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Registry No. MAOTPP, 110528-82-0; poly(MAOTPP), 110528-83-1; AOTPP, 87345-23-1; poly(AOTPP), 87366-09-4; HOTPP, 87345-22-0; MMA, 80-62-6; O_2, 7782-44-7; $H_2C{=}C(CH_3)COCl$, 920-46-7; $H_2C{=}CHCOCl$, 814-68-6.

References and Notes

(1) Ovchinnikov, A. A. *Dokl. Acad. Nauk USSR* **1978**, *236*, 928.
(2) Buchachenko, A. L. *Dokl. Acad. Nauk USSR* **1979**, *244*, 1146.
(3) Kamachi, M.; Akimoto, H.; Mori, W.; Kishita, M. *Polym. J.* **1984**, *16*, 23.
(4) Kamachi, M.; Tamaki, M.; Morishima, Y.; Nozakura, S.; Mori, W.; Kishita, M. *Polym. J.* **1982**, *14*, 363.
(5) Kamachi, M.; Enomoto, H.; Shibasaka, M.; Mori, W.; Kishita, M. *Polym. J.* **1986**, *18*, 439.
(6) More, K. M.; Eaton, S. S.; Eaton, G. R. *J. Am. Chem. Soc.* **1981**, *103*, 1087.
(7) Kamachi, M.; Akimoto, H.; Nozakura, S. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 693.
(8) Lautch, W.; Broser, W.; Rothkegel, W.; Biederman, W.; Doering, U.; Zoschke, H. *J. Polym. Sci.* **1952**, *8*, 191.
(9) Lautch, W.; Broser, W.; Biederman, W.; Gnichel, H. *J. Polym. Sci.* **1955**, *17*, 479.
(10) Kamogawa, M. *J. Polym. Sci., Part B* **1972**, *10*, 711.
(11) Tsuchida, E. *J. Macromol. Sci., Chem.* **1979**, *A13*, 545.
(12) Finkenauer, A. L.; Dickinson, L. C.; Chien, C. W. *Macromolecules* **1983**, *16*, 728.
(13) Kamogawa, M. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 2317.
(14) Nishide, H.; Shinohara, K.; Tsuchida, E. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 1109.
(15) Kamachi, M.; Fujii, M.; Ninomiya, S.; Katsuki, S.; Nozakura, S. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 1489.
(16) Little, R. G.; Anton, J. A.; Loach, P. A.; Ibers, S. A. *J. Heterocycl. Chem.* **1975**, *12*, 343.
(17) Fineman, R.; Ross, S. D. *J. Polym. Sci.* **1950**, *5*, 269.
(18) Blythe, A. R. *Electrical Properties of Polymers*; Cambridge University Press: London, 1979; pp 132–139.
(19) Belami, L. J. *The Infrared Spectra of Complex Molecules*; Methuen: London, 1985; p 179.
(20) Brookfield, R. L.; Ellul, H.; Harriman, A.; Porter, G. *J. Chem. Soc., Faraday Trans. 2* **1986**, *82*, 219.
(21) White, I. W. *Porphyrins*; Dolphin, M., Ed.; Academic Press: New York, 1973; Vol. 4, pp 306–325.
(22) Goutermann, M.; Holten, D.; Libermann *Chem. Phys.* **1977**, *25*, 139.
(23) Young, L. J. In *Polymer Handbook*, 2nd ed.; Brandrup, J., Immergut, E. H., Eds.; Wiley: New York, 1975; p II-398.
(24) Kamachi, M.; Liaw, D. J.; Nozakura, S. *Polym. J.* **1981**, *13*, 41.
(25) Kamachi, M.; Liaw, D. J.; Nozakawa, S. *Polym. J.* **1977**, *9*, 307.
(26) Kamachi, M.; Cheng, X. S.; Kida, T.; Kajiwara, A.; Shibasaka, M. to be published in *Macromolecules*.

Characterization of Functionalized Polymers: Synthesis of Cyanomethylated Polystyrenes and Reaction Chemistry with Palladium(II)

Julian A. Davies,* Randy J. Shaver, and Anup Sood

Department of Chemistry, University of Toledo, Toledo, Ohio 43606

Michael W. Phillips* and Michael Watkins

Department of Geology, University of Toledo, Toledo, Ohio 43606

Colin A. Fyfe* and Michael McKinnon

Department of Chemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1.

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ABSTRACT: The reactions of linear and cross-linked chloromethylated polystyrenes with NaCN/DMSO have been investigated. Unlike the model compound benzyl chloride, which reacts exclusively by substitution, these functionalized polystyrenes react by substitution and oxidation, producing products bearing both cyanomethyl and aldehyde functional groups. The substrates and reaction products have been fully characterized by solid-state ^{13}C NMR spectroscopy and diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy, in conjunction with more routine methods. The differences in reactivity of benzyl chloride and chloromethylated polystyrenes are attributed to a matrix effect which is believed to be operative in the case of polymeric substrates. Penetration of the ionic reactant and/or the polar solvent through the nonpolar polymer network is shown to be limited in the case of cross-linked resins by use of electron probe analysis and energy dispersive spectroscopy. An alternative route to cyanomethylated polystyrenes free of aldehyde functionality has been developed. Palladium(II) complexes of polystyrenes bearing cyanomethyl groups have been prepared by displacement of weakly bound nitromethane ligands from solvated palladium(II) precursors. Such complexes are of interest as immobilized promoters and catalysts in organic syntheses.

