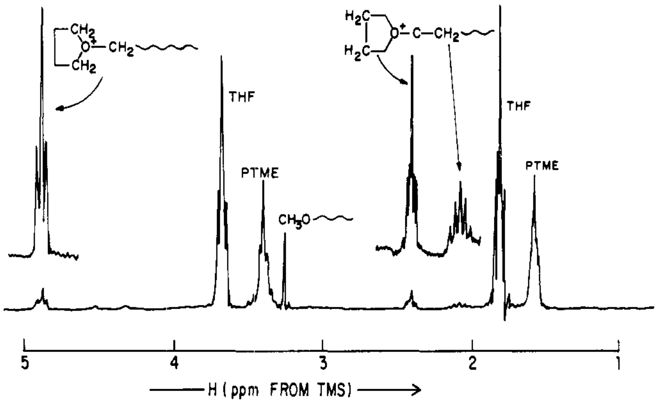
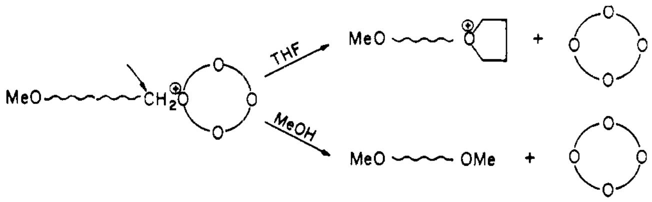


Figure 3. ^{1}H NMR spectrum (220 MHz) of THF/methyltriflate. THF/CD_3NO_2/$CF_3SO_3CH_3$ = 55.4/41.5/3.1 mol %; 30 min: endo/exo = 2; 360 min: endo/exo = 1.6 (PTME = polytetramethylene ether).

exo-cyclic α-methylene group of these macrocyclic oxonium ions:



Attack on endo-cyclic α-methylene groups will only produce linear chains. The formation of THF crown ethers is therefore rather inefficient, but since they represent "dead" polymer, they will tend to accumulate until an equilibrium concentration is reached. This is in agreement with the present finding of an increase in the concentration of crown ethers with time in living THF polymerization systems.

References and Notes

(1) (a) Elastomers Department; (b) Plastic Products and Resins Department; (c) Industrial Chemicals Department.
(2) J. Dale, G. Borgen, and K. Daasvatn, *Acta Chem. Scand., Ser. B*, **28**, 378 (1974).
(3) (a) P. Dreyfuss and M. P. Dreyfuss, *Polym. J.*, **8**, 81 (1961); (b) J. B. Rose, *J. Chem. Soc.*, 542 (1956).
(4) (a) J. M. Andrews and J. A. Semlyen, *Polymer*, **12**, 642 (1971); (b) E. J. Goethals, *Adv. Polym. Sci.*, **23**, 103 (1977).
(5) J. B. Lambert, H. F. Shurvell, L. Verbit, R. G. Cooks, and G. H. Stout, "Organic Structural Analysis", Macmillan, New York, N.Y., 1976.
(6) (a) H. Jacobson and W. Stockmayer, *J. Chem. Phys.*, **18**, 1600 (1950); (b) J. M. Andrews and J. A. Semlyen, *Polymer*, **13**, 142 (1972).
(7) C. J. Pedersen, *J. Am. Chem. Soc.*, **89**, 7017 (1967).
(8) J. L. Lambert and E. J. Goethals, *Makromol. Chem.*, **133**, 289 (1970).
(9) T. Saegusa and S. Kobayashi, *Prog. Polym. Sci.*, **6**, 107 (1973).
(10) G. Pruckmayr and T. K. Wu, paper presented at Central Regional Meeting of the American Chemical Society, Akron, Ohio, May 21, 1976.
(11) G. Pruckmayr and T. K. Wu, *Macromolecules*, **8**, 954 (1975).
(12) T. K. Wu and G. Pruckmayr, *Macromolecules*, **8**, 77 (1975).
(13) R. Hoene and K. W. Reichert, *Makromol. Chem.*, **177**, 3545 (1976).

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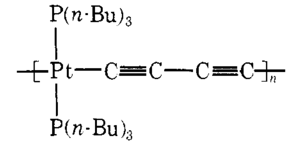
Received March 30, 1977

A New Extended Chain Polymer. Poly[*trans*-bis(tri-*n*-butylphosphine)platinum 1,4-butadiynediyl]

Recently, a large variety of polymers containing ferrocene or related transition metal complexes have been prepared. However, polymers containing σ-bonded transition metal atoms in the main chain have not yet been reported. The interest in functional polymeric materials is growing rapidly. We expected that the polymers having the backbone composed of conjugated poly-yne and platinum metal atoms might have straight rodlike structures and particular properties in solution or in catalysis. In the previous paper[1] we reported the syntheses of oligomers composed of such repeat units and here we wish to report on the synthesis and characterization of high molecular weight poly[*trans*-bis(tri-*n*-butylphosphine)platinum 1,4-butadiynediyl] (1) prepared by the following method.



$$-\!\!\left[\underset{P(n\text{-}Bu)_3}{\overset{P(n\text{-}Bu)_3}{Pt}}-C\equiv C-C\equiv C\right]_n$$

1

$$H\underline{D}\text{-}\underline{Pt}\text{-}\underline{D}H + Cl\text{-}\underline{Pt}\text{-}Cl \xrightarrow[Et_2NH,\ reflux]{CuX} \underset{1}{(\text{-}\underline{Pt}\text{-}\underline{D}\text{-})_n}$$

$\underline{Pt}$ and $\underline{D}$ represent *trans*-$(n\text{-}Bu_3P)_2Pt$– and –C≡C–C≡C–, respectively.

