Butatriene-Based Polymer Chemistry. 2. Synthesis and Characterization of Poly[1,1,4,4-bis(pentamethylene)-1,2,3-butatriene][†,1]

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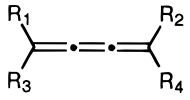
ABSTRACT: The cumulene 1,1,4,4-bis(pentamethylene)butatriene has been shown to undergo a thermally induced 1,4 free-radical polymerization to yield a crystalline polymer with a unique nonconjugated acetylene containing backbone. This polymerization occurs in both the melt and in solution. Typical free-radical inhibitors prevent the thermally induced polymerization. The reaction occurs in the presence or absence of free-radical initiators. The polymer is crystalline with a triclinic unit cell (a = 9.87 Å, b = 6.10 Å, c = 4.97 Å, α = 113.7°, β = 85.2°, γ = 100.6°). No melting or glass transition is observed via differential calorimetry, but an irreversible exothermic transition is observed from both solution and melt polymerized material. This is interpreted as a cold crystallization process. Trapping of the polymerizing monomer with TEMPO leads to soluble oligomers.

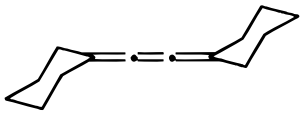
Introduction

Organic chemists and spectroscopists have noted that simple 1,2,3- butatrienes

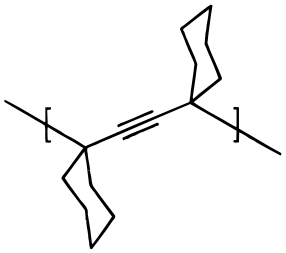


are prone to polymerization both in the presence and absence of oxygen.[3−6] The former produces polymeric peroxides,[7] while the latter mode of polymerization produces materials with ill-defined structures. This spontaneous polymerization proved a point of frustration for many spectroscopic studies of the parent molecule and simple alkyl substituted systems. Carothers recognized the potential for butatriene as a reactive monomer and was awarded a patent in 1937.[8] The structure of this polymer, described as an intractable white material, was not known.

Recently, we[9] described initial studies on the structure of polymers derived from the monomer bis(pentamethylene)-1,2,3-butatriene (BPMB)



with the structure



consistent with a 1,4 addition of the original bis(pentamethylene)butatriene. This reaction occurs both in solution and in the molten state. In this work, we provide further details on the homopolymerization of BPMB and on the solid state properties of its homopolymer.

Experimental Section

Unless otherwise noted, reagents were used as received. All solvents were purified using standard procedures. BPMB was prepared using a modification of the method of Macomber.[10,11] Melting points were obtained using a Fisher-Johns melting point apparatus and are reported uncorrected. Solution NMR data were obtained on a General Electric QE-300 FT-NMR system equipped with a Tecmag data system and were referenced either to an internal TMS standard or to solvent peaks. Solid state CP/MAS/DD ^{13}C spectra (carbon frequency of 68.055 MHz) were obtained from Spectral Data Services, Inc. (Champaign, IL). X-ray diffraction data were obtained on a Scintag, Inc. Model XDS 2000 powder diffractometer operating in reflection geometry with Ni filtered Cu Kα radiation. The system was calibrated using reflections from the copper sample holder. Infrared data were obtained using either a Perkin Elmer 1600 Fourier transform infrared spectrometer or a Bio-Rad Model FTS-40 Fourier transform infrared spectrometer. Fourier transform Raman data were obtained using a Biorad FTS-60A spectrometer. Differential scanning calorimetry data were obtained using a Polymer Laboratories PL-DSC or a Perkin-Elmer DSC 7 system. Simultaneous thermal analysis data (TGA-DTA) were obtained using a Polymer Laboratories STA-1500 system. Gel permeation chromatographic (GPC) analysis was carried out using a system consisting of a GBC isocratic pump, a GBC UV/vis detector, a Knauer refractive detector and Rheodyne manual injector and a single Polymer Laboratories Plgel 3 μm mixed bed E Linear column (300 mm x 7.5 mm) interfaced to a data acquisition system of local design. Samples were eluted with toluene. Mass spectrometric data were obtained using a Finnigan Model 3500 GC/MS or a Hewlett Packard 5980 GC/5971A MSD system. X-ray diffraction simulations were carried out using the Cerius[2] package of programs (Molecular Simulations Inc., San Diego, CA). For the simulations, an X-ray wavelength of 1.5418 Å (corresponding to Cu Kα radiation) was utilized and the crystallite sizes for the three crystallographic axes were set to 50 Å. For a given unit cell calculation, the chain structure was minimized using molecular mechanics with the Drieding II force field[11] and then the unit cell was minimized using the same methodology, but taking into account interchain interactions as well.

