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A Facile Synthetic Method of Poly(Propargyltriphenylphosphonium-Tetraphenylborate) Via Ion Exchange Reaction of Poly(Propargyltriphenylphosphonium Bromide) Using Tetraphenylboron Sodium

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**A FACILE SYNTHETIC METHOD OF
POLY(PROPARGYLTRIPHENYLPHOSPHONIUM-
TETRAPHENYLBORATE) VIA ION EXCHANGE REACTION
OF POLY(PROPARGYLTRIPHENYLPHOSPHONIUM
BROMIDE) USING TETRAPHENYLBORON SODIUM**

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ABSTRACT

A Novel conjugated salt polymer having a highly bulky substituent, methylene triphenylphosphonium-tetraphenylborate from the simple ion exchange reaction of poly(propargyl triphenylphosphoniumbromide) by tetraphenylboron sodium. The yellow poly(propargyltriphenylphosphonium-tetraphenylborate) was formed. The polymer showed different physical and chemical properties in comparison to the precursor polymer. The polymer structure was characterized by various instrumental methods such as NMR (^1H -, ^{13}C -), IR, and UV-visible spectroscopies.

[Keywords: ion exchange reaction, sodium tetraphenylborate, conjugated salt polymer, poly(propargyltriphenylphosphonium-tetraphenylborate), molybdenum (V) chloride]

INTRODUCTION

The polymers having conjugated backbone are expected to show unique properties such as electrical conductivity,¹⁻³ gas and liquid mixture

separation,^{4,5} radiation degradation,^{6,7} side-chain liquid crystalline,⁸⁻¹⁰ and nonlinear optical properties.¹¹⁻¹³

The polyelectrolites having conjugated backbone were scarce and restricted to a few cases as follows: the solid-state polymerization of propiolic salts by γ -irradiation,¹⁴ the water-soluble polyene polymers by quaternarization of poly(6-bromo-1-hexyne),¹⁵ and the synthesis of mono- and di-substituted polyacetylenes by the activation of the acetylene bond in ethynylpyridines by introduction of a strong electron withdrawing substituents in conjugation to it.¹⁶⁻¹⁸

In recent years, we have synthesized the conjugated polyelectrolytes by the polymerization of mono-, di-, and tri-propargyl salt monomers.¹⁹⁻²⁴ In the polymerization of simple phosphonium salt, propargyltriphenylphosphonium bromide (PTPB), it was found that the polymerization reaction by W- and MoObased transition metal catalysts are well proceeded.¹⁹

Now we report a facile synthetic method of polyacetylene derivatives having a highly bulky substituent (methylenetriphenylphosphonium-tetraphenylborate) by the simple ion exchange reaction of poly(PTPB) using tetraphenylboron sodium.

EXPERIMENTAL

Propargyltriphenylphosphonium bromide (Aldrich Chemicals, 98%, mp 162-164°C) was used after recrystallization with ethyl alcohol. The polymerization catalyst MoCl₅ (Aldrich Chemicals., resublimed, 99+%) was used as received. Chlorobenzene was dried with calcium hydride and fractionally distilled. All procedures for catalyst solution preparation and polymerization were carried out under dry nitrogen atmosphere. MoCl₅ was dissolved as 0.2 M solution. A typical polymerization procedure of PTPB is as follows. Into a 20ml ampule, PTPB (1.0g, 2.62 mmol) and chlorobenzene (3.72 mL, [M]₀=0.5 M) were added in that order given, and sealed with rubber septum after flushing with nitrgen. After standing at 90 °C for 30 min, the MoCl₅ catalyst solution (0.1M, 0.52 mL) was added. The polymerization seemed to be proceeded by a heterogeneous phase (solid-state) before a viscous oily phase was formed at the bottom of ampoule (polymerization temperature 90°C). After decanting the upper layer, the 10ml of chloroform was added to the polymerization ampule. This polymer solution was precipitated into an excess hexane, filtered from the solution, and then dried under vacuum at 40°C for 24 hrs to give a light-brown powder. The polymer yield was calculated by gravimetry.

