Solvents and Molecular Weights of Nitrated Poly(*p*-phenylene) and Poly(pyridine-2,5-diyl)

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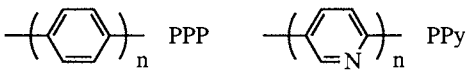
Poly(*p*-phenylene), PPP, becomes soluble by nitration and two types of nitrated PPPs give an *M*n of 5800 ± 400 in the GPC analysis. Poly(pyridine-2,5-diyl), PPy, has been found to be soluble in hexafluoro-*i*-propanol, and its GPC analysis gives an *M*n and *M*w of 6800 and 23000, respectively.

Poly(*p*-phenylene), PPP, and poly(pyridine-2,5-diyl), PPy, are typical π-conjugated poly(arylene)s.[1,2] They are electrically conducting and show interesting optical properties. For example, PPy is a useful material for an electron-transporting layer of organic light emitting diodes.[2c] Preparation of graphite for lithium ion battery from PPP is also actively investigated.[3] However, information about the molecular weight of these polymers has been limited.



PPy is soluble in formic acid and information about its molecular weight can be conveniently obtained from its viscosity in formic acid.[2] However, its GPC analysis was not possible. For PPP, it is completely insoluble and the information about its molecular weight has mainly been based on mass spectroscopic analysis of vacuum evaporated PPP.[4] In the course of our studies to reveal chemistry of PPP and PPy, we have found that nitrated PPP becomes soluble in DMF and that PPy is soluble in a new solvent $(CF_3)_2CHOH$ suited to GPC analysis. We here report new information about the molecular weights of PPP and PPy obtained based on these findings.

Two types of PPPs, PPP prepared by Kovacic's cationic oxidative polymerization of benzene (K-PPP)[5a] and PPP prepared by organometallic polycondensation of *p*-dibromobenzene with magnesium in the presence of a nickel catalyst (OM-PPP),[5b] were nitrated with mixed acid.[6]

Powdery PPP was treated with an excess amount of mixed acid (95% H_2SO_4: 61% HNO_3: H_2O = 1 : 0.17 : 0.13 vol/vol). The mixture of PPP and mixed acid was stirred in an ice bath. After that, the mixture was stirred at 40 °C for 4 h. The nitrated product was poured into cold water, washed with water, and dried under vacuum. Yield = 98% and 94% for K-PPP and OM-PPP, respectively. The nitrated K-PPP and OM-PPP were denoted by K-PPP-NO_2 and OM-PPP-NO_2, respectively. Analytical data of OM-PPP-NO_2 roughly agreed with $Br(C_6H_3NO_2 \cdot 0.4H_2O)_{45}Br$; 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 the found and calculated values seems, at least partly, to be due to high thermal stability of the polymer. TGA analysis of OM-PPP-NO_2 showed 5% wt-loss at 272 °C. Both the nitrated PPPs gave only one broad XRD peak at about d = 4.2 Å, although the original OM-PPP gave several sharp XRD peaks.[5] IR spectra of the nitrated polymers showed strong new peaks at 1340 and 1520 cm^{-1} due to the nitro group. The ^{1}H-NMR spectra of the two types of nitrated PPPs exhibited an analogous complex peak pattern in a range of δ 7.5 - 9.0. The nitrogen contents indicated that both K-PPP-NO_2 and OM-PPP-NO_2 contained about 1.0 nitro groups per the *p*-phenylene unit, respectively. Since the introduced NO_2 group deactivates the benzene ring, essentially only one NO_2 group per the *p*-phenylene unit seemed to be introduced. A repeated nitration experiment for OM-PPP at 40 °C for 4 h gave essentially the same results.

The nitrated PPP became soluble in DMF and DMSO and the GPC analysis (eluent = DMF containing LiBr (0.006 M)) gave *M*n (number average molecular weight) of 6100 and 5400 (*vs* polystyrene standards) for K-PPP-NO_2 and OM-PPP-NO_2, respectively. They showed the *M*w/*M*n (*M*w = weight average molecular weight) ratios of 3.8 and 1.7, respectively. Figures 1a and 1b exhibit GPC traces of K-PPP-NO_2 and OM-PPP-NO_2, respectively.