† This paper is dedicated to Professor Shelton Bank on the occasion of his 65th birthday.

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Synthesis of Pentamethylene Allenic Phosphonate (1):[10] Under a dry nitrogen atmosphere, 2 g (16.1 mmol) of 1-ethynyl-1-cyclohexanol in 30 mL of dry dichloromethane was added dropwise to a stirred mixture of 4.4 g (28.2 mmol) of diethyl chlorophosphite and 3.47 g (43.4 mmol) of freshly distilled pyridine. The resulting mixture was stirred for 48 h. The reaction was followed by IR and was complete after 48 h. The solvent was removed by rotary evaporator under reduced pressure. The product (5.1 g) was dissolved in 35 mL of THF and the suspension was added dropwise to 100 mL of stirring 8:1 mixture of THF and water at 0 °C. After stirring at room temperature for 1 h the product was extracted several times with diethyl ether, dried over anhydrous magnesium sulfate, and filtered and the solvent was removed by rotary evaporator. The product was purified by column chromatography using Florosil (100−200 mesh, Fisher). After purification, the allenic phosphonate was an oil and the yield was 81%. ^{1}H NMR 1.33 (t, J = 7.0 Hz, 6 H, 2*-CH_3), 1.5−1.7 (m, 6 H, −$(CH_2)_3$−), 2.19 (q, J = 3.4 Hz, 4 H, −$(CH_2)_2$C=C=C−), 4.1 (m, 4 H, −OCH_2 CH_3), and 5.18 ppm (b, d, 1 H, −C=C=CH−). ^{13}C NMR ($CDCl_3$): 15.9,16.1 (−OCH_2CH_3); 25.4, 26.5, 29.6 (−$(CH_2)_5$−); 61.4, 61.7 (−OCH_2CH_3); 78.8 (−C=C=CH); 103 (C=C=CH); 128.2 ppm (−C=C=CH). IR (cast from $CDCl_3$): 2985, 2930, 2854; 1958 (C=C=C); 1444, 1259 cm^{-1}. MS : 244 (40, M = $C_{12}H_{21}PO_3$), 216 (22, M − C_2H_4), 188 (89), 171 (71), 135 (100), 105 (75), 91 (82), 81 (76), 65 (63).

Synthesis of 1,1,4,4-Bis(pentamethylene)-1,2,3-Butatriene[7] (BPMB, 2). Under a dry nitrogen atmosphere, 2.6mL (4.2 mmol) of *n*-butyllithium was added dropwise (over 10 m) to a stirred mixture of freshly distilled diisopropylamine in 20 mL of dry THF at −78 °C to form lithium diisopropylamide (LDA) in situ. The yellow solution was warmed to room temperature for 30 min and then cooled to −78 °C and 0.94 mL (4 mmol) of **1** added dropwise over 10 min followed immediately by 0.5 mL (4.8 mmol) of cyclohexanone. The mixture was stirred at room temperature for 16 h. Solvent removal via rotary evaporator (2 h, room temperature) left a viscous yellow oil. The product was purified by column chromatography (under nitrogen using Florosil as the stationary phase and petroleum ether (degassed for several hours) as an eluent. ^{1}H NMR 1.43 (b, m, 10 H, −$(CH_2)_3$−), 2.07 ppm ($(CH_2)_2$C=C=C−). ^{13}C NMR ($CDCl_3$): 26.1, 27.7, 34.9 (−$(CH_2)_5$−); 116 (C=C=C=C); 151 ppm (−C=C=C=C−). IR (cast from $CDCl_3$): 2940, 2852, 2875 (−$(CH_2)_5$−); 1650 (C=C=C=C); 1434 cm^{-1} (CH_2 bend). MS: 188 (64, M = $C_{14}H_{20}$), 159 (6, M − C_2H_4), 131 (30), 105 (22), 91 (100), 65 (21).

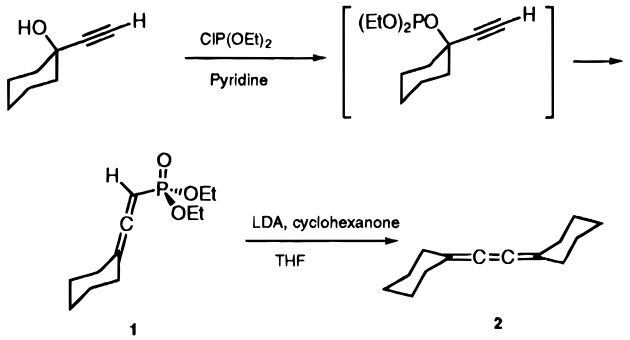
Synthesis of the homopolymer of BPMB. Monomer **2** (4 mmol, 0.752g) was dissolved in 20 mL of freshly distilled benzene in a pressure tube. To this was added 65.6 mg (0.4 mmol) of AIBN initiator. This solution was subjected to five freeze−pump−thaw cycles, and the tube was then sealed under vacuum. The polymerization was carried out in a temperature controlled oven at 60 °C for 48 h. At the end of this period, the insoluble polymer was isolated by filtration and vacuum-drying to give 0.331 g (44.0%) of the polymer. Raman (acetylenic): 2221, 2204 cm^{-1}.

