

Linear Structure and Viscometric and Electrical Properties of Nitrated Poly(*p*-phenylene)s

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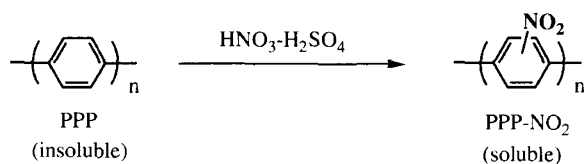
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(Received January 13, 2000)

KEY WORDS Poly(*p*-phenylene) / Nitration / Viscometric Properties / Light Scattering / Linear Structure / Conductivity /

Poly(*p*-phenylene), PPP, is a fundamental π -conjugated poly(arylene), and various methods have been developed for its synthesis.^{1–10} The polymer is transformed into organic metals by oxidation and reduction (*p*- and *n*-doping).^{10a,b} Recently, conversion of the polymer into graphite for lithium ion batteries was also reported.^{10f} In spite of its importance as a standard π -conjugated polymer and its interesting properties, information on the molecular structure of PPP remains limited due to tough insolubility. Recently various soluble PPPs with side chains have been prepared by palladium catalyzed organometallic polycondensation and their rod-like structures have been investigated.¹¹ However, obtaining further information on the structure of PPP itself is considered to be still important.

This paper deals with two PPPs prepared by Kovacic's cationic polymerization of benzene in the presence of AlCl₃ and CuCl₂ (PPP-a)¹ and Ni-catalyzed organometallic dehalogenative polycondensation of *p*-dibromobenzene with magnesium (PPP-b).² These PPPs have been the objective of various instrumental analyses including mass spectroscopy^{10c} and ESR spectroscopy.^{10e} These insoluble PPPs can be converted into soluble polymers by nitration, and in this paper a linear molecular



structure of the nitrated PPPs as well as interesting viscometric and electronic properties of the nitrated polymers are discussed.

EXPERIMENTAL

The two PPPs were prepared according to the literature^{1,2} and nitrated with mixed acid under similar conditions used for the nitration of low molecular weight aromatic compounds and polystyrene.^{12a,b} The reaction time was 4 h at 40°C. The reaction mixture was poured into ice-water. The nitrated product was collected by filtra-

tion, washed with water and methanol, and dried under vacuum. Analytical data of PPP-b-NO₂ roughly agreed with a partly hydrated structure, Br(C₆H₃NO₂ · 0.4 H₂O)₄₅Br. Found: C, 54.9; H, 2.5; N, 10.2; Br, 2.6%. Calcd: C, 54.7; H, 2.9; N, 10.6; Br, 2.7%. The discrepancy between found and calculated values seems, at least in part, due to the high thermal stability of the polymer. TGA showed 5% weight loss at 272°C. PPP-a-NO₂ gave the following analytical data: C, 52.2; H, 2.3; N, 10.0%. PPP-a is considered to contain irregular components (*cf.* text).^{10e} The nitrogen content suggests occurrence of similar nitration to introduce about 1 NO₂ group to the benzene ring.

IR spectra were recorded on a JASCO IR-810 spectrometer. Both nitrated PPPs showed peaks at 1600, 1520, 1340, and 830 cm⁻¹. ¹H and ¹³C NMR spectra were recorded on a JEOL JNM-EX-400 NMR spectrometer by using dimethyl sulfoxide (DMSO)-*d*₆ as the solvent. The ¹H NMR spectrum of PPP-b-NO₂ gave overlapping peaks in a region of δ 7.5–9.0. The ¹³C NMR spectrum of PPP-b-NO₂ showed peaks at δ 124.3, 128.5, 132.6–134.1 (overlapped), 138.4, 147.5, and 148.1. Assignment of the peaks has not been successful. GPC analysis was carried out with a Tosoh HPLC 8120 equipped with polystyrene gel columns and by using a *N,N*-dimethylformamide (DMF) solution of LiBr (0.006 M) as the eluent. Viscosity was measured with a Ubbelohde viscometer. Light scattering data were obtained using an He-Ne laser (632.8 nm where the nitrated PPP did not show absorbance) and according to a method reported previously.¹³

