the presence of both PBV and PN. The ratio of the two polymers is readily determined by integration of the ^{1}H 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,[26] photochemically,[27] and with transition-metal catalysts.[28] The analogous transformation for PBV produces PA as shown in Scheme III.

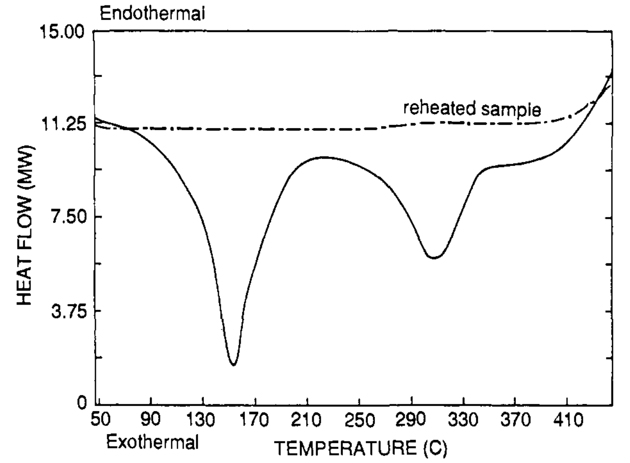


Figure 4. DSC thermogram of PBV at 10°/min. The solid line is for the first scan and the broken line is for the reheated sample. Integration from 50 to 420 °C reveals the liberation of 59 kcal/mol for the first scan.

Scheme IV

The thermal transformation of PBV into PA is an attractive goal. Bicyclobutanes rearrange to 1,3-dienes at approximately 150–200 °C.[26] 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.[29]

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 I_2 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 I_2 or AsF_5 treatment.

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(25) The heat of formation was determined experimentally by bomb calorimetry and was performed by Morton Thiokol, Inc.

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(27) (a) Renner, C. A.; Katz, T. J.; Pouliquen, J.; Turro, N. J. *J. Am. Chem. Soc.* **1975**, *97*, 2568. (b) Adam, W.; Oppenlander, T. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 661–672 and references therein. (c) Adam, W.; Oppenlander, T.; Zang, G. *J. Am. Chem. Soc.* **1985**, *107*, 3921–3924. (d) Becknell, A. F.; Berson, J. A.; Srinivasan, R. *J. Am. Chem. Soc.* **1985**, *107*, 1076–1078.

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(29) DSC of PBV samples that had been stored at room temperature for 2 months displayed a similar thermogram. Integration showed the samples to contain ~75% the chemical energy of fresh samples. The peaks were broader and the 153 °C exotherm was shifted to 172 °C.

Scheme V

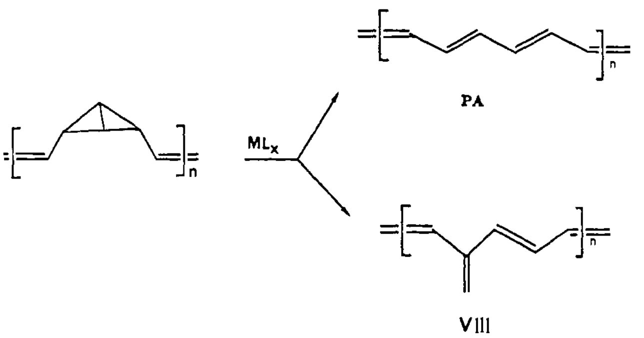

Table I. Results of the Catalytic Isomerizations

catalyst	appearance	conductivity, Ω^{-1} cm^{-1}		isomerization of V,[a] % yield of products	
		un-doped	saturated with I_2	VI	VII
$AgBF_4$	silvery-black, dull	10^{-8}	10^{-4}	100	
ZnI_2	black, shiny	10^{-6}	0.2	88	11
$HgBr_2$	black, shiny	10^{-7}	0.1	85	8
$HgCl_2$	silvery-black, shiny	10^{-5}	1.0		
$[Rh(COD)Cl]_2$[b]	burgundy-red		10^{-6}	0	98

[a] From ref 28b. [b] $[Rh(CO)_2Cl]_2$ was used in ref 28b.