Diradical Trapping Experiments. TEMPO (2,2,6,6-tetramethyl-1-piperidinoxy) (63 mg, 0.4 mmmol) in 8 mL of toluene was placed in a sealable tube, degassed (freeze−thaw−pump) several times and kept under nitrogen atmosphere. The solution was cooled to −78 °C, and 36 mg (0.19 mmol) of **2** was added. The tube was then sealed, and the mixture was warmed to room temperature and allowed to stand for 4 days. The solution was then added to acetonitrile, but no precipitation was observed. Removal of the solvent on a rotatory evaporator yielded an oily product which after 4 h solidified to a low melting solid (26% yield). (For peak labeling, see below.) ^{1}H NMR ($CDCl_3$): 1−1.17 (s, Me); 1.17−1.37 (b, s, β); 1.43−1.90 (b,multiplet, 3,4,δ,δ'); 1.95−2.29 (γ, γ'). ^{13}C NMR ($CDCl_3$) (for assignments, see below). IR (neat) 2210, 2240 cm^{-1} (acetylenic).

Results and Discussion

BPMB can be synthesized by the Horner−Emmons modification to the Wittig reaction.[10] Starting with a commercially available propargylic alcohol and diethyl chlorophosphite, the allenic phosphonate is formed through rearrangement of the phosphonate ester. Deprotonation of the allenic phosphate at the acidic vinyl proton and subsequent reaction with cyclohexanone afford the butatriene in reasonable yield. It was found that flash chromatography on Florisil under a nitrogen atmosphere provided pure butatriene monomer in reasonable yields. Recrystallization from solution is not a viable purification procedure due to the rapid polymerization of BPMB in solution. However, by slow sublimation at high vacuum, we have been able to obtain single crystals of BPMB suitable for X-ray structural analysis and were able to obtain a solid state structure of the monomer. We will report on that study in a subsequent publication.[12]

Scheme 1. Synthesis of BPMB



BPMB when dissolved in either ethereal or aromatic hydrocarbon solvents produces a white fibrous precipitate upon standing. No initiator is required for BPMB to undergo 1,4 polymerization. The presence of an initiator does not appear to effect the course of the polymerization. The reaction occurs either in solution or in the melt. A DSC scan (10 °C/min) of BPMB exhibited a melting transition at 80 °C followed by an exothermic polymerization process at 98 °C followed by a second, distinct exotherm at 200 °C. For solution polymerized materials, only the 200 °C exotherm is present, but in both cases this peak is absent in a subsequent heating run. No difference in the infrared or Raman spectra is discernible after heating the material above 200 °C (but below the decomposition point). The presence of conventional free-radical inhibitors such as BHT (bis-*tert*-butylated hydroxytoluene) inhibits solution polymerization. When excess dodecanethiol was added as a chain transfer agent, no polymer was observed but a foul smelling soluble residue was obtained. The spectra of the yellow oil proved too complex for analysis.

Attempts to analyze the polymer via solution NMR techniques have not been successful. The polymer is insoluble in common solvents. Attempts to dissolve it in strong mineral acids gave a dark brown solution with spectra too complex to be interpreted. In addition to the aliphatic carbons, the solid state ^{13}C NMR spectrum of the precipitate exhibits no peaks due to the cumulene carbons but, instead, has a single acetylenic resonance at δ 80 ppm (Figure 1). The large spinning side bands are consistent with the large chemical shift anisotropy expected for these acetylenic carbons.[13]

Raman and infrared spectra of the solid are shown in Figure 2. As stated in our previous publication, the strong Raman band at 2221/2204 cm^{-1} (inset, Figure 2) with a corresponding absence of band in the infrared gives a strong indication of a symmetrically substituted alkyne.[14] The doublet nature of this vibration in the Raman is seen in systems with high symmetry and is