Introduction

Functionalized polymers have found numerous applications in solid-phase synthesis,[1] as supports in chromatography,[2] as macromolecular ligands for the immobilization of catalytically active metal complexes,[3] and as reagents in organic synthesis.[4]

Despite widespread interest in the chemistry of functionalized polymers there is a paucity of structural and mechanistic data on these solid-phase systems. The problems encountered in acquiring structural and mechanistic data of such materials revolve around the low concentration of functional groups typically encountered and the lack of solubility of cross-linked polymeric systems. These two factors lead to acute analytical problems which eliminate the use of many standard instrumental methods.

We have previously reported[5-10] that structural information may be acquired by the application of solid-state NMR techniques,[11] employing cross-polarization,[12] magic angle spinning,[13] and high-power proton decoupling (CP/MAS NMR), to both inorganic and organic substrates

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bearing pendant ligand groups and to transition-metal complexes of such support systems. Similarly we have described the application of diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy to the characterization of organic[14] and inorganic[15] substrates bearing Lewis base groups and to the structural analysis of transition-metal complexes of these ligated support materials.

A combination of solid-state NMR and DRIFT spectroscopic methods is particularly valuable in the chemical characterization of functionalized polymers and yet even this powerful combination of analytical techniques provides no information on the spatial distribution of functionality within a polymer matrix. Such information can, however, be acquired by the application of electron microprobe analysis or allied surface techniques.[16,17]

In this paper we describe the synthesis of cyanomethylated polystyrene and its reaction with palladium(II) chloride. A combination of CP/MAS NMR and DRIFT techniques has been employed to analyze reaction products and electron microprobe analysis has shed light on matrix effects observed during reactivity studies. There is considerable interest in this class of functionalized polystyrene and its palladium(II) complexes since low molecular weight analogues, such as $[PdCl_2(NCCH_3)_2]$ and $[PdCl_2(NCC_6H_5)_2]$, are ubiquitous catalysts and promoters in organic synthesis.[18] Applications include acetylene oligomerization,[19] α,β-dehydrogenation of aldehydes and ketones,[20] amination of conjugated dienes,[21] selective cleavage of epoxides,[22] and other transformations of synthetic utility.

After completion of this work, Darling and Frechet[23] reported some observations on the reaction of chloromethylated polystyrene with $DMSO/CN^-$ and described contamination of the cyanomethylated product by oxidation byproducts. These workers went on to develop a phase-transfer catalyzed route to cyanomethylated polystyrene using dry DMF as a solvent. The problem that they describe and their solution to it agree entirely with the results we describe here.

Experimental Section

Physical Measurements. Diffuse reflectance infrared Fourier transform (DRIFT) spectra[14,15] were obtained by using a Nicolet 5DX FT-IR spectrometer equipped with a 64K × 20-bit high-speed data processor, a DTGS room temperature pyroelectric bolometer with a KBr window, a Harrick "preying mantis" diffuse reflectance accessory and a Zeta 8 printer/plotter. The 5DX spectrometer has f5 optics and all spectra were recorded with 4-cm^{-1} resolution over the range 4600–400 cm^{-1} at a maximum gain setting. Happ–Ganzel apodization was applied and the spectra are presented without Kubelka–Munk transformation since they are for qualitative interpretation only. Polymer samples were prepared for DRIFT analysis by dilution with dried KBr (ca 1:20 w/w) and the spectra were obtained by ratioing against a KBr background by using a dry nitrogen purge system.

^1H and ^{13}C high-resolution NMR spectra were obtained for $CDCl_3$ solvent swollen gels at 89.56 and 22.49 MHz, respectively, on a JEOL FX 90 Q NMR spectrometer operating in the Fourier transform mode. Chemical shifts are relative to internal tetramethylsilane, with more positive values of the chemical shift representing deshielding.

^{13}C CP/MAS NMR spectra were obtained at 22.6 MHz by using a Bruker CXP 100 spectrometer equipped with a homemade probe with an Andrews-Beams type of spinning apparatus.[13] Sample spinners of ca. 460-μL capacity were constructed of Kel-F [poly(chlorotrifluoroethylene)] and were spun at ca. 3 kHz. Spectra were typically acquired with a 1-ms contact time and a 1-s delay between sequences. The number of scans acquired and the line broadening applied are cited in the appropriate figure legends. Spectra in which signals due to protonated carbon atoms have been reduced in intensity by delayed acquisition were typically acquired with a 1-ms contact, a 1-s recycle delay, and decoupler gated off for 50 μs before acquisition.

An ARL electron microprobe coupled with a Kevex energy dispersive spectrometer was employed for the sulfur and chlorine analyses of bead cross sections. A relatively large beam size (diameter = 80 μm) was chosen to minimize sample damage and analyses were performed in 100-μm step intervals across traverses passing through the approximate centers of the sectional samples. The intensities of the Kα X-ray emission lines of chlorine (2.622 keV) and sulfur (2.307 keV) were measured by using counting intervals of 20 s (excluding dead time). Intensities were integrated for peak widths taken at one-half maximum peak intensity, which corresponded to window widths of 21 and 15 channels for chlorine and sulfur, respectively. Raw counts were corrected for background by subtraction of a visually estimated linear background for each element.

Elemental analyses were performed by Micanal, AZ, and Galbraith, TN.

Syntheses. Linear biological grade polystyrene was obtained from Baker Chemicals. Other reagents were obtained as follows: polyvinyl alcohol (MCB, Inc., 99% hydrolyzed); divinylbenzenes (Pfaltz and Bauer, ca. 80% para by NMR spectroscopy); chloromethylstyrene (Polysciences, Inc., ca. 60% meta and ca. 40% para by NMR spectroscopy).