Solid-state CPMAS ^{13}C NMR spectra of the heated samples revealed extremely broad signals ($w_{1/2} \approx$ 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.$0^{2,7}$]heptane (V) by a variety of Lewis acidic catalysts.[28b] In this investigation it was reported that isomerization of V with $AgBF_4$, ZnI_2, and $HgBr_2$ 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 $AgBF_4$, $HgBr_2$, $HgCl_2$, and ZnI_2 were semiconductive in their undoped form, as is observed for PA. CPMAS ^{13}C NMR spectroscopy (Figure 5) confirms that PA was formed with the $AgBF_4$ and $HgCl_2$ treatment. The CPMAS ^{13}C NMR spectrum of material from the $AgBF_4$ isomerization of PBV displays peaks at 135 and 127 ppm which correspond to *trans*- and *cis*-PA, respectively.[30] Ag^+ salts have been demonstrated to oxidatively dope PA.[31] Hence, as PA is produced, Ag^0 is also deposited in the material. This material exhibits a conductivity before doping of $\sim 10^{-8}$ Ω^{-1} cm^{-1}. I_2 doping produced materials with modest conductivities of $\sim 10^{-4}$ Ω^{-1} cm^{-1} and had a noticeable amount of light yellow AgI on the surface of the film. The deposition of metallic silver in the polymer and its subsequent conversion during doping is the likely cause of the low conductivities observed for this material.

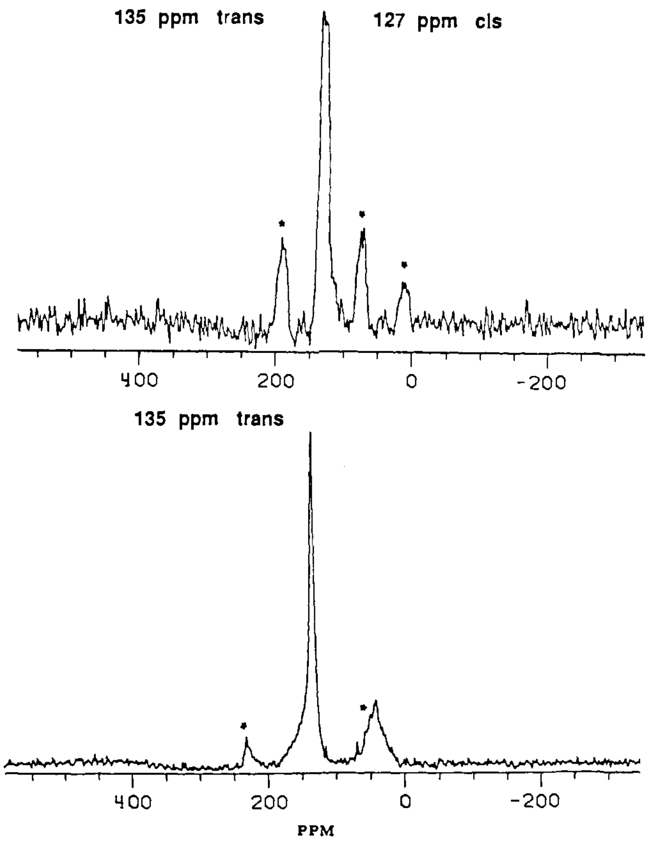

Figure 5. (a) CPMAS ^{13}C NMR spectrum of PA produced from the isomerization of PBV with $AgBF_4$. (b) CPMAS ^{13}C NMR spectrum of PA produced with $HgCl_2$ after thermal isomerization to *trans*-PA by heating at 150 °C for 6 h. The sp^3 peak at 40 ppm is the result of cross-linking. The asterisks represent spinning sidebands.

Isomerization with $HgCl_2$, in addition to yielding materials exhibiting the highest conductivity with I_2 doping (1 Ω^{-1} 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. To distinguish the PA formed by the $HgCl_2$ isomerization of PBV from the other forms of PA discussed, this material will be called "precursor polyacetylene" or PPA.

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 $HgBr_2$ and ZnI_2 display similar spectra. A small infrared band at 895 cm^{-1} is present in materials produced with $HgBr_2$, $HgCl_2$, and ZnI_2. This band is indicative of the vinylidene moiety and indicates that some VIII is likely to have been produced in the isomerization. The absorption bands of PPA are wide in comparison with those of Shirakawa PA[2] 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.[32] The broad nature of the infrared spectra of PPA precludes a quantitative determination of the cis to trans content. However,

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(30) See: Clarke, T. C.; Scott, J. C. in ref 1, pp 1127–1156.

(31) Clarke, T. C.; Geiss, R. H.; Kwak, J. F.; Street, G. B. *J. Chem. Soc., Chem. Commun.* **1978**, 489–490.

(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.