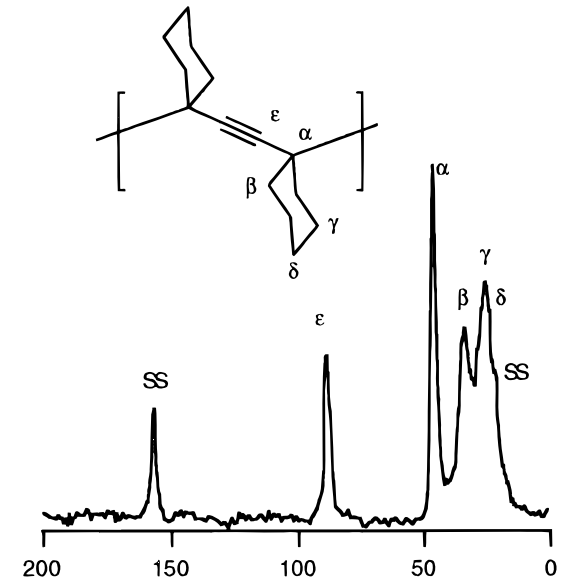


Figure 1. CP/MAS/DD ^{13}C spectra and assignments of the homopolymer of BPMB. Spinning sidebands of the acetylenic carbons (ϵ) are denoted by SS.

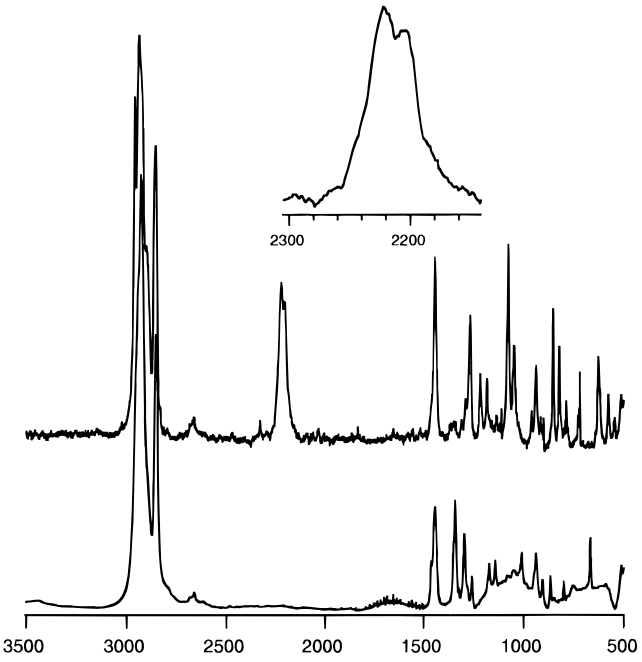


Figure 2. Vibrational spectroscopy of homopolymer of BPMB. Upper trace, infrared specta, obtained as a KBr pellet. Lower trace, Nd:YAG excited Raman spectra. The inset is an expansion of the acetylenic peak in the Raman.

usually ascribed to a Fermi resonance.[15] However, there is no evidence for a band at 1102 cm^{-1} as would be anticipated for such as resonance. It is also possible that this band is a consequence of a lattice splitting in the crystaline phase.[15,16] There is a complete absence of other bands due to other unsaturation confirming the conversion from the cumulene to the acetylenic structure.

X-ray diffraction studies of the precipitate reveal three strong reflections with *d* spacings of 9.951, 5.583, and 4.417 Å. The peaks are present in polymer freshly prepared from solution, and no change is noted in their breadth or intensity after heating above 200 °C. Utilizing the Cerius[2] software package, were able to obtain a sutiable unit cell structure which had a powder diffraction pattern with the three observed reflections. For a fulled extended backbone, there are two reasonable

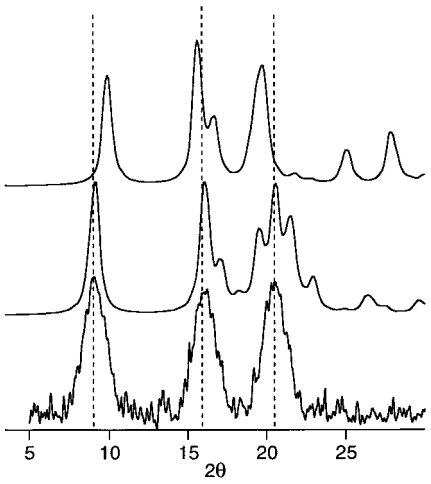
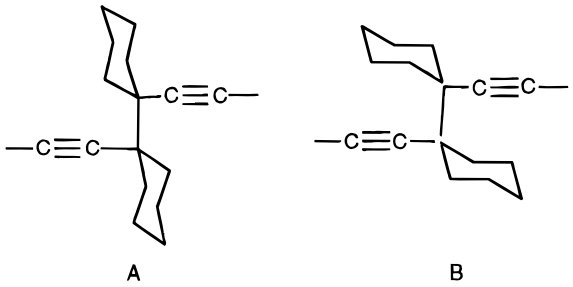