Preparation of Linear Chloromethylated Polystyrene 1.[24] Chloromethyl methyl ether (60 mL; 0.79 mol; **NOTE**, chloromethyl methyl ether is a carcinogen—use all appropriate precautions in handling and disposal) was added with stirring (using a high-speed mechanical stirrer) to polystyrene (10 g; 96 mmol) at 50 °C. After the polymer beads were dissolved, a further aliquot of chloromethyl methyl ether (60 mL) containing anhydrous stannic chloride (3.04 g; 11.6 mmol) was added and the reaction mixture was stirred at 50 °C for 7.5 h. It was then quenched with methanol at which time precipitation occurred. The polymer was filtered off; washed with methanol, water, ethanol, and methanol; dried under vacuum; and characterized.

Preparation of Cross-Linked Chloromethylated Polystyrene 2. Polyvinyl alcohol (0.054 g) was added to degassed water (32 mL) under a nitrogen atmosphere in a three-necked round-bottomed flask fitted with a high-speed mechanical stirrer. The mixture was heated to dissolve the polyvinyl alcohol and then styrene (0.667 g; 6.41 mmol), divinylbenzenes (1.273 g; 9.78 mmol), (chloromethyl)styrene (a mixture of isomers, 5.0 g; 32.80 mmol), azobisisobutyronitrile (0.037 g; 0.22 mmol), and acetonitrile (1.8 mL) were added and the reaction mixture was stirred at 90 °C for 8 h. The polymer beads were collected on a filter and washed with methanol, ethanol, and acetone and then dried in vacuum prior to characterization.

Preparation of Polymer 3.[25] Polymer 1 (0.50 g) and sodium cyanide (excess, 0.30 g) were dissolved in dimethyl sulfoxide (DMSO, 25 mL) and heated with stirring on a boiling water bath for 6 h. The reaction mixture was then diluted with water and filtered. The polymer was washed with water, methanol, and acetone and then dried in vacuum prior to characterization.

Preparation of Polymer 4.[14] Polymer 1 (0.75 g) and sodium bicarbonate (0.41 g) dissolved in excess DMSO (50 mL) were heated at 110 °C with stirring for 24 h. The reaction mixture was then diluted with water, filtered, washed with water, followed by methanol, and dried in vacuum for analysis.

Reaction of 3 and 4 with Schiff's Reagent. Polymers 3 and 4 (about 0.05 g of each) were suspended separately in 2-mL portions of Schiff's reagent (prepared by dissolving 0.1 g of *p*-rosaniline hydrochloride in 100 mL of water, adding 4 mL of saturated aqueous sodium bisulfite solution, and then, after 1 h, adding 2 mL of concentrated hydrochloric acid), heated on a steam bath for 1 min, and then allowed to cool. Both cooled samples showed the characteristic purple color indicative of the presence of aldehyde groups. As a control, both polystyrene itself and polymer 1 were similarly treated with Schiff's reagent. Neither sample gave a purple coloration.

Reaction of 3 and 4 with Thionyl Chloride. Polymers 3 and 4 (about 0.05 g of each) were suspended separately in thionyl chloride (excess, 5 mL) and refluxed with stirring for 3 h. After they were cooled, the polymeric products were filtered off and dried under vacuum.

Preparation of Polymer 5. Polymer 4 (0.50 g) was suspended in excess acetone (25 mL) and an excess of Jones' reagent (10 mL, prepared by dissolving 26.72 g of chromium trioxide in 23 mL of concentrated sulfuric acid and diluting to 100 mL with water) was added to this mixture. The reaction mixture was stirred at room temperature for 6 h. The polymer was then filtered off; washed with cold water, hot water, methanol, and acetone; and then dried in vacuum. The washing procedure used here was not effective at removing entrapped impurities and the resulting product had a green color, presumably due to chromium-containing byproducts from the oxidation process.

Preparation of Polymer 7. Polymer 2 (1.00 g) was suspended in DMSO (25 mL), sodium cyanide (excess, 0.50 g) was added, and the suspension was heated with stirring on a boiling water bath for 6 h. The reaction mixture was then cooled, diluted with water, and filtered. The polymer was washed with water, methanol, and acetone and then dried under vacuum.

Preparation of Polymer 8. Polymer 8 was prepared by using the method described above for polymer 3 except that the DMSO solvent was replaced by an equal volume of *N*,*N*-dimethylformamide (DMF).

Preparation of the Palladium(II) Complex of Polymer 3. Method 1. Following the literature method,[25] polymer 3 (0.10 g) was packed into a small glass column. Through this column a 0.1 M aqueous solution of palladium(II) chloride was passed slowly. The column was then washed through with water, methanol, and acetone and then dried in vacuum. **Method 2.** Polymer 3 (0.10 g) and palladium(II) chloride (0.065 g; 0.37 mmol) in nitromethane (25 mL) were refluxed with stirring for 3.5 h. The reaction mixture was then filtered while hot, to prevent unreacted palladium from precipitating out of solution during cooling and contaminating the product. The filtered polymer was washed with methanol and acetone and then dried in vacuum.