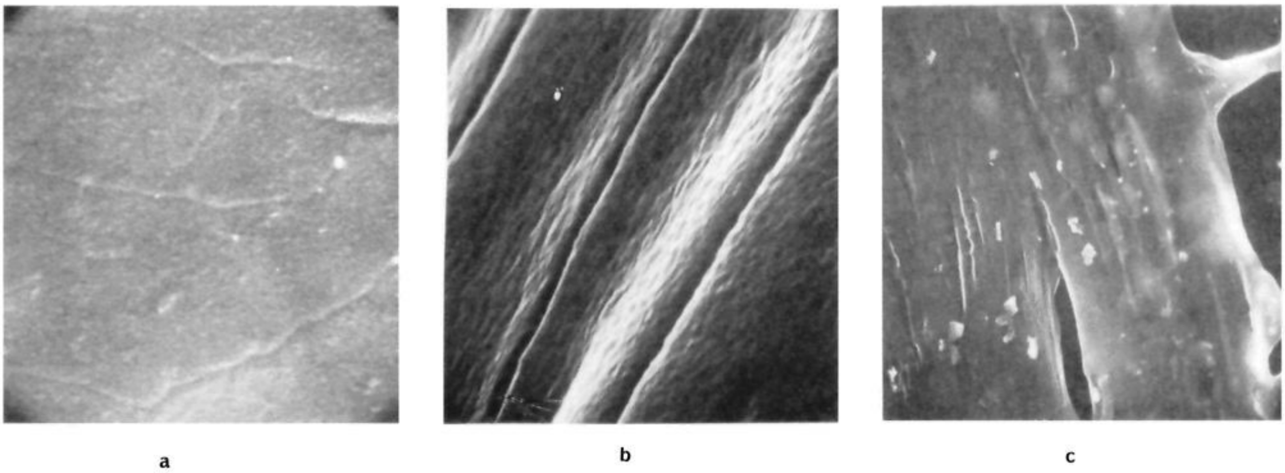

Figure 6. (a) SEM photograph of unoriented PPA (magnification 12 000) showing a textured surface and stress-induced lines. (b) An SEM photograph of oriented PPA $l/l_0 = 6$ at 30 000 magnification is shown. The oriented material shows channels in the direction of stretching which are approximately 0.5 μm apart. Fibrils approximately 200 Å in diameter are also observed. (c) An SEM photograph of an oriented $l/l_0 = 6$ PPA:PN (1:1.2) block copolymer at a magnification of 3000 is shown. The block copolymer has a much smoother surface and the material appears to have relaxed or undergone some flow to relieve the stress induced with orientation. (Note: the photographs have been reduced by 63% for publication.)

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.[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 ^{13}C NMR experiment.[33] *trans*-PA is considerably more brittle than *cis*-PA,[2] and thus ^{13}C NMR samples were first isomerized to *trans*-PPA at 150 °C for 6 h and then ground. Thus, the CPMAS ^{13}C NMR spectrum shown in Figure 5 is of *trans*-PPA. The CPMAS ^{13}C NMR spectrum also exhibits an additional peak at 40 ppm which is the result of sp^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 $T_{1\rho}$ relaxation time than the 135.5 ppm signal.[34] A more rigid environment is consistent with these sp^3 carbon centers resulting from cross-linking. Quantitative measurements of the amount of sp^3 carbons in PPA were performed at a cross-polarization contact time of 2 ms. Integration determined the PPA to contain ~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 (~150 °C).[2,4a,11] A crankshaft mechanism for the isomerization of *cis*- to *trans*-PA has recently been proposed.[36] Cross-linking would inhibit the crankshaft motion, thus resulting in the higher isomerization temperature.

The product of Rh$^{\rm I}$-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^{-1} indicates there is considerable saturated material present. DSC reveals the absence of the 153 °C exotherm exhibited by PBV. This suggests that residual bicyclobutanes are not present. On the basis of Gassman's results,[28b] we anticipated the formation of VIII with Rh$^{\rm I}$ isomerization. Hence, if VIII is formed, it is prone to cross-linking and decomposition to give saturated material. Our previous studies of polymers similar to to VIII indicated that conjugated vinylidene groups are prone to cross-linking which produces saturated centers.[37]