Figure 3. X-ray diffraction data (Ni filtered Cu Kα radiation) from the homopolymer of BPMB. Lower trace: experimental data. Middle trace: simulation (see text) of unit cell for polymer with lowest energy conformation (A) of cyclohexane rings. Upper trace: simulation (see text) of unit cell for polymer with higher energy conformation (B) of cyclohexane rings.

conformations for the cyclohexane rings, a low-energy conformer A having nearly a perpendicular relationship



to the polymer backbone, or a slightly higher energy form B with the rings lying back along the backbone. When crystal lattices of lowest energy for both conformers are calculated and the diffraction pattern simulated, the low energy conformer A provides the best match with experiment (Figure 3, middle trace). The unit cell we derived from this simulation is triclinic with unit cell parameters of $a = 9.87$ Å, $b = 6.10$ Å, $c = 4.97$ Å, $\alpha = 113.7°$, $\beta = 85.2°$, $\gamma = 100.6°$. The packing of the polymer in this structure is given in Figure 4.

As stated above, there is an irreversible exothermic transition observed by DSC at 200 °C. Spectroscopic analysis of the material subsequent to heating above 200 °C shows no obvious chemical changes. As we shall describe below, we ascribe this peak to a crystallization phenomenon. Simultaneous thermogravimetric/differential thermal analysis (TGA−DTA) analysis of the homopolymer shows a maximum rate of weight loss at 350 °C corresponding to the decomposition of the polymer. On the basis of the observation of monomers and oligomers in the solid probe, mass spectroscopic studies of the polymer,[9,17] we presume that this process is a radical mediated depolymerization.

In addition, we observe at 200 °C in the DTA trace an exotherm with no accompanying weight loss event. This exothermic event is also observed in the DSC scan of melt-polymerized material. This is an irreverisble thermal event. Bis(pentamethylene)butatriene polymerizes in a 1,4 fashion to provide a poly(2-butyne-1,4-diyl) backbone. This behavior is quite similar to the reactivity of *p*-xylylenes, which undergo a 1,6

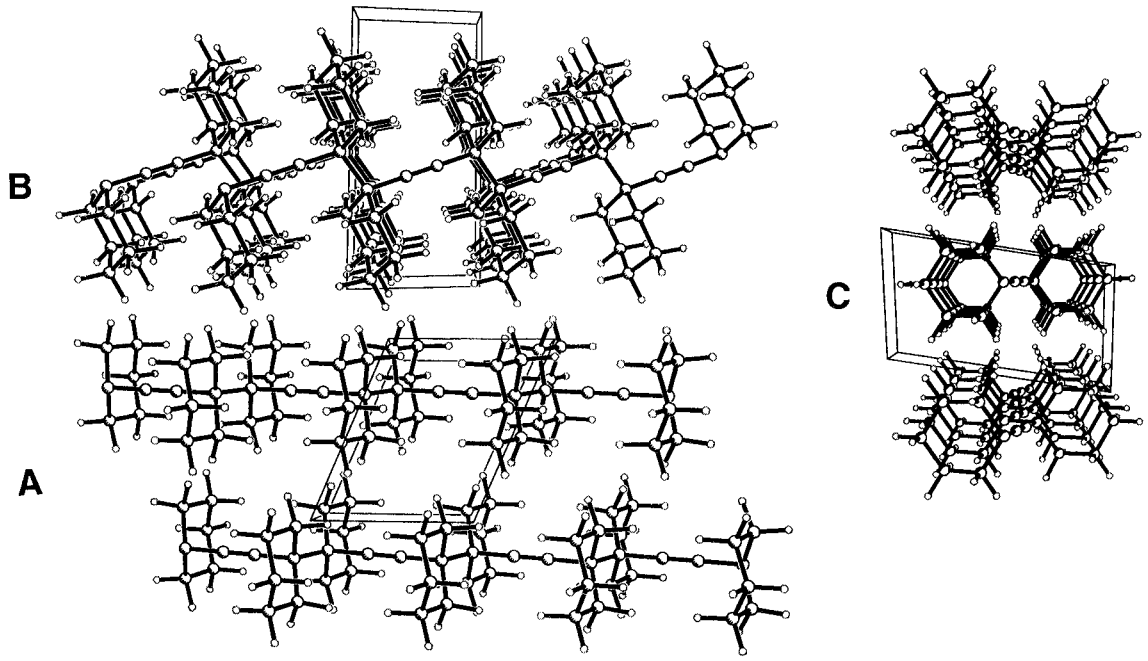


Figure 4. Unit cell for crystal structure of conformer A: (a) view down *a* axis; (b) view down *b* axis; (c) view down *c* axis.

