Free-Radical Polymerization of Bis(pentamethylene)butatriene. A Novel Monomer for the Preparation of Poly(2-butyne-1,4-diyl)s

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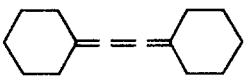
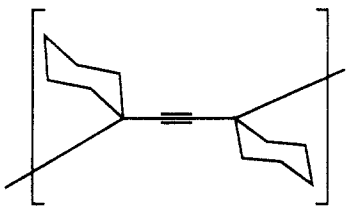
In the course of investigating bis(pentamethylene)-butatriene (BPMBT) as a model compound for the



synthesis of compounds with hidden functional groups,[1] it was observed that the material, when dissolved in THF and heated in the absence of air or light, formed an insoluble white precipitate. This material, from ^{13}C CP/MAS NMR spectroscopic evidence, posseses only aliphatic carbons at 48.2 (propargylic), 33.7, and 25.8 (ring carbons) ppm and acetylenic carbons at 88.8 ppm (Figure 1). The Raman data for this material also exhibited a symmetric –C≡C– doublet at 2222 and 2203 cm^{-1}. The doublet is typical of symmetrical dialkylacetylenes and has been ascribed to a Fermi resonance. The possibility also exists that this doublet is due to a crystallographic splitting of the alkyne band rather than a Fermi resonance.[2] The infrared spectrum of the precipitate did not exhibit an acetylenic stretch, consistent with a symmetric environment around the triple bond (Figure 2). Mass spectrometric data were consistent with monomer, dimer, and trimers of the parent $C_{14}H_{20}$ structure. Based on these findings, the following polymer structure was postulated



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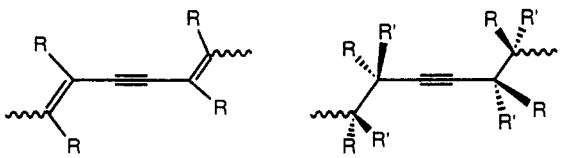
poly[1,4-bis(pentamethylene)-2-butyne-1,4-diyl] (1). The polymer backbone is analogous to that of poly(diacetylene)s (2), the difference being the presence of single bonds replacing the backbone double bonds.



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While the double bonds in the poly(diacetylene) provide for rigidity in the system, we have determined using AM1 semiempirical calculations[3] for 1 that the trans versus

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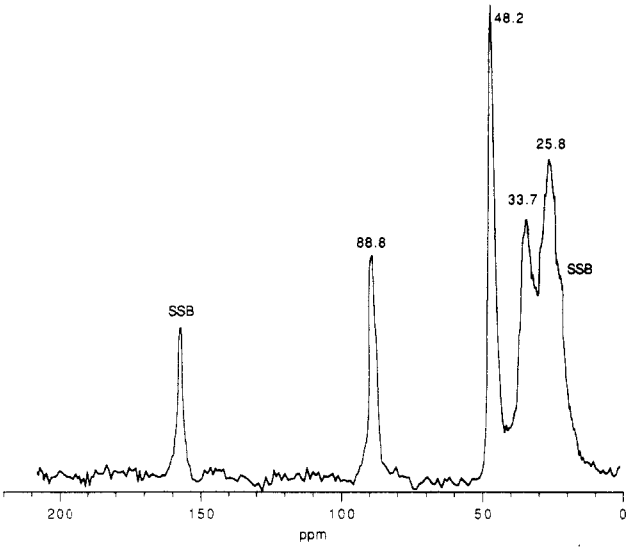

Figure 1. 68-MHz solid-state CP/MAS/DD ^{13}C NMR of the homopolymer. The peaks labeled SSB are spinning sidebands of the peak at 88.8 ppm.

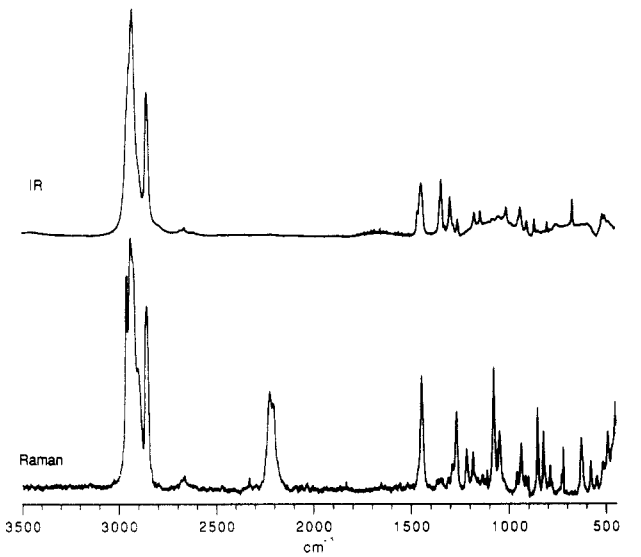

Figure 2. Infrared and Raman (excitation at 1064 nm) spectra of the homopolymer.