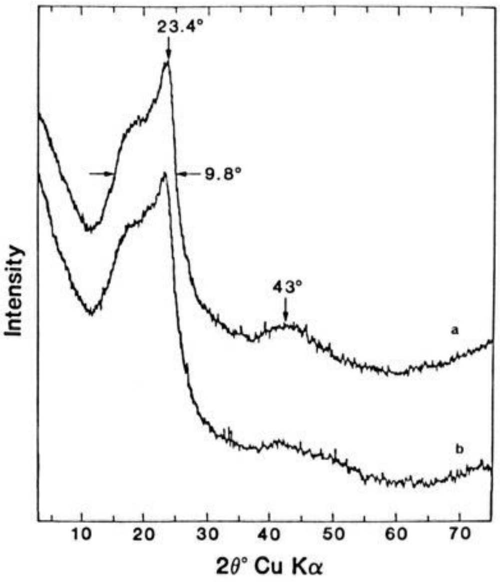

Figure 7. Wide angle X-ray diffraction intensity of unoriented PPA as produced (a) and after thermally annealing at 120 °C for 48 h (b). The tail of an amorphous halo is observed at low angles and the characteristic *d* spacing of 3.80 Å (23.4°) of PA is also observed. The broad nature of the diffraction peak ($w_{1/2} = 9.8°$) indicates a low level of crystallinity.

Morphology of PPA. The conductivity of conductive polymers is known to increase with increasing crystallinity.[1] This is a consequence of factors such as greater carrier mobility in a more rigid lattice, higher conjugation lengths, and better interchain interaction. An advantage of a precursor route is the fact that a variety of morphologies may be produced depending on the processing.[4] Hence, the manipulation of the morphology of PPA was studied.

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(33) Spinning rates of 3.5–5 kHz are required to reduce the sidebands in the CPMAS ^{13}C NMR experiment at a carbon frequency of 50.36 MHz.

(34) Eckert, H.; Yesinowski, J. P.; Sandman, D. J.; Velazquez, C. S. *J. Am. Chem. Soc.* **1987**, *109*, 761.

(35) Ito, T.; Shirakawa, H.; Ikeda, S. *J. Polym. Sci., Polym. Chem. Ed.* **1975**, *13*, 1943.

(36) Gibson, H. W.; Kaplan, S.; Mosher, R. A.; Prest, W. M.; Weagley, R. J. *J. Am. Chem. Soc.* **1986**, *108*, 6843.

(37) We have investigated the ROMP of 3,4-dimethylenecyclobutene and found the resulting polymer to be highly susceptible to cross-linking reactions. Swager, T. M. Ph.D. Thesis, California Institute of Technology, May 1988.

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 fibular morphology observed in Shirakawa PA. The bulk density of PPA is 0.87 g/cm^3, which is higher than that of Shirakawa PA, but lower than Durham PA ($\rho > 1$). 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.[38] 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 $2\theta = 23°$ with a d spacing of 3.80 Å, which is the dominant peak observed in other forms of PA.[2,5b] The full width at half height ($w_{1/2}$) of this peak is $2\theta = 9.8°$. This is considerably broader than PA produced by other methods. For example, Shirakawa *cis*-PA has a $w_{1/2}$ of $2\theta = 1.5°$,[2] and unoriented, Durham *cis*-PA has a $w_{1/2}$ of $2\theta = 4°$.[5b] There is no noticeable change in PPA upon annealing at 120 °C whereas the 23° peak of Durham PA was observed to narrow with thermal annealing to widths of $2\theta \approx 2.0°$.[5b] The $2\theta = 23.4°$ peak of PPA is noticeably asymmetric with a shoulder at lower angles. This shoulder at higher 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 23° peak.[5b] The tail of an intense amorphous halo is also observed in Figure 6 and results in a sloping baseline under the $2\theta = 23.4°$ peak. At larger angles there is a hint of the $2\theta = 43°$ diffraction peak observed in other forms of PA.[2,5b]

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 eV[2] and unoriented Durham *trans*-PA has a band gap of 1.5 eV and an absorption maximum of 2.3 eV.[5a] 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 PPA 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 $l/l_0 = 2.3$ and $l/l_0 = 6.0$ displayed conductivities of 13 and 49 Ω^{-1} cm^{-1}, respectively, when doped to saturation with I_2 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.[2] The fibrils of the oriented material are ~200 Å in diameter. Stretching polymers is known to induce crystallinity,[39] and thus X-ray diffraction of the oriented PPA was investigated. The X-ray diffraction intensity of oriented PPA ($l/l_0 = 6$) 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 $2\theta = 23.4°$ peak shape is qualitatively the same for the $l/l_0 = 2.3$ elongation. However, this material still exhibits some tailing at low angles (≤10°) from an amorphous halo.