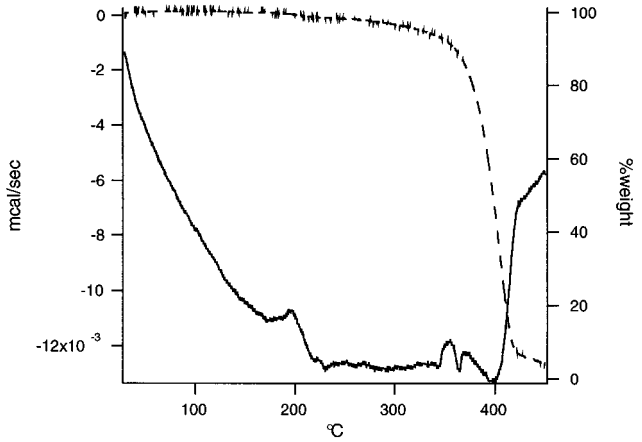
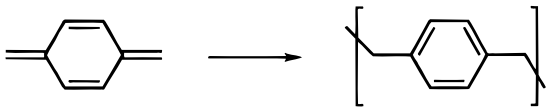


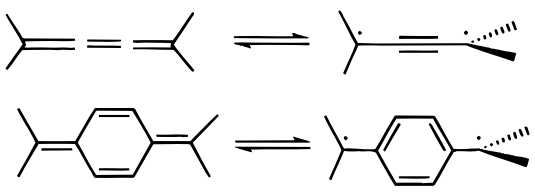
Figure 5. STA data for homopolymer of BPMB: (upper trace) TGA data; (lower trace) DTA data. Note exotherm at 200 °C.

polymerization

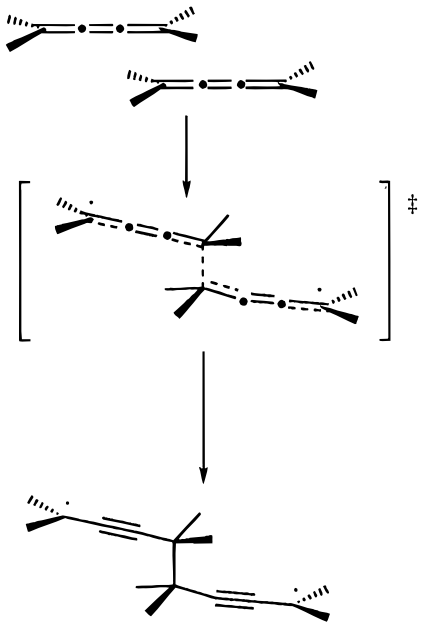


to give a metastable solid state structure.[18−21] This metastable phase is destroyed upon heating and cannot be recovered. We speculate that as with poly(*p*-xylylene), the as-polymerized BPMB is "trapped" in a high energy state and, with the addition of sufficient thermal energy, undergoes a solid state crystallization yeilding the exothermic transition.

These two system share other similarities. In both cases there is the opportunity for the formation of a nonplanar diradical species.



We and others[5,22] had initially speculated that the ease with which butatrienes polymerize might be due to a low lying triplet structure. Kloster-Jensen et al.[5] have shown that for the parent butatriene, a substantial quantity of cyclic dimer, 1,5-cyclooctadiyne, is formed along with polymeric material when 1,2,3-butatriene is allowed to warm above 0 °C. These authors argue that the easy formation of the diradical is responsible for this process. However, recent *ab initio* molecular orbital calculations on the parent butatriene[23] have shown the nonplanar triplet to be approximately 40 kcal mol^{-1} less stable than the planar singlet for the parent butatriene. The planar diradical triplet state is 56 kcal mol^{-1} above the planar singlet state. If the formation of the triplet diradical state was the rate determining step, this 40 kcal mol^{-1} activation barrier would imply a very low concentration of the 1,4-diradical present in solution. This is inconsistent with the rapid rate of polymerization observed. Alternatively, reaction of 2 molecules of the planar singlet to form the 1,8 singlet or (following a spin flip) triplet diradical