Results and Discussion

It is reported[25] that commercial chloromethylated styrene–divinylbenzene (80%/20%) copolymer, containing 16.7% chlorine, reacts with sodium cyanide in DMSO at boiling water bath temperatures over a 6-h period to yield a cyanomethylated polymer containing 5.7% nitrogen and 2.6% residual chlorine. The analytical data imply a ca. 85% conversion of chloromethyl groups to cyanomethyl groups. We have employed this literature method with two types of well-characterized chloromethylated polystyrene as follows:

(i) Linear Chloromethylated Polystyrene 1. A biological grade high-purity polystyrene was chloromethylated under conditions to minimize cross-linking via dehydrohalogenation.[24] The chloromethylated product (20.2% chlorine; calcd for 85% chloromethylation = 20.6%) was characterized by ^{1}H and ^{13}C high-resolution NMR and solid-state ^{13}C NMR methods and by DRIFT spectroscopy. The ^{1}H NMR spectrum of a chloroform d_1 gel showed the expected resonances for the aliphatic and aromatic protons of the polystyrene matrix and an additional resonance at 4.51 ppm due to the benzylic protons of the chloromethyl groups. The high-resolution ^{13}C NMR spectrum similarly showed the expected resonances for the aliphatic and aromatic carbons of the polystyrene matrix and a new resonance at 46.3 ppm for the benzylic carbon of the chloromethyl group.

The solid state ^{13}C NMR spectra of the polystyrene substrate before and after chloromethylation are shown in Figure 1. Prior to chloromethylation the spectrum shows overlapping resonances for the aliphatic carbon atoms of the polystyrene backbone (46.1–41.0 ppm) and discrete resonances for the protonated (128.1 ppm) and nonprotonated (146.7 ppm) aromatic carbon atoms of the phenyl residues. After chloromethylation, new resonances appear due to the pendant benzylic carbon atom (47.4 ppm) and the quaternary carbon atom (135.9 ppm) of the aromatic residue which bears the pendant functionality.

Both the high-resolution and solid-state ^{13}C NMR methods give useful structural data for sample 1 since it is a linear polymer capable of forming a relatively mobile gel and since it has a high degree of functionalization. In cases where the mobility of the matrix is restricted (e.g., cross-linked polymers) the usefulness of the high-resolution method decreases and the solid-state technique becomes the method of choice. Thus, high-resolution measurements give rise to substantially smaller line widths for the ^{13}C resonances of mobile (typically linear) polymers, but the solid-state ^{13}C NMR technique is superior for cases where the mobility is restricted (typically for cross-linked polymers) and the line widths obtained by high-resolution techniques are large.

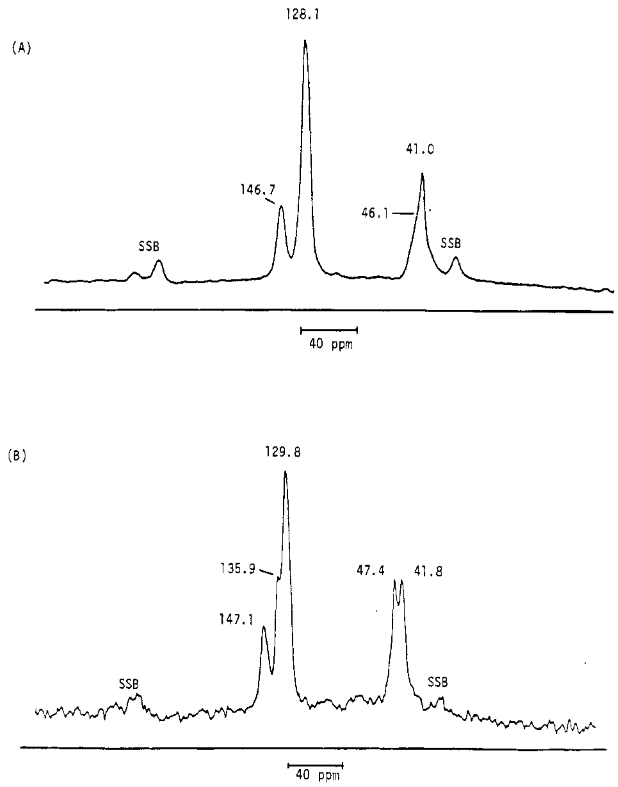

Figure 1. (A) ^{13}C CP/MAS NMR spectrum of linear polystyrene: 38 586 scans; 20-Hz line broadening. (B) ^{13}C CP/MAS NMR spectrum of chloromethylated polystyrene 1: 8100 scans; 20-Hz line broadening.

The DRIFT spectra of this substrate before and after chloromethylation have been described previously,[14] with the chloromethylated polystyrene exhibiting new bands at 1266 and 677 cm^{-1}. The former is diagnostic of the CH_2Cl group while the latter is attributed to ν(C–Cl). We have found the DRIFT technique to be valuable in obtaining well-resolved IR spectra of functionalized polymers. A major advantage lies in the simplicity of sample preparation. Thus, we find that polymer particles with elastic properties resist preparation as pressed KBr pellets and are similarly difficult to prepare as mulls for IR study. The DRIFT technique bypasses these practical problems and offers a useful alternative.

(ii) Cross-Linked Chloromethylated Styrene–Divinylbenzene (80%/20%) Copolymer (2). A cross-linked chloromethylated resin was prepared by suspension polymerization of styrene (13.1 mol %), divinylbenzenes (20.0 mol %), and chloromethylstyrenes (66.9 mol %). Elemental analysis indicated a chlorine content of 14.1% and DRIFT spectroscopy confirmed the presence of chloromethyl groups (vide supra).