gauche conformational preference about the single bonds is at least 99:1 with a barrier to interconversion of at least 15 kcal mol^{-1}. This provides a rigidity similar to that resulting from the double bonds of 2 and may explain the insolubility of the polymer as well as the lack of any observable glass transition below the decomposition temperature of 350 °C.

Homopolymerization has been shown to occur under conventional free-radical conditions, using azobis(isobutyronitrile) (AIBN) as an initiator, as well as through thermally induced polymerization using benzene or THF as the solvent. The presence of free-radical inhibitors such as 2,6-di-*tert*-butyl-4-methylphenol (BHT) suppresses polymerization. Chain transfer agent was added in an attempt to lower the molecular weight and increase solubility. The presence of 10 mol % of *n*-dodecanethiol still yielded insoluble material whose Raman spectrum is essentially identical to that of 1. When 50 mol % of thiol was utilized, a yellow oil with the characteristic odor of thiol and trace amounts of insoluble polymer were isolated. We take these findings to indicate that the polymer formed in this process is of relatively low molecular weight but is of sufficient rigidity to render it intractable.

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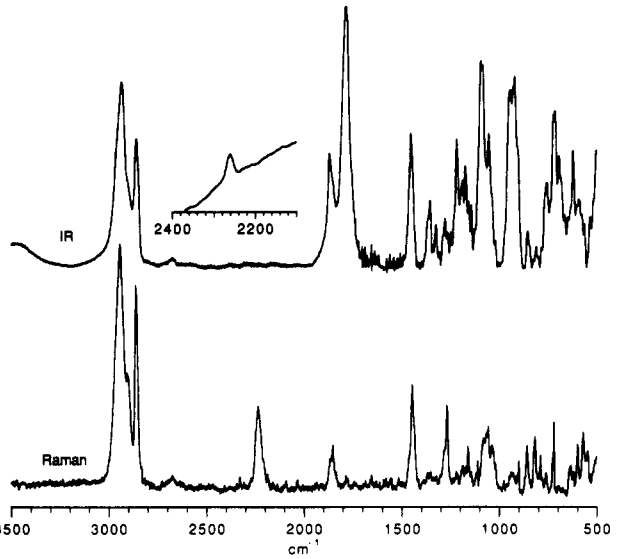
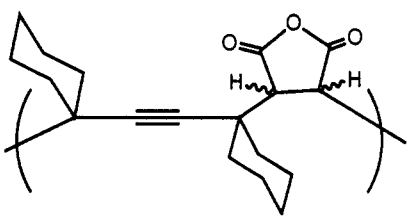


Figure 3. Infrared and Raman (excitation at 1064 nm) spectra of the copolymer.

This is in analogy to poly(oxybenzoate), which at a degree of polymerization of 8 can no longer be readily melted nor dissolved without decomposition due to its rigidity.[4]

When BPMBT is copolymerized with maleic anhydride (MAH) in the presence or absence of free-radical initiators, a soluble copolymer is formed which is capable of being cast to form tough transparent films. Molecular weight analysis of the copolymers via GPC using polystyrene standards yields typical values for M_w and M_n of 187 000 and 70 000, respectively. Raman data confirm the presence of both anhydride and acetylenic bands. However, unlike the homopolymer, the Fermi resonance at 2204 cm^{-1} is absent, and the copolymer exhibits only a single –C≡C– stretch at 2234 cm^{-1} (Figure 3). In the copolymer, there is a weak but measurable acetylenic stretch in the infrared, implying a nonsymmetric environment for the acetylene. The chemical structure of the alternating copolymer is symmetric with respect to the acetylenic bond, so the presence of the acetylenic stretch, while very weak, is somewhat surprising. Its presence could be attributed to breaking of local symmetry due to differing conformations of the MAH monomers at either end of the butatriene monomer. This same argument is consistent with a high degree of conformational and possibly crystalline order in the homopolymer.