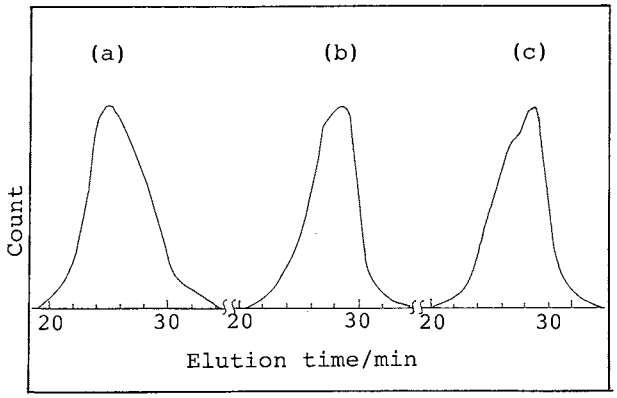


Figure 1. GPC traces of (a) K-PPP-NO_2 (reaction time = 4 h at 40 °C), (b) OM-PPP-NO_2 (reaction time = 4 h at 40 °C), and (c) OM-PPP-NO_2 (reaction time = 0.5 h at 40 °C). 1 min = 60 s.

It has been reported that K-PPP highly likely contains irregular units like a fused ring unit,[7] and the presence of the irregular units may give the wide molecular weight distribution of K-PPP-NO_2. On the other hand, OM-PPP is considered to have a linear regular structure as judged from its sharp XRD peaks and ordered alignment in a vacuum deposited thin film.[8a] Therefore, the molecular weight distribution of OM-PPP is considered to obey the theory of usual polycondensation, as previously observed for the molecular weight distribution of polymethylene prepared by an analogous method.[8b]

K-PPP-NO_2 showed an η_{sp}/c value of 0.29 dlg^{-1} (dl = 100

cm^3) at c = 2.5 gdm^{-3} in a DMF solution containing LiCl (0.50 M) at 30 °C. Since it is known that even a extensive nitration of polystyrene does not lead to crosslinking of polystyrene,[6b] crosslinking of PPP by the nitration is unlikely. Actually OM-PPP-NO_2 prepared at shorter nitration time[9] showed essentially the same *M*n (5400) and *M*n and *M*w ratio (1.8), supporting the above described assumption. The GPC trace of OM-PPP-NO_2 prepared at the shorter nitration time is exhibited in Figure 1c.

As described in the introduction part of this communication, PPy is soluble in hexafluoro-*i*-propanol suited to the GPC analysis. PPy prepared by an organometallic polycondensation[2] and showing an [η] value of 1.02 dlg^{-1} in formic acid gives a GPC trace exhibited in Figure 2. The GPC trace gives *M*n and

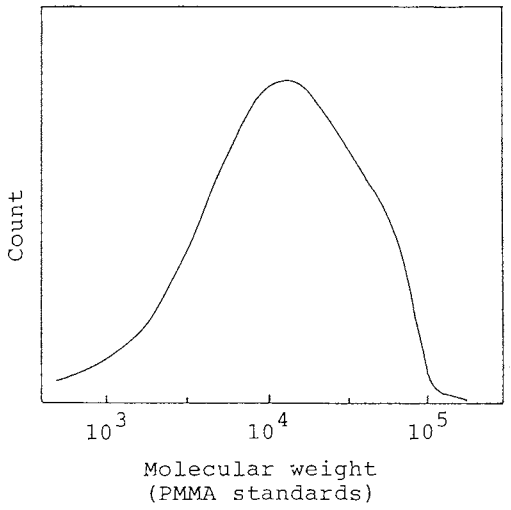


Figure 2. GPC trace of PPy. Eluent = hexafluoro-*i*-propanol.

*M*w of 6800 and 23000 (*vs* poly(methyl methacrylate) standards), respectively. The large [η] value for the molecular weight is consistent with the rigidly linear molecular structure of PPy, which was confirmed by the light scattering analysis of the polymer.[2b]

As described above, information about the molecular weight of PPP and PPy can now be obtained by the GPC analysis. The obtained information will contribute to better understanding of the chemistry of the polymers as well as to design of electronic and optical devices using the polymers.

References and Notes

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9 Reaction time = 0.5 h at 40 °C. Analytical data indicated that this OM-PPP-NO_2 contained 0.92 NO_2 group per the *p*-phenylene unit.