Preparation and Characterization of Polymer. Cuprous iodide (7 mg, 0.037 mmol) was added to a stirred deoxygenated solution of $\underline{Pt}(\underline{D}H)_2$ (1.3968 g, 2.0 mmol) and $\underline{Pt}Cl_2$ (1.3404 g, 2.0 mmol) in 50 mL of diethylamine under a nitrogen atomosphere. The reaction mixture was heated to a gentle reflux for 1 day and then evaporated to dryness under reduced pressure. The residue was dissolved in methylene chloride and the resulting solution was filtered by alumina column chromatography. After evaporation of the filtrate, a pale yellow product was collected and purified by repeated precipitation from methylene chloride into methanol. Finally, a benzene solution of the product was frozen and then freeze-dried under reduced pressure to afford a pale yellow polymer 1, yield 2.5 g (96%). The elemental analyses were in good agreement with calculated values. Anal. Calcd for $C_{28}H_{54}P_2Pt$: H, 8.40; C, 51.92; P, 9.56, Found: H, 8.63; C, 51.89; P, 9.81. The IR spectrum of polymer 1 shows a peak at 1999 cm^{-1} attributed to $\nu_{C\equiv C}$ and no trace of the 3307 cm^{-1} acetylenic hydrogen band of the monomer H$\underline{D}$-$\underline{Pt}$-$\underline{D}$H. The UV spectrum of polymer 1 is very similar to that of the model compound Cl-$\underline{Pt}$-$\underline{D}$-$\underline{Pt}$-$\underline{D}$-$\underline{Pt}$-Cl. The λ_{max} have shifted to slightly longer wavelengths in the polymer. These facts indicate that the polymerization proceeds through the expected route without any side reactions. Polymer 1 was easily dissolved in methylene chloride, diethylamine, THF, benzene, toluene, and even in *n*-hexane at a reflux condition, but not in methanol. The high solubility of polymer 1 is thought to be attributed to butyl substituents on phosphorus which would protect the polymer backbone and decrease intermolecular interaction. Intrinsic viscosity measurement in THF varied from 0.9 to 1.3 dL/g for a series of polymers made using this technique. A sample of polymer 1 ($[\eta]$ = 1.20 dL/g) was fractionated from a methylene chloride solution using methanol as the precipitant to afford a fraction having $[\eta]$ of 2.11 dL/g (yield 60%). Sedimentation equilibrium of the fraction in toluene provided a weight-average molecular weight ($\overline{M}_w$) of 119000–122000 ($\bar{n}_w$ = 184–188).[2] Thermogravimetric analysis at a heating rate of 5 °C/min of polymer 1 showed a rapid decomposition in air at 270 °C and 42% weight loss in vacuo at 325–400 °C.

^{31}P Nuclear Magnetic Resonance Spectra of the Polymer. In structural studies of the Pt-diyne polymer, configurational analysis of platinum moiety in polymer using ^{31}P NMR provides a method which proves the rodlike structure of the polymer. Previously we have reported that the spectra of several monomers and model compounds illustrated the utility of ^{31}P NMR for the configurational analysis of platinum.[3] The spectra of trans-configurational phosphorus on platinum bis(acetylide) showed a signal at −3.0 to −4.5 ppm and those of the cis-configurational one showed a signal at +2.6 to +3.6 ppm (based on 85% phosphoric acid standard).

The ^{31}P Fourier transform NMR spectrum of high molecular weight polymer 1 showed a large resonance at −4.2 ppm attributable to the trans-configurational phosphorus with attendant satellites due to coupling ($J = 2384$ Hz) with ^{195}Pt ($I = \frac{1}{2}$, 33%). Since no trace of absorption at +2.6 to +3.6 ppm assigned to *cis*-configurational phosphorus was observed, it was concluded that polymer 1 has all-trans configurations at platinum moiety and the extended chain structure.

Thus, we could first obtain a high molecular weight representative of a new class of extended chain polymers possessing relatively good solubility and thermal stability. The details of the polymerization reactions, the polymer characterization, and properties of the polymer will be the subject of a forthcoming series of publications, and studies on analogous polymers containing other metal-diyne moieties are in progress.

Acknowledgment. The authors wish to thank Mr. S. Kataoka, Mr. M. Kariya, and Mr. T. Yatake for their excellent assistances.

References and Notes

(1) Y. Fujikura, K. Sonogashira, and N. Hagihara, *Chem. Lett.*, 1967 (1975).
(2) Thanks are due Dr. K. Kakiuchi for his determination of the molecular weights.
(3) K. Sonogashira, S. Kataoka, T. Yatake, S. Takahashi, and N. Hagihara, The 24th Symposium on Organometallic Chemistry, Japan, The Chemical Society of Japan, 1975, Abstract p 97.

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Received April 13, 1977