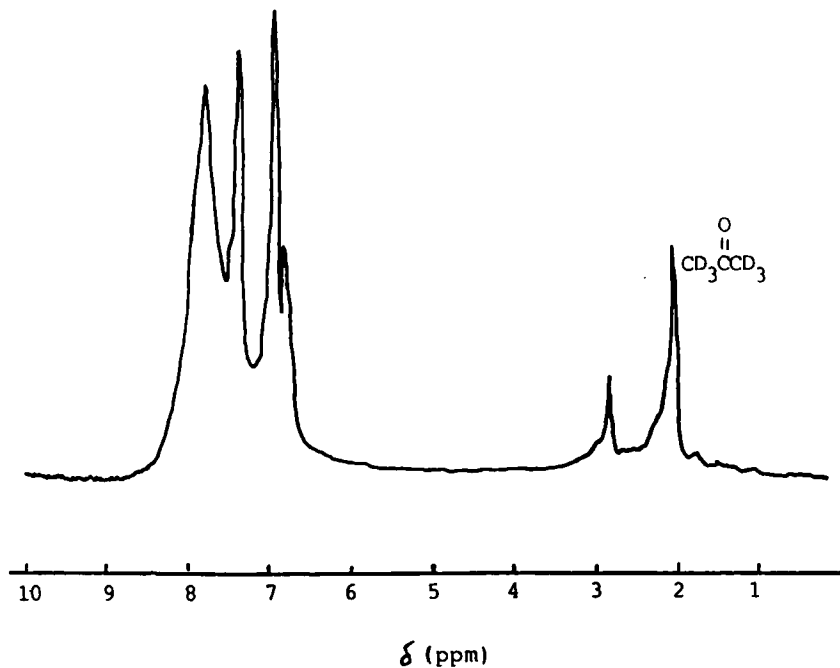
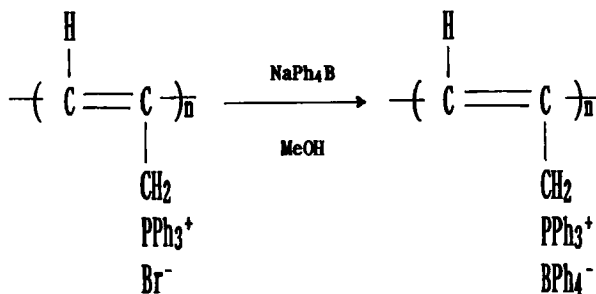


Figure 1 ¹H-NMR spectrum of poly(PPB) prepared by ion exchange reaction.

RESULTS AND DISCUSSION

Poly(PPB), a substituted polyacetylene having a highly bulky substituent was easily synthesized by the ion exchange reaction of poly(PTPB) by NaPh₄B in methanol.



Ion Exchange Reaction

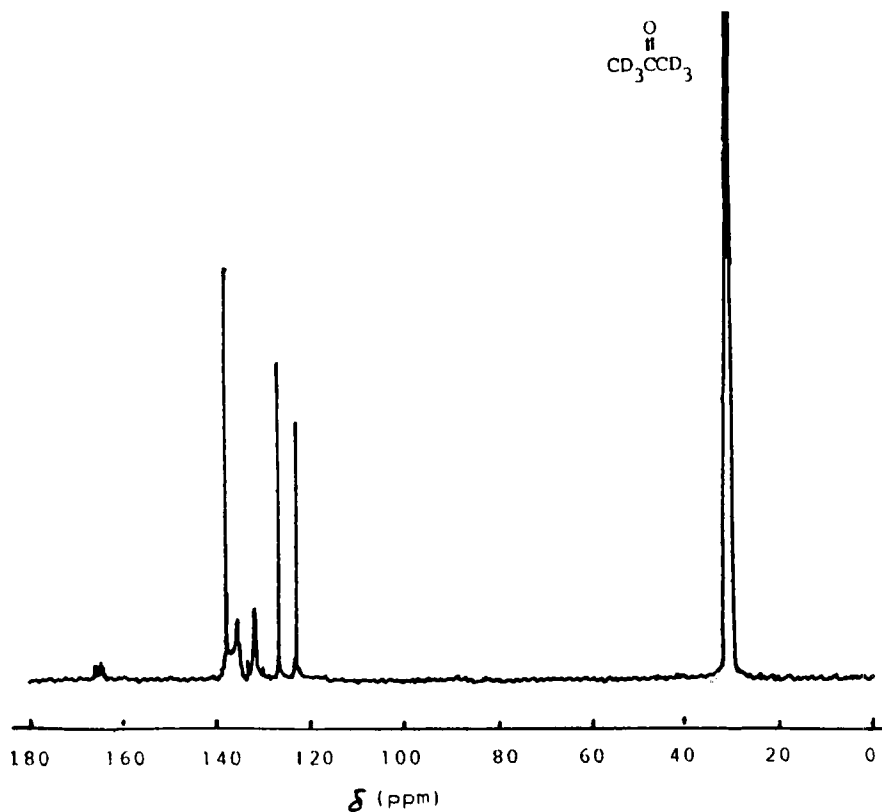


Figure 2 ^{13}C -NMR spectrum of poly(PPB) prepared by ion exchange reaction.