Reaction of the linear substrate 1 with sodium cyanide in DMSO under the reported[25] reaction conditions yielded a product, 3, whose DRIFT spectrum showed the complete disappearance of bands due to the chloromethyl groups and the presence of new bands due to both nitrile- and

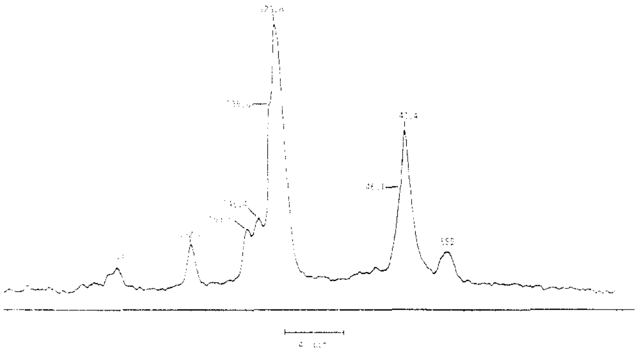

Figure 2. ^{13}C CP/MAS NMR spectrum of polymer 4: 9300 scans; 20-Hz line broadening.

carbonyl-containing functionalities at 2250 and 1709 cm^{-1}, respectively. Elemental analysis confirmed the presence of a nitrogen-containing functionality (% N = 6.50), indicating a conversion of ca. 74% of the chloromethyl groups to cyanomethyl groups.

The appearance of carbonyl-containing functionality during this reaction is significant since under similar reaction conditions benzyl chloride, as a model substrate, produced only the substitution product, as determined by gas chromatography and ^{1}H NMR analysis, with the reaction being complete in just 15 min.[26] The carbonyl-containing functionality is believed to be aldehydic, since the DMSO oxidation of chloromethylated polystyrene in the presence of base ($NaHCO_3$) leads to aldehyde formation, eq 1.[14] Thus, treatment of the linear chloromethylated polystyrene 1 with DMSO/$NaHCO_3$ produces a polymer, 4, whose DRIFT spectrum shows the disappearance of the chloromethyl groups and the presence of new bands at 1702 cm^{-1} (cf. 1709 cm^{-1}, above) and 2734 cm^{-1}, attributed to the carbonyl and carbon–hydrogen stretching modes of the aldehyde functionality.[14] The solid-state ^{13}C NMR spectrum, Figure 2, shows that the resonance due to the benzylic carbon atom of the chloromethyl group is no longer present but that a resonance due to carbonyl carbon atoms (192.8 ppm) has appeared. Both the products 3 and 4, obtained from the treatment of chloromethylated polystyrene with DMSO/NaCN and DMSO/$NaHCO_3$, respectively, give positive tests for aldehyde groups in their reactions with Schiff's reagent.

$$\text{Ⓟ-}C_6H_4CH_2Cl \xrightarrow[NaHCO_3]{DMSO} \text{Ⓟ-}C_6H_4CHO \qquad (1)$$

Identification of the carbonyl-containing functionality of 3 as aldehydic is thus based on comparisons of DRIFT spectroscopic data with those of 4, in conjunction with the results of testing with Schiff's reagent. However, we were surprised to find that both 3 and 4 react with thionyl chloride, in contrast to the model substrate benzaldehyde, which of course does not. The DRIFT spectra of the products of these reactions show new bands at 1771 and 1735 cm^{-1} in the polymer derived from 3 and at 1773 and 1734 cm^{-1} in the polymer derived from 4. On the basis of these results alone it would seem possible that the carbonyl-containing functionalities of 3 are carboxyl groups, which could arise from hydrolysis of the cyanomethyl groups and which react with thionyl chloride to produce an acyl chloride functionality. However, other data exclude this possibility. Thus, 4 is assigned a structure-bearing aldehyde functionality on the basis of definitive DRIFT and solid-state ^{13}C NMR data and yet this polymer also reacts with thionyl chloride to produce a product with a DRIFT spectrum essentially identical with that of the product derived from 3. Also, 4 reacts with Jones' reagent to produce a new polymer, 5, whose DRIFT spectrum shows the presence of carboxyl groups ($\nu(CO)$ = 1700, 1718 cm^{-1}; $\nu(OH)$ = 3500–2400 cm^{-1}) and is characteristically different from the DRIFT spectra of 3 and 4. These results suggest that the reaction of 1 with DMSO/NaCN produces a polymer containing not only cyanomethyl groups but also an aldehyde functionality and that the reactivity of the aldehyde groups toward thionyl chloride is modified by the polymer matrix.

This modification of reactivity is not entirely unexpected and, indeed, a comparison of the reactions of benzyl chloride and chloromethylated polystyrene with DMSO/NaCN illustrates this very effect. Thus, benzyl chloride reacts with DMSO/NaCN under the present reaction conditions to give exclusively substitution[26] whereas chloromethylated polystyrene gives both substitution and oxidation. In the reaction of benzyl chloride with DMSO in the absence of base, the ionic intermediate 6 may be isolated whereas in the presence of base this intermediate is deprotonated rapidly to produce benzaldehyde, eq 2.[25]

$$C_6H_5CH_2Cl \xrightarrow{DMSO} C_6H_5CH_2\text{—}O\text{—}\overset{+}{S}(CH_3)_2Cl^- \xrightarrow{B^-} C_6H_5CHO + HB + Me_2S \quad (2)$$

If an intermediate analogous to 6 is formed when chloromethylated polystyrene is heated in DMSO, then substitution at either these pendant ionic sites or residual chloromethyl functionalities will lead to the formation of cyanomethyl groups. However, if cyanide ion is unable to penetrate the matrix to certain sites analogous to 6, then thermally promoted deprotonation (e.g., by chloride ion) will lead to aldehyde formation. Indeed, at 105 °C, in the absence of base, compound 6 slowly produces benzaldehyde. Thus, penetration of cyanide ion through the nonpolar polymer matrix would appear to be central in determining the extent of substitution and/or oxidation. Penetration of the cyanide ion through the polymer network would presumably be limited by the extent to which the polar solvent, DMSO, could transport through the nonpolar matrix environment. This effect may be of particular importance with cross-linked resins where the flexibility of the matrix is limited. We have examined this situation in detail for the cross-linked resin 2.