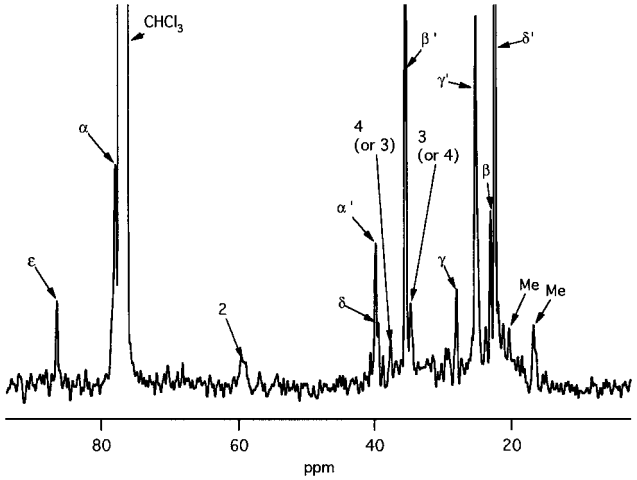
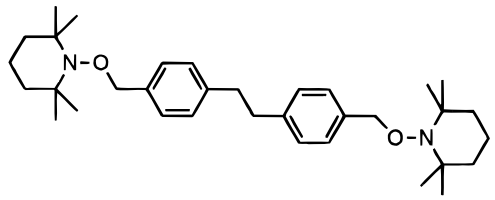
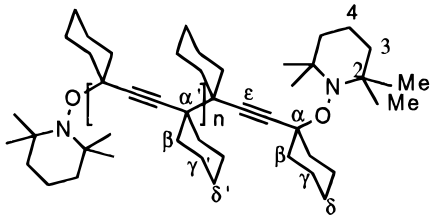


Figure 6. ^{13}C NMR data for TEMPO adduct.

provides a more plausible reactive intermediate. This diradical would then act as the initiator. Recently,[24] it has been shown that *p*-xylylene undergoes this type of dimerization to form the α,ω diradical which is then trapped by 2,2,4,4-tetramethylpiperidinyloxy (TEMPO) giving the compound



and no evidence of the α,α′ adduct to the *p*-xylylene. We attempted a similar study. When BPMB is reacted with TEMPO, we obtained a low melting solid which is soluble in common organic solvents (THF, $CHCl_3$, CH_2Cl_2, etc.) unlike the homopolymer itself. The ^{13}C NMR and infrared data are consistent with the presence of



From the ^{13}C NMR data, there is no indication of allenic type carbons due to unreacted starting material. The line width in both the ^1H and ^{13}C NMR spectra give no indication of the presence of unreacted paramagnetic species. Thus all of the TEMPO has been removed or reacted. Based on the proposed structure, there are three sets of cycloaliphatic carbons, those due to TEMPO, those due to the cyclohexane rings of the monomers at the chain termini, and those midchain. Using the reaction products of TEMPO and benzylic Grignards described by Hawker and co-workers[25,26] as models for the chain ends and other model compounds, we have assigned the ^{13}C resonances at 17.6, 20.3 (axial and equitorial methyls) 34.7, 39.4 (C3 and C4), and 59.5 (C2) to the TEMPO carbons. Those at 23.1, 24.9, 39.8 (Cβ, Cγ, and Cδ), and 78.3 (Cα) are the terminal cyclohexane rings. Finally, those at 35.4, 25.2 , 22.4 (Cβ', Cγ', and Cδ'), and 39.9 (Cα') are due to the midchain rings. There is an acetylenic resonance at

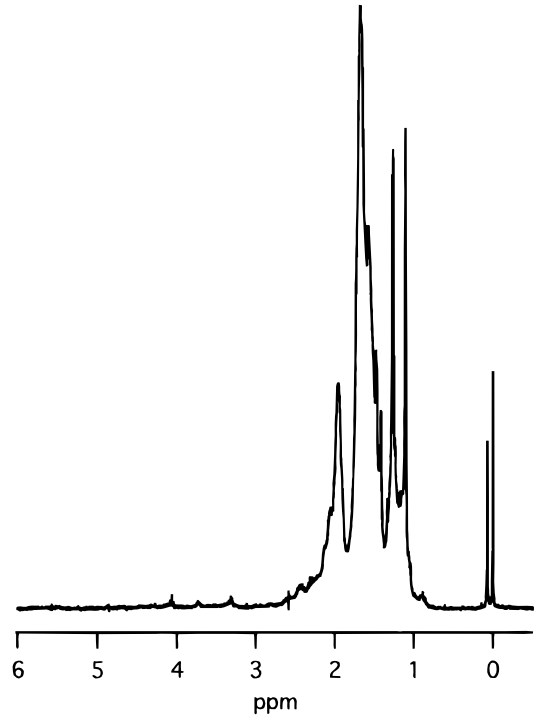


Figure 7. ^1H NMR data for TEMPO adduct.