The ion exchange reaction of poly(PTPB) was carried out in methanol at room temperature. Into a 15 ml methanol solution of 0.5g poly(PTPB) [1.31 mmol as monomeric unit], the 10mL NaBPh_4 (0.493g, 0.144 mmol) methanol solution was gradually added. The yellow precipitate were immediately formed as soon as the NaBPh_4 solution is added into the poly(PTPB) solution. The precipitated poly(PPB) was filtered from the solution and wased several times with methanol. The polymer was dried under vacuum at 40°C for 24 hrs. The polymers were mostly yellow powder and soluble in DMF, DMSO, acetone, nitrobenzene, but insoluble in chlorobenzene, ethanol, methanol, n-hexane, etc.

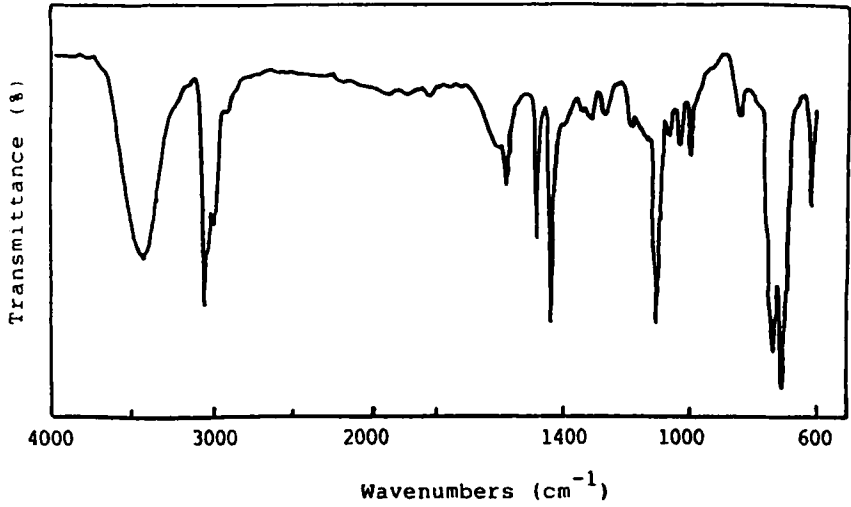


Figure 3 FT-IR spectra of poly(PPB) in KBr pellet.