RESULTS AND DISCUSSION

After nitration, both polymers became soluble in DMF and *N*-methylpyrrolidone (NMP). The strong out-of-plane δ (CH) IR peak of PPP^{1,2} at about 805 cm⁻¹, characteristic of the *p*-phenylene unit, became very weak and new peaks (1340 and 1520 cm⁻¹) due to the NO₂ group appeared. Since the nitro group deactivated for the next nitration, distribution of the NO₂ group is probably uniform. Nitrated PPPs (PPP-a-NO₂ and PPP-b-NO₂) contained 10.3 ± 0.3% of nitrogen corresponding to about one NO₂ group per the *p*-phenylene unit. GPC using a DMF solution of LiBr (0.006 M) as the eluent gave *M_n* of 6100 and 4900 for PPP-a-NO₂ and PPP-b-NO₂, re-

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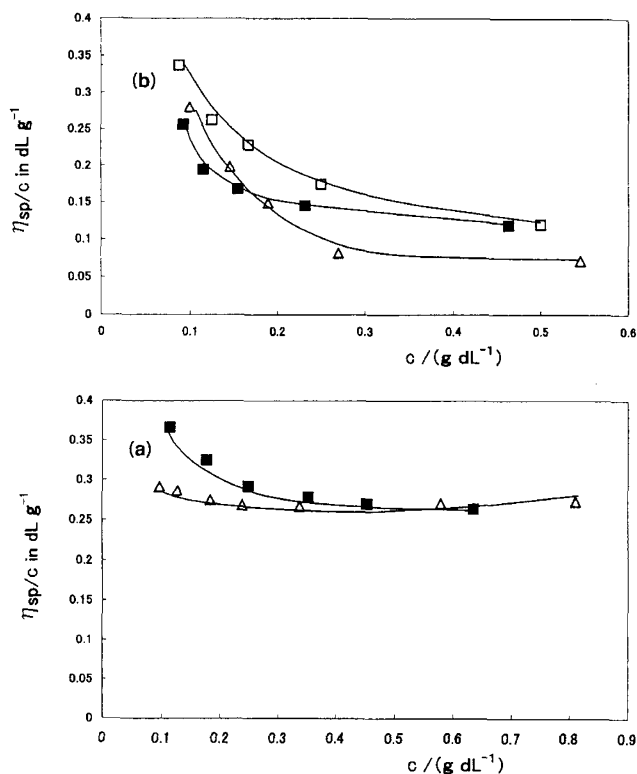


Figure 1. Plots of η_{sp}/c vs. c in DMF for (a) PPP-a- NO_2 and (b) PPP-b- NO_2 . $[\text{LiCl}] = 0$ (Δ), 0.10 M (\square), or 0.50 M (\blacksquare).

spectively.

Light scattering analysis (in DMF solution) indicated that PPP-a- NO_2 and PPP-b- NO_2 had ρ_v (degree of depolarization)¹³ of 0.13 and 0.12, respectively. ρ_v can be taken as a measure of stiffness and linearity of the polymer, and the limiting ρ_v for ideally stiff polymer is $1/3$.¹³ Observed ρ_v is comparable to those of stiff and linear all-aromatic polyamides (e.g., ρ_v = about 0.1 for poly(*p*-benzanilide terephthalamide) with a similar molecular weight).^{13c}

Thus, both nitrated PPPs assume, as a whole, an analogous stiff structure in DMF, although PPP-a prepared by using CuCl_2 and AlCl_3 is considered to contain some irregular components, such as fused aromatic units.^{10e} Nitration of polystyrene does not lead to increase in the viscosity of polystyrene and thus crosslinking of PPP by nitration is unlikely. The stiff structure of the nitrated PPP supports this view. Rod-like linear π -conjugated polymers are the subject of recent interest.¹⁴ However, enough evidence for such a linear structure of PPP has not been given due to insolubility.