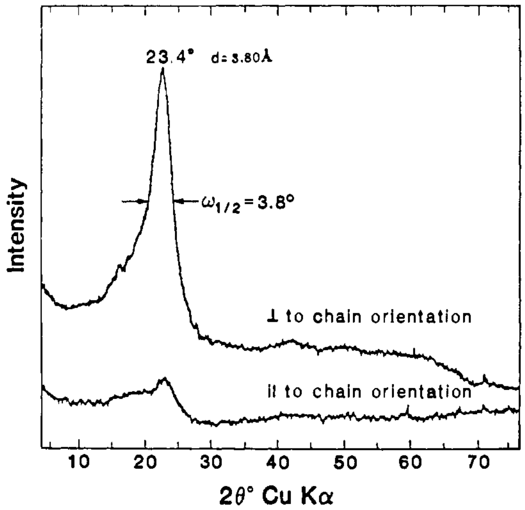

Figure 8. Wide angle X-ray diffraction intensity of oriented $l/l_0 = 6$ PPA at different orientations of the polymer film. The peak intensity is most intense for the diffraction perpendicular to the orientation, indicating that the polymer chains are oriented in the stretching direction. The narrowing of the diffraction peak to $w_{1/2} = 3.8°$ indicates that the level of crystallinity has been increased greatly from that of the unoriented material. In addition, the diffraction from the amorphous halo at low angles is greatly reduced.

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.[10] The PBV:PN block copolymers were shown to exist as a single phase, as DSC showed no detectable glass transition (T_g) for PN. Phase separated PN should have a T_g 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.[10] 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 T_g 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 I_2. Orientation (l/l_0) of the block copolymers resulted in an increase of the conductivity to 0.37 Ω^{-1} cm^{-1} when saturated with I_2. The decrease in the conductivity of the oriented copolymer from that of the oriented PPA homopolymer ($l/l_0 = 6$) 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 $2\theta = 19.6°$ 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

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[38] PBV forms clear films with no birefringence and hence is an amorphous material. The X-ray diffraction of PBV exhibits a peak at $2\theta = 17°$ ($d = 5.2$) and a very broad asymmetric peak from ~2–20°.

[39] Alexander. L. E. *X-Ray Diffraction Methods in Polymer Science*; Wiley-Interscience: New York, 1969.

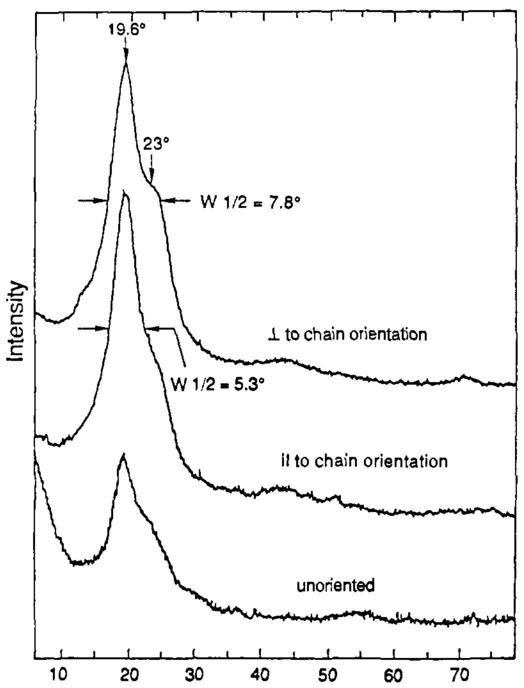

Figure 9. Wide angle X-ray diffraction intensity of the PPA:PN (1:1.2) block copolymer. The unoriented material displays the tail of an amorphous halo at low angles and a peak at 19.6° (d = 4.67 Å) with a slight shoulder at 23°. In the oriented material, $l/l_0 = 6$, the 19.6° peak is isotropic with respect to orientation while the 23° peak is not. The fact that the 23° shoulder displays a stronger diffraction in the perpendicular orientation indicates that the phase-separated PPA is aligned in the stretching direction.