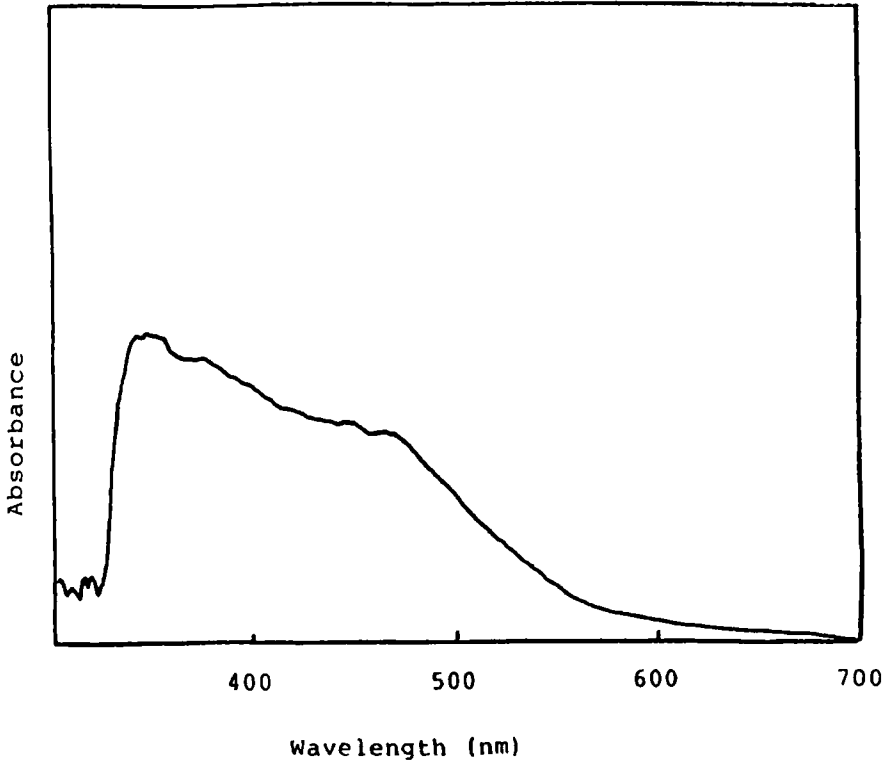


Figure 4 UV-visible spectrum of poly(PPB) prepared by ion exchange reaction.

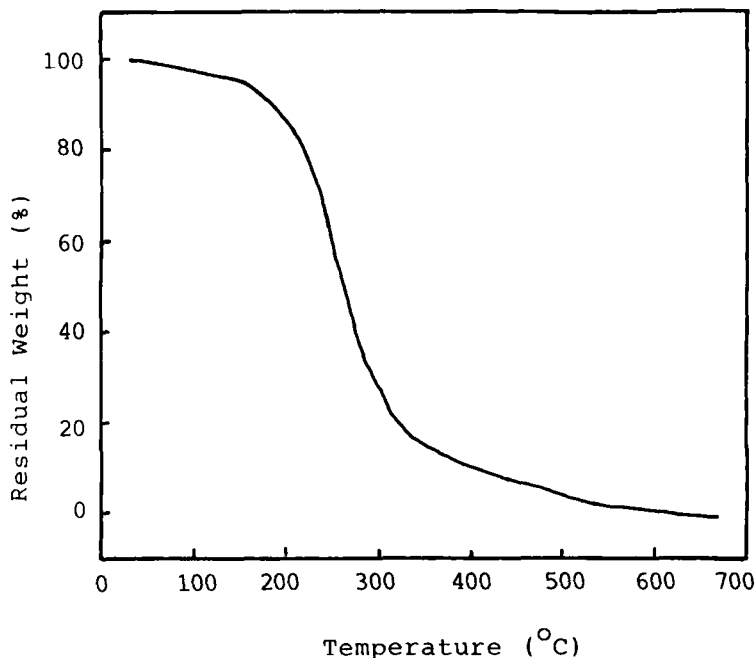


Figure 5 TGA thermogram of poly(PPB) prepared by ion exchange reaction.

Figure 1 shows the $^1\text{H-NMR}$ spectrum of poly(PPB) in acetone- d_6 . The phenyl hydrogen peaks of Ph_3P and Ph_4B were observed at 7.71ppm and 6.72-7.31 ppm, respectively. The methylene hydrogen peaks were observed at 2.81ppm.

Figure 2 shows the $^{13}\text{C-NMR}$ spectrum of poly(PPB) in acetone- d_6 . The aromatic carbon peaks of Ph_3P and Ph_4B were observed at 122.2-137.0 ppm. The methylene carbon peak was nearly seen at $^{13}\text{C-NMR}$ spectrum.

Figure 3 shows the FT-IR spectrum of poly(PPB). Aromatic and aliphatic C-H stretching frequencies were observed at 3151cm^{-1} and $2907\text{-}2987\text{ cm}^{-1}$, respectively. The peak of conjugated double bond on the polymer backbone was observed at 1615 cm^{-1} .

Figure 4 shows the UV-visible spectrum of poly(PPB) in acetone. The absorption spectra of poly(PPB) exhibits a large absorption band at 324-600nm that is due to the $\pi \rightarrow \pi^*$ transition of conjugated polymer backbone. This indicated that the present polymer is highly conjugated.

Figure 5 shows the TGA thermogram of poly(PPB) under nitrogen atmosphere. This polymer showed an abrupt weight loss at 150–350°C, which indicated the decomposition of polymer. It retains 96% of its original weight at 150°C, 86% at 200°C, 57% at 250°C, and 4% at 500°C.

CONCLUSIONS

In this paper, a facile synthetic method of ionic polyacetylene derivatives having a highly bulky substituent by the simple ion exchange reaction was presented. This method may be applied for many similar polyelectrolytes having bromide or chloride ion as counter anion in order to modify the polymer properties.

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