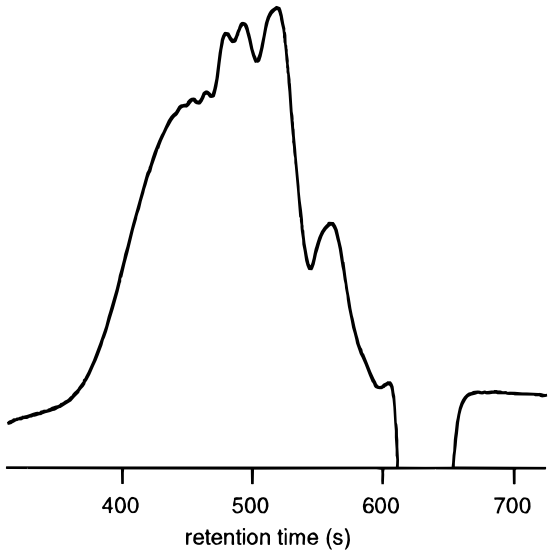


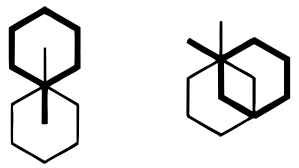
Figure 8. GPC trace for TEMPO adduct.

86.4 (ϵ). The relative intensity of the TEMPO and terminal ring carbons is significanly smaller than those due to the midchain carbons. This observation suggests that the adduct is mainly oligomers. One can obtain a crude composition of the TEMPO trapped oligomers by integration of the ^1H NMR data using the methyl group's integral as a measure of the end groups. This leads to a ratio of TEMPO:monomer in the oligomer of 1:6. Gel permeation chomatographic data of the product reveals a distribution of oligomers, with individual peaks evident for the lower oligomers. Due to the significant difference in structure between this material and available polystyrene molecular weight standards, no attempt has been made to assign the degree of polymerization to peak positions. Electron impact solid probe mass spectral analysis of the mixture produces mainly a characteristic hydrocarbon pattern, with small but significant high molecular mass ions at 501, 424, and 362 amu. The peak at 501 is the correct mass for the protonated form of the $n = 0$ adduct, that is

monomer plus 2 molecules of TEMPO. However, these data are not strong enough to support this hypothesis. We are hoping to perform MALDI and/or chemical ionization solid probe mass spectrometry on this sample and will report on these results in future publications. The infrared data show two well resolved peaks in the acetylenic region. We assign the band at 2210 cm^{-1} to the chain termini and the weaker band at 2240 to the midchain acetylenes. The former group is assymetrically substituted and would be anticipated to have a stronger infrared absorption.[14]

While there is evidence for the formation of a limited quantity of the bis-TEMPO adduct of the monomer, there is also evidence of higher oligomers, in contrast to the behavior of the *p*-xylene. This may be due to the difference in reaction conditions used to perform the trapping experiments or to the more bulky nature of the BPMB monomer. We are planning similar studies with the parent butatriene. The fact that added BHT stops the polymerization of BPMB lends credence to the trapping of either the 1,4 or 1,8 diradical initiating species. We are currently conducting a theoretical study of the potential energy surface for the spontaneous dimerization of butatriene to the 1,8 diradical and hope to be able to report on these findings in the near future.

Given the bulky nature of the side group in this homopolymer of BPMB, it is somewhat surprising that the material exhibits such a high degree of crystallinity. The single−triple−single bond linkage connecting cyclohexane rings within a structural repeat unit has no formal rotation barrier, whereas one would anticipate that the high steric demands of the rings in adjacent SRUs forces a trans conformation about the single bond linking two adjacent monomer units. Molecular mechanics calculations utilizing the Sybyl force field[26] predict the barrier to rotation around this single bond to be 15 kcal mol^{-1}, but the difference in energy between the trans and gauche comformers is predicted to be only 1 kcal mol^{-1}.



We would anticipate that the polymer, as formed, would have a high degree of these gauche conformers. Upon heating, sufficient energy is provided for surmounting the 15 kcal mol^{-1} barrier. Thereafter, crystallization of the material ensues, giving rise to the exotherm observed in the DSC at around 200 °C. If one carefully examines the packing predicted from the powder simulations, adjacent chains interdigitate the cyclohexane rings, giving a structure with little free volume. This may explain both the absence of an observable glass transition and the inability to observe a melting transition prior to the thermal decomposition of the polymer.

Conclusions

The hindered cumulene bis(pentamethylene)butatriene undergoes a thermally induced 1,4 polymerization to produce a crystalline polymer with nonconjugated acetylenic groups in the backbone. The polymerization is free-radical in nature, involving either a nonplanar triplet state or more probably a dimer-diradical as the initiating species. The solid state structure of the material has been determined and is shown to undergo an irreversible thermal transition at 200 °C. Trapping of the growing macroradical by stable nitroxide free radicals yields soluble oligomers. Present experimental work in our laboratories focuses on other substituted and unsubstituted butatrienes as homopolymers and as comonomers with more conventional free-radical monomers.

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References and Notes

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