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[40] 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 d 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.[7,8] 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. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL FX-90Q spectrometer (89.6 MHz for ^{1}H, 23.53 MHz for ^{13}C). Chemical shifts were referenced to the solvent (^{13}C NMR) or to residual protons in the solvent (^{1}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–vis analysis were films ~0.1-μm thick. The conductivity measurements were made with the four-point method[41] 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 160B 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 Alltech TSK-gel GMH6 column with toluene 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 1 300 000. CPMAS ^{13}C NMR spectra were obtained on a home-built spectrometer at a carbon frequency of 50.36 MHz. A commercial Doty Scientific CPMAS probe was used and spinning speeds of 3.5–5 KHz were obtained. The samples were ground with Na_2SO_4 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 Na_2SO_4. Data collection was performed with a Nicolet 1280 computer and Nicolet NMC 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° ^{1}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 home-built Guinier camera in a vacuum with monochromatic Cu Kα radiation. Plots of the X-ray data were obtained by scanning the developed film with a LKB Bromma Ultrascan XL laser densitometer. X-ray photographs of the oriented films at different orientations were of the same sample 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 detonation of the PBV samples. SEM photographs were obtained on an ETEC autoscan 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 with a thermocouple which was put in the furnace next 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 H_2SO_4 for 3 weeks. CH_2Cl_2 and chlorobenzene were dried with P_2O_5. Catalysts I and II were made by the published procedure[8b] and purified by recrystallization from pentane (20–50 °C). Catalyst III was made by the method of Kress and Osborn.[8h] The methanol or acetone used to precipitate the polymer was not dried but was deoxygenated by pumping on the solvent multiple times and then bubbling argon through the solvent for half an hour or more. $HgCl_2$ (Baker) was purified by sublimation under dynamic vacuum. ZnI_2 (Aldrich) was purified by heating at 100 °C under vacuum for 12 h. $AgBF_4$ (Alfa), $HgBr_2$ (Allied Chemical), and $(RhCl(COD))_2$ (Strem) were used without purification. Polyethylene was used as a substrate for

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(40) Bates, F. S.; Baker, G. L. *Macromolecules* **1983**, *16*, 1013.

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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 of beer or soft-drink cans together. This material could be stretched to 6.0 times its length. The stretching was found to be uniform by measuring the distance between marks on the substrate before and after elongation. BV is explosive in pure form and must be handled in solution. Solutions of BV were prepared by the published procedure[15] with the condition that the second equivalent of alkyllithium is butyllithium. By using a concentrated butyllithium solution in hexanes, BV could be obtained as a 1.0–1.5 M solution in hexanes (other residual solvents are also present). The concentration of BV was determined by NMR integration against an internal standard of mesitylene. Solutions of BV were degassed, placed under inert atmosphere, and stored over 4-Å molecular sieves at −50 °C. The synthesis of BV may result in residual dimethyl ether and diethyl ether in the solution of BV, which will decrease the activity of the catalysts and, hence, change reaction times. The polymerization procedures presented below are based on a concentration of diethyl ether of approximately 1 M with no residual dimethyl ether. Both PBV and BV are *potentially dangerous materials* and should be handled with caution.

General Synthesis of PBV. The polymerization of BV 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 a white or slightly yellow powder by slow addition of the polymerization 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 precipated 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 seem to be most prone to decomposition and were observed to decompose when scraped away from the walls of glassware. Films should be gently cut with a razor blade since tearing may also cause decomposition. NMR samples were prepared by removing an aliquot of the polymerization solution and subjecting it to repeated evaporation of the solvent and the addition of C_6D_6. 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 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 BV, 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 I (10.7 mg, 0.019 mmol). After 2.5 h the yellow, homogeneous reaction mixture is viscous. At this time the reaction mixture is cast directly into films on glass microscope slides in a glovebox. Once dry, the smooth films are light yellow in appearance, ~0.03-mm thick, and soft and rubbery. The reaction yield was approximately 70%. ^{1}H NMR (C_6D_6): 6.35 (br s), 6.06 (br s), 5.83 (2 H, br s), 3.29 (2 H, br s), 2.58 (br s), 1.72 (2 H, br t) ppm. ^{13}C NMR (C_6D_6): 133.0, 47.8, 12.8 ppm and multiple smaller peaks in the region of 20–40 ppm (Figure 3). Infrared: 3450 (m, br), 3025 (s), 2920 (s), 1590–1720 (w), 1460 (m, sh), 1440 (m, sh), 1360 (s, sh), 1075 (m, sh), 980 (s, br), 965 (s, br), 750 (s, br) cm^{-1}. UV–vis (film): λ_{max} 190 nm with a shoulder at 270 nm. GPC analysis indicated a broad molecular weight distribution ranging from 600 000 to 3500 with the average molecular weight estimated to be 30 000.