A sample of the polymer 2 was treated with DMSO/NaCN by using the reported reaction conditions and the product, 7, analyzed by DRIFT spectroscopy. The DRIFT spectrum of a sample prepared from small beads of 7 (<0.5-mm diameter) showed the presence of both unreacted chloromethyl groups and new cyanomethyl groups (1266 and 2250 cm^{-1}, respectively), along with a small band at 1699 cm^{-1} indicating probable formation of low levels of aldehyde functionality. Several larger beads of 7 (ca. 2-mm diameter) were separated and sliced in half and the middle portion of the beads was removed. DRIFT analysis of samples prepared separately from the central and exterior portions of the beads indicated that reaction is extensive at the surface, but is much less at the center. This observation again implies that the penetration of the polar solvent and ionic reactant is restricted by the nonpolar matrix environment.

In order to confirm this penetration effect, samples of 2 and 7 were embedded in an epoxy matrix and sectioned for X-ray spectroscopic analysis by using an electron microprobe equipped with an energy dispersive spectrometer (EDS).[16,17] The relative abundance of chlorine was measured in the first instance in background-corrected counts taken in 20-s intervals at 100-μm steps across each bead section. Plots of the relative chlorine content across each bead are shown in Figures 3 and 4. Prior to reaction with DMSO/NaCN, the chlorine content in 2 is approximately

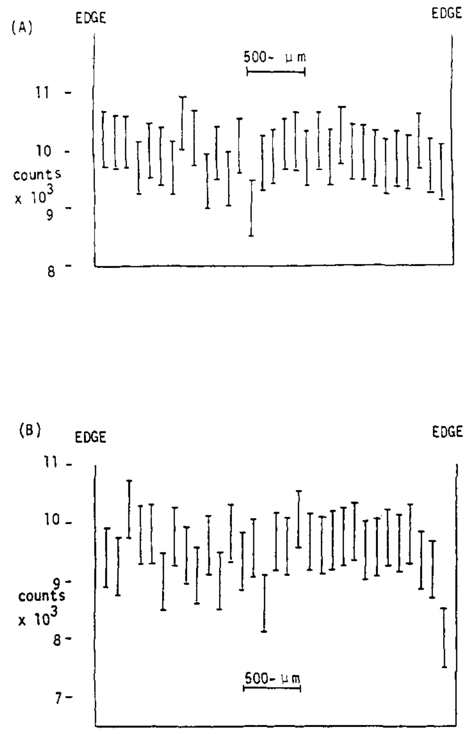

Figure 3. EDS analysis for chlorine across a sectional sample of chloromethylated polystyrene **2**. Plots A and B represent traverses along the *x* and *y* axes of a single polymer bead.

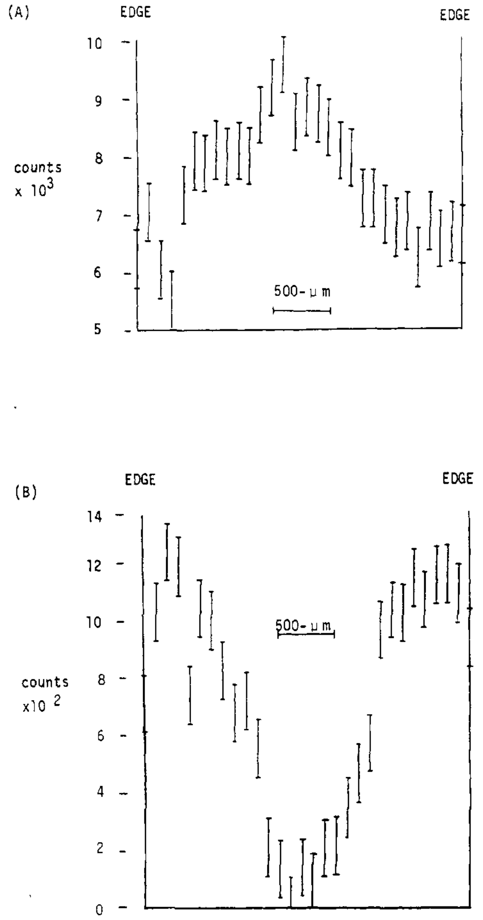

Figure 4. EDS analyses for (A) chlorine and (B) sulfur across a sectional sample of polymer **7**. Both plots represent traverses along one axis of a single polymer bead.

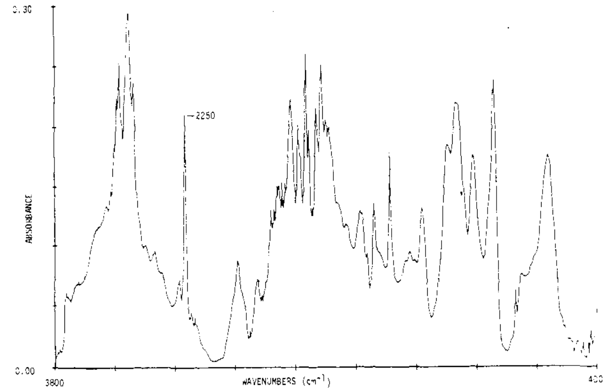

Figure 5. DRIFT spectrum of cyanomethylated polystyrene **8**.