One interesting property of the DMF solution containing PPP- NO_2 is that it behaves like a polyelectrolyte solution. As depicted in Figure 1, the η_{sp}/c increases as the concentration of the polymer decreases. Various polyelectrolyte¹⁵ solutions give similar η_{sp}/c vs. c patterns, and it has recently been reported that PPPs with ionic side chains behave as polyelectrolytes.^{11d} The strongly electron-withdrawing NO_2 group seems to introduce a highly polarized structure in the π -conjugated polymer, and this may be the reason for the polyelectrolyte-like behavior of nitrated PPP. In contrast to nitrated PPP, nitrated polystyrene does not seem to show such a

polyelectrolyte-like behavior,^{12b} and the present results indicate the unique properties of PPP with the nitro group.

Light scattering analysis gave higher M_w of 6×10^4 and 5×10^4 for PPP-a- NO_2 and PPP-b- NO_2 , respectively, than by GPC. Electrostatic interactions between the polar PPP- NO_2 molecules may lead to seemingly larger molecular weight in the light scattering analysis carried out in a static solution. PPP-b- NO_2 showed a π - π^* absorption band at 320 nm in DMF. Light scattering analysis indicated that coagulation of PPP-a- NO_2 and PPP-b- NO_2 took place when LiBr was added to the DMF solution, probably due to a decrease in electronic repulsion between the nitrated PPP molecules with polyelectrolyte-like nature. In DMF containing LiBr (0.10 M), PPP-a- NO_2 and PPP-b- NO_2 gave M_w of 12×10^4 and 29×10^4 , respectively, in light scattering analysis.

PPP-a- NO_2 and PPP-b- NO_2 showed dc electrical conductivities of 1×10^{-11} and $3 \times 10^{-9} \text{ Scm}^{-1}$, respectively, although these values were lower than previously reported for other π -conjugated polymers with NO_2 groups.¹⁶ These electrical conductivity was considered to originate from electronic conduction, since the dc measurement did not show time dependence. Evaporating a DMF solution containing PPP-a- NO_2 and LiBF_4 (1 : 0.2 wt ratio) gave a mixture showing higher electrical conductivity of about $1 \times 10^{-4} \text{ S cm}^{-1}$ as measured at 1 kHz at room temperature, presumably due to ionic conduction. Various polymers with flexible main chains (e.g., poly(ethylene oxide)) have been used as matrices of polymer solid electrolytes.^{17a,b} However, only a few polymers having rigid aromatic units and thermal stability and usable as a matrices of polymer solid electrolytes (or ion conducting polymer) have been reported.^{17c}

Due to the stiff molecular structures of nitrated PPPs, they serve as base polymer film for the alignment of liquid crystalline materials. Spin-coating (500 rpm) from an NMP solution of the polymer (concentration: 0.5–1.0 wt%) and drying at 80°C (5 min) and 150°C (5 min) gave a film of the polymer on a glass substrate. After rubbing the polymer film with a rayon cloth, a ferroelectric cholesteric liquid crystalline composite, which takes a smectic C* liquid crystalline phase at room temperature,¹⁸ was spread on the rubbed film. Alignment of the liquid crystalline molecules in the direction of the rubbing was confirmed under crossed nicols conditions at room temperature. The two nitrated PPPs exhibited similar effect for alignment of the liquid crystalline molecules.

The nitrated PPP gave basic information of PPP and showed interesting properties. Although nitration of PPP was carried out in the early stages of PPP chemistry,^{11c} such interesting properties were not reported before. Other PPPs are to undergo similar nitration reaction and the nitrated PPPs will give further basic information on the structures and properties of PPP. We are grateful to Canon Inc. for examining the alignment of the liquid crystalline material on the rubbed film of nitrated PPP.

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 18. The composite contained 98 wt% of a host mixture (68 wt% of a liquid crystalline compound containing a phenylpyrimidine unit + 30 wt% of a liquid crystalline compound containing a two *p*-phenylene groups and 2,5-pyrimidinediyl group) and 2 wt% of a chiral liquid crystalline compound containing a phenylpyrimidine unit. Phase transition temperatures of the composite:

$$\begin{array}{l} \text{crystalline} \xrightleftharpoons[-16.9^\circ\text{C}]{-4.4^\circ\text{C}} \text{smectic C}^* \text{ (ferroelectric)} \\ \xrightleftharpoons[61.3^\circ\text{C}]{61.9^\circ\text{C}} \text{smectic A.} \end{array}$$