Synthesis of PBV with II. The activity of the fluorinated catalyst (II) is considerably greater than that of the nonfluorinated catalyst (I).[8a,b] A monomer concentration of 0.15 M is used (balance toluene) and a 50:1 monomer to catalyst ratio. For example: 1.9 mL of a 1 M solution of BV (1.9 mmol) is added to 11 mL of a toluene solution of II (30 mg, 0.038 mmol) at −20 °C. The reaction mixture is initially yellow. After 0.5 h at −20 °C the reaction mixture is slowly allowed to warm to 0 °C over the course of 1.5 h. The reaction mixture is light orange and the presence of polymer is apparent from the increased viscosity. The catalyst is deactivated by the addition of 10 equiv of acetone (based on the number of moles of catalyst). The reaction mixture is concentrated in vacuo to approximately one-third the original volume and cast into light orange films in a glovebox. These films are soft and rubbery and are ~0.03-mm thick. The reaction yield was found to be approximately 70%. ^{1}H NMR (C_6D_6): 5.83 (2 H, br d), 3.28 (2H, br d), 1.72 (2H, br t) ppm. ^{13}C NMR (C_6D_6): 133.0, 47.8, 12.8 ppm. Infrared: 3450 (m, br), 3025 (s), 2970 (s), 2920 (s), 1590–1720 (w), 1495 (m), 1450 (m, br), 1360 (m), 1320 (m), 1080 (s), 1023 (s), 995 (s), 983 (s), 750 (s), 724 (s), 693 (s) cm^{-1}. GPC indicated a very broad molecular weight distribution ranging from 600 000 to 1000, with the average molecular weight estimated to be 20 000. This distribution had three components: a low molecular weight peak at approximately 2000, a maxima at 50 000, and a shoulder at a high molecular weight which extended to 600 000.

Synthesis of PBV with III. Catalyst III is an oil which is not readily purified. The activity of this catalyst has been found to be greatly enhanced by Lewis acids. The last step in the synthesis of III involves reaction with $AlBr_3$, and hence, small amounts of Lewis acidic material may be present. As a result, in our hands this catalyst has been found to have a varied activity in the absence of additional Lewis acid. If the catalyst was too impure, considerable gel was produced in the polymerization. Polymerization conditions were 0.50 M BV and 0.010 M III with a monomer to catalyst ratio of 50. A reaction time of 7 h at room temperature produced a yield of 80% PBV. An example of a preparation is as follows. A solution of III (88 mg, 0.15 mmol) in 5 mL of benzene is prepared. Five milliliters of a 1.5 M solution of BV is diluted with 5 mL of benzene and then added to the solution of III. The reaction turns from a light orange-brown to a darker red-brown color in approximately 1 min. This solution was stirred for 7 h at room temperature and then cast into soft, rubbery films which were orange-brown. ^{1}H NMR (C_6D_6): 6.48 (br s), 6.08 (br s), 6.83 (br s), 3.37 (br s), 2.93 (br s), 2.87 (br s), 2.13 (br s), 2.65 (br s), 2.03 (br s), 1.73 (vbr s) ppm. ^{13}C NMR (C_6D_6): 132.9, 124.9, 47.9, 42.6, 38.3, 32.3, 28.4, 21.3, 12.8, −2.2 ppm. Infrared: 3450 (m, br), 3025 (s), 2930 (br), 1699 (m, br), 1675 (m, br), 1635 (m, sh), 1595 (m, sh), 1510 (w, sh), 1435 (m, br), 1360 (s, vbr), 1015 (s, vbr), 890 (m, sh), 735 (s, vbr), 615 (w, br) cm^{-1}.

Synthesis of PBV:PN Block Copolymers with I. The synthesis of the PN living polymer is a procedure adapted from the literature[9b] and was run in a glove box. Norbornene (0.245 g, 2.6 mmol) in 1.5 mL of 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 6 mL of benzene and then 2.6 mL of a 1 M solution of BV (2.6 mmol) was added. The reaction was stirred for three more hours and then cast into films. The films were slightly yellow, ~0.06-mm thick, and soft and rubbery. The ^{1}H NMR is a composite of PN[9] and PBV. From integration of the olefinic peaks in the ^{1}H NMR the ratio PBV to norbornene was determined to be 1:1.2. GPC analysis indicated a broad, nearly isotropic distribution from approximately 300 000 to 4000 with an average molecular weight of approximately 80 000.