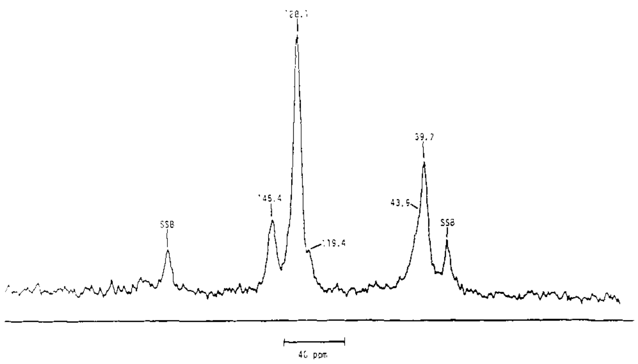

Figure 6. ^{13}C CP/MAS NMR spectrum of cyanomethylated polystyrene **8**: 3900 scans; 10-Hz line broadening.

constant across the bead. After reaction, the chlorine content is low at the edges, but high in the middle. These results thus confirm the DRIFT spectroscopic data, showing that the chloromethyl groups only undergo extensive reaction at the edges of the bead. Although the EDS study was unable to monitor oxygen or nitrogen content across the polymer bead, which would have allowed us to correlate substitution/oxidation phenomena with matrix penetration, we were able to monitor sulfur content in sample **7**, the product of reaction with DMSO/NaCN. Clearly the sulfur detected results from entrapped solvent, which is retained even after drying in vacuum. The plot of sulfur content as a function of penetration is shown in Figure 4, which indicates how effectively the polar DMSO solvent penetrates the polymer matrix. It is immediately apparent that penetration of the solvent is accompanied by a decrease in chlorine content and hence that cyanomethylation and/or oxidation phenomena are limited by the ability of the polar DMSO solvent to transport the ionic reactant through the nonpolar polymer matrix.

In order to prepare cyanomethylated polystyrene free of any oxidized functionality[25] it is necessary to use a nonoxidizing solvent. We have found that reaction of **1** with NaCN in *N,N*-dimethylformamide (DMF) yields a product, **8**, whose DRIFT spectrum, Figure 5, shows the complete disappearance of chloromethyl groups, the absence of any carbonyl-containing functionality, and a new band at 2250 cm^{-1} due to cyanomethyl groups. The solid-state ^{13}C NMR spectrum, Figure 6, shows resonances due to both aliphatic (43.9, 39.7 ppm) and aromatic (145.4, 128.1 ppm) carbon atoms and a weak resonance at 119.4 ppm which is assigned to the cyano carbons. This assignment was confirmed by repeating the solid-state NMR experiment with a cross-polarization sequence in which a short delay was inserted between the cross-polarization step and the free induction decay acquisition during which the decoupling field was turned off. The overall effect of this pulse sequence is to suppress resonances which are due to protonated carbon atoms and to enhance resonances which are due to nonprotonated carbon atoms.[11] The

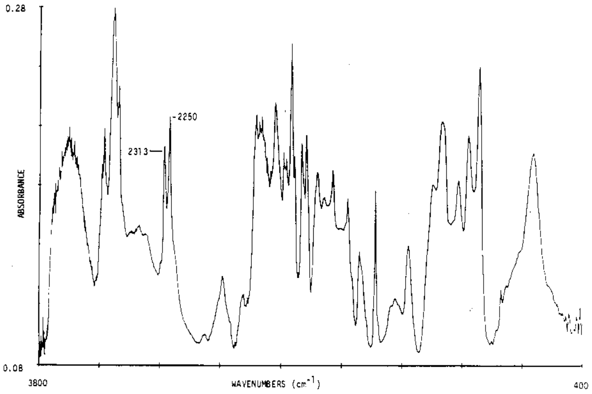

Figure 7. DRIFT spectrum of polymer **3** after reaction with palladium(II) chloride in refluxing nitromethane.

resulting spectrum showed large enhancements of the peaks assigned to the quaternary aromatic carbon atoms and the cyano carbon atoms.

It is reported[25] that cyanomethylated styrene–divinylbenzene copolymer and other polymers bearing cyanide groups separated from the polymer backbone by at least one methylene group react with palladium(II) chloride to form immobilized complexes of the type $[PdCl_2(nitrile)_2]$. The technique used in synthesis was to pass solutions of palladium(II) chloride down a column packed with resin and to elute excess $PdCl_2$ by washing. The presence of palladium in the product was confirmed by elemental analysis. We have used this method[25] to treat the cyanomethylated polystyrene **3** with palladium(II) chloride. The DRIFT spectrum of the product, however, shows no positive shift in the ν(CN) band, which would be expected upon complexation (vide infra). Indeed, the pale brown color of the product that we obtained suggests that palladium(II) chloride is simply physically entrapped in the resin. Accordingly, results relating to the hydrolysis of olefins promoted by such samples[25] may refer solely to the activity of entrapped palladium(II) chloride and not to immobilized nitrile complexes.