The ^1H NMR of the copolymer exhibits bands due to the maleate ring protons and the cyclohexane ring protons. The ^{13}C and ^1H NMR as well as the elemental analysis of the copolymer are consistent with the structure



3

There is no evidence of MAH–MAH diads in the NMR spectra,[5] indicating that the product is an alternating copolymer. This is not surprising due to the steric hindrance of both the triene and MAH. The peak assignments based on standard spectral correlations[6] as well as DEPT and HETCOR experiments[7] (to be presented at a later time) are given in Figure 4.

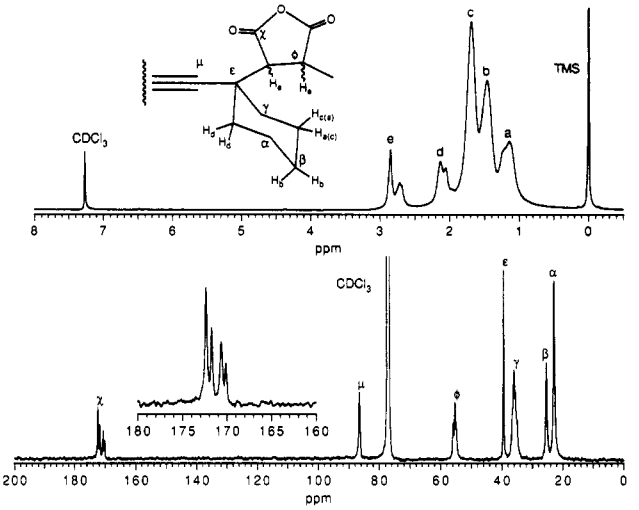


Figure 4. Proton (400 MHz) and carbon (100 MHz) NMR spectra of the copolymer with peak assignments.

The low propensity for self-reaction of the triene during the copolymerization is consistent with the prediction that the homopolymer is oligomeric in nature. The presence of four different carbonyl carbons in the ^{13}C NMR spectrum of 3 cannot be attributed to hydrolysis of the anhydride groups, as there is no evidence in the infrared or Raman spectra for ester or acid carbonyls. We interpret these four peaks as being due to asymmetric conformations of the cis- and trans-substituted maleates. A study to model the available conformations and their relative importance is currently underway.

Neither polymer exhibits a measurable T_g or a melting endotherm as determined via DSC. Both exhibit high thermal stability, the homopolymer showing negligible weight loss in N_2 up to 350 °C and the copolymer exhibiting similar stability up to 370 °C. Both systems exhibit a nonreversible exothermic transition at 200 °C of varying magnitude which does not involve any weight change, as determined via simultaneous TGA–DSC. This transition may correspond to either a relaxation of trapped high-energy conformers or possibly a cross-linking reaction involving the acetylenic bonds. This is currently under investigation.

In conclusion, we have reported the first use of butatrienes as free-radical monomers. They yield polymers containing acetylenic units in the backbone which may prove useful as reactive sites for graft polymerization and polymer modification. We are currently investigating the generality of other butatrienes as 1,4-addition monomers, as well as the solid-state behavior of these materials with respect to crystallinity, liquid crystallinity, and conductivity. We are also interested in the potential of these monomers to undergo topochemical polymerization in analogy to the diacetylenes.[8] These studies will be described in subsequent publications.

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References and Notes

(1) Rardon, D. E. Chemistry Thesis, University of Cincinnati, 1991.
(2) Colthrup, N. B.; Daly, L. H.; S. E., W. *Introduction to Infrared and Raman Spectroscopy*; Academic Press: Boston, 1990.
(3) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(4) Donald, A. M.; Windle, A. H. *Liquid Crystalline Polymers*; Cambridge University Press: New York, 1992.
(5) Regel, W.; Schneider, C. *Makromol. Chem.* **1981**, *182*, 237.
(6) Silverstein, R. M.; Bassler, G. C.; Morril, T. C. *Spectrometric Identification of Organic Compounds*, 5th ed.; John Wiley & Sons: New York, 1991.
(7) DEPT (distortionless enhancement by polarization transfer): a ^{13}C NMR experiment for identifying methyl, methylene, and methine carbons. HETCOR (heterogeneous correlation): a 2-D $^{13}C/^{1}H$ NMR experiment for identifying proton–carbon connectivity.For examples, see: Bovey, F. A. *Nuclear Magnetic Resonance Spectroscopy*; Academic Press: New York, 1987.
(8) Sandman, D. J. *Crystallographically Ordered Polymers*; ACS Symposium Series 337; American Chemical Society: Washington, DC, 1987.