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, they were immersed in the solution of the catalyst. 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 with Schlenk techniques.

Isomerization of PBV with $HgCl_2$ and $HgBr_2$. A 5% solution of $HgCl_2$ 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, to blue-green over the next 30 s, and finally to a black, silvery, shiny film within 2–3 min. Films were soaked in this solution 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 the $HgBr_2$ with similar results. With $HgBr_2$ the rate of color change was ~10 times slower and the films were not quite as silvery as those obtained with $HgCl_2$. The residual $HgCl_2$ 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 $HgCl_2$. It is interesting to note that these peaks did not index with those of $HgCl_2$ with or without exposure to THF. Soxhlet extraction with THF for 48 h resulted in the disappearance of these peaks. 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 (Caltech Microanalytical Facility) with a carbon and hydrogen content of 91.55 (C/H = 0.955). CPMAS ^{13}C NMR: 135.5 (s) and 40 (br) ppm. Infrared: 3100 (s, sh), 2900 (m, br), 1497 (m, br), 1395 (w, sh), 1005 (s, vbr), 740 (s, vbr) cm^{-1}. UV–vis (film isomerized at 150 °C in 6 h) λ_{max} 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 block copolymer was soluble in THF and hence produces poor-quality films.

Isomerization of PBV with $AgBF_4$. The isomerization with $AgBF_4$ was much slower than was observed with $HgCl_2$. Films soaked in a 2% solution of $AgBF_4$ 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, dull 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: 3100 (s, sh), 2900 (m, br), 1410 (s, vbr), 1395 (w, sh), 1005 (s, vbr), 760 (s, vbr) 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 slowly became red over this period and were brittle. These films were rinsed multiple times with THF. Infrared: 3090 (s, sh), 2900 (s, br), 1715 (s, vbr), 1650 (m, sh), 1430 (m, sh), 995 (s, br), 970 (s, br), 866 (s, br), 740 (s, br), 685 (s sh) cm^{-1}.

Acknowledgment. We gratefully acknowledge the NSF (Grant CHE 8520517) and Office of Naval research (contract NOOO14-88-K-0208) for financial support. T.M.S. gratefully acknowledges IBM for a predoctoral fellowship for 1984–1987. T.M.S. was supported in part (1987–1988) by a fellowship from Caltech's Program in Advanced Technologies sponsored by Aerojet General, General Motors, and TRW.

Supplementary Material Available: Figures showing ^1H NMR of PBV produced with I and III and of PBV:PN block copolymer, thermogravimetric 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.

Some Reactions and Properties of Molecular C_2. An Experimental and Theoretical Treatment

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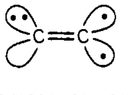
Abstract: Diatomic carbon, C_2, reacts with propylene and (*E*)- and (*Z*)-2-butene in the condensed phase at 77 K. Products can be rationalized by a mechanism involving initial addition of C_2 to the alkene to generate a 1,4-diradical. This diradical may then either abstract hydrogens or add another alkene molecule to give a 1,6-diradical which disproportionates to an enyne. Thus, reaction of C_2 with propene gives 1-pentyne, 3-methyl-1-butyne, 4-methylhept-6-en-1-yne, 6-methylhept-1-en-4-yne, and oct-1-en-4-yne. Ab initio calculations at the HF/3-21G level predict that both $^1C_2$ and $^3C_2$ will add to ethylene without barrier. At the MP2/6-31G*//3-21G level, the triplet adduct is calculated to be more stable than $^3C_2$ and ethylene by 46.0 kcal/mol. The reactions of $^1C_2$ and $^3C_2$ with methane and hydrogen have also been investigated theoretically.

Diatomic carbon has been the subject of theoretical,[1-5] spectroscopic,[6-8] and kinetic studies,[9-17] but little is known of the mechanisms and products of its reactions. Ballik and Ramsay[6] have demonstrated that there are two low-lying electronic states of C_2, the singlet ($^1\Sigma_g$) and the triplet ($^3\Pi_u$), 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[1a] indicates the structure $\cdot C{\equiv}C\cdot$ for the ground state singlet and



for the triplet.[1b] 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.[9-17]

Skell and co-workers have reported the products in the reaction of diatomic carbon at low temperature, in condensed phase, with alcohols,[18] carbonyl compounds,[19,20] alkenes,[21] alkanes, and ethers.[22,23] 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 alkylidenecyclopropanes.[21] 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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