Immobilized nitrile complexes may be prepared by treatment of the cyanomethylated polystyrene **3** with palladium(II) chloride in refluxing nitromethane. In such a reaction system, the polymeric halide bridged structure of palladium(II) chloride is broken down by the weakly coordinating solvent to form nonisolable solvated complexes of the type $[PdCl_2(O_2NCH_3)_2]$.[27] Displacement of the weakly bound nitromethane ligands by the immobilized nitrile groups leads to formation of the polymer-supported complex. The DRIFT spectrum of the product, Figure 7, shows ν(CN) bands due to unreacted cyanomethyl groups at 2250 cm^{-1} and due to complexed cyanomethyl groups at 2313 cm^{-1}. For comparison,[25] the ν(CN) mode of $[PdCl_2(NCC_6H_5)_2]$ occurs at 2316 cm^{-1}. The spectrum shown in Figure 7 also indicates that water is present in the sample, which may imply the presence of species such as $[PdCl_2(H_2O)(nitrile)]$ which could form in instances where the spatial requirements of the polymer matrix prohibit coordination of two nitrile groups to a single metal center.

Further studies with these characterized palladium–nitrile systems will focus on reactivity with small organic molecules, such as olefins, and will attempt to exploit the modifications in reactivity as a function of matrix penetration that we have observed as a means to control selectivity in catalytic processes.

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Registry No. NaCN, 143-33-9; $SOCl_2$, 7719-09-7; $PdCl_2$, 7647-10-1; $C_6H_5CH_2Cl$, 100-44-7; (styrene)(divinylbenzene)-((chloromethyl)styrene) (copolymer), 55844-94-5; *p*-rosaniline hydrochloride, 569-61-9.

References and Notes

(1) Blossey, E. C.; Neckers, D. C. *Solid Phase Synthesis*; Dowden Hutchinson and Ross, Inc.: Pennsylvania, 1975; Vol. 2.
(2) Grushka, E. *Bonded Stationary Phases in Chromatography*; Ann Arbor Science: Ann Arbor, MI, 1974.
(3) Hartley, F. R.; Vezey, P. N. *Adv. Organomet. Chem.* **1977**, *15*, 189.
(4) Mathur, N. K.; Narang, C. K.; Williams, R. E. *Polymers as Aids in Organic Chemistry*; Academic: New York, 1980.
(5) Bemi, L.; Clark, H. C.; Davies, J. A.; Drexler, D.; Fyfe, C. A.; Wasylishen, R. E. *J. Organomet. Chem.* **1982**, *224*, C5.
(6) Bemi, L.; Clark, H. C.; Davies, J. A.; Fyfe, C. A.; Wasylishen, R. E. *J. Am. Chem. Soc.* **1982**, *104*, 438.
(7) Fyfe, C. A.; Bemi, L.; Childs, R.; Clark, H. C.; Curtin, D.; Davies, J. A.; Drexler, D.; Dudley, R. L.; Gobbi, G. C.; Hartman, J. S.; Hayes, P. J.; Klinowski, J.; Lenkinski, R. E.; Lock, C. J. L.; Paul, I. C.; Rudin, A.; Tchir, W.; Thomas, J. M.; Wasylishen, R. E. *Philos. Trans. R. Soc. London, A* **1982**, *No. 305*, 591.
(8) Clark, H. C.; Davies, J. A.; Fyfe, C. A.; Hayes, P. J.; Wasylishen, R. E. *Organometallics* **1983**, *2*, 177.
(9) Fyfe, C. A.; Clark, H. C.; Davies, J. A.; Hayes, P. J.; Wasylishen, R. E. *J. Am. Chem. Soc.* **1983**, *105*, 6577.
(10) Fyfe, C. A.; Bemi, L.; Clark, H. C.; Davies, J. A.; Gobbi, G. C.; Hartman, J. S.; Hayes, P. J.; Wasylishen, R. E. In *Inorganic Chemistry: Toward the 21st Century*; Chisholm, M. H., Ed.; American Chemical Society: Washington, DC, 1983; p 405.
(11) Fyfe, C. A. *Solid State NMR for Chemists*; C.F.C. Press: Guelph, Ontario, Canada, 1983.
(12) Pines, A.; Gibby, M. G.; Waugh, J. S. *J. Chem. Phys.* **1972**, *56*, 1776; **1973**, *59*, 569.
(13) Andrew, E. R. *Prog. Nucl. Magn. Reson. Spectrosc.* **1971**, *8*, 1.
(14) Davies, J. A.; Sood, A. *Am. Lab.* **1984**, 122.
(15) Davies, J. A.; Sood, A. *Makromol. Chem.* **1985**, *186*, 1631.
(16) Grubbs, R. H.; Su, S. C. H. *J. Organomet. Chem.* **1976**, *122*, 151.
(17) Grubbs, R. H.; Sweet, E. M. *Macromolecules* **1975**, *8*, 241.
(18) Tsuji, J. *Organic Synthesis with Palladium Compounds*; Springer-Verlag: New York, 1980.
(19) Maitlis, P. M. *Acc. Chem. Res.* **1976**, *9*, 93.
(20) Mukaiyama, T.; Ohshima, M.; Nakatsuka, T. *Chem. Lett.* **1983**, 1207.
(21) Akermark, B.; Backvall, J. E.; Lovenborg, A.; Zetterberg, K. *J. Organomet. Chem.* **1979**, *166*, C3.
(22) Afza, N.; Malik, A.; Voelter, W. *J. Chem. Soc., Perkin Trans. 1* **1983**, 1349.
(23) Darling, G. D.; Frechet, J. M. J. *J. Org. Chem.* **1986**, *51*, 2270.
(24) Pepper, K. W.; Paisley, H. M.; Young, M. A. *J. Chem. Soc.* **1953**, 4097.
(25) Kraus, M.; Tomanova, D. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 1785.
(26) Sood, A. Ph.D. Thesis, University of Toledo, 1985.
(27) Davies, J. A.; Hartley, F. R. *Chem. Rev.* **1981**, *81*, 79.