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Novel materials from bis(arene)metal-containing polyacrylonitrile†

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Novel bis(arene)metal-containing polyacrylonitrile materials have been prepared by the polycyanoethylation reaction between acrylonitrile and $(arene)_2M$ ($M = Cr$ or V; arene = PhH, $C_6H_4Et_2$ or mesitylene) in the absence of solvent. The resulting star-shaped molecules consist of a central $(arene)_2M$ species with up to four polyacrylonitrile arms covalently bonded to the arene ligands. The materials are readily soluble and films can be cast from solutions in acetonitrile. The IR and solid state ^{13}C NMR spectra (or EPR spectrum for the oxidized chromium-containing polymer) are consistent with the presence of a metal–arene bond and confirm the persistence of the sandwich structure. The properties of the thermolysed materials are consistent with the formation of conjugated naphthyridine-type structures. The value of $|n_2|$ determined by the degenerate four-wave mixing technique at 1064 nm with a 6 ns pulse duration for a solution in conc. H_2SO_4 ($1\,g\,l^{-1}$) of the chromium-containing polymer pyrolysed at 350 °C was found to be $0.8 \times 10^{-13}\,cm^2\,W^{-1}$ corresponding to $|\mathrm{Re}\chi^{(3)}| = 0.4 \times 10^{-11}$ esu. Copyright © 2001 John Wiley & Sons, Ltd.

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There is current interest in soluble polymers containing transition metals because of the requirements for advanced materials in molecular electronics, electro- or magneto-optics and catalytical processes. We expect that polymers containing CN groups and having transition metal sandwich complexes in their macrochains should be promising precursors of organometallic metal-containing nanomaterials with interesting magnetic, optical and perhaps magneto-optical properties following chemical, photochemical or thermal treatment. Miller and co-workers have shown that such materials can be formed by the reaction between bis-benzenevanadium and tetracyanoethylene, which gives rise to a high-temperature ferromagnet.[1,2] Similarly, high temperature ferro- and ferri-magnetic behaviour has been observed for cyanometallate (Prussian blue type) compounds, such as mixed valence chromium cyanides, with excellent photochromic properties.[3] The present report focuses on the synthesis and the characterization of new polymer materials based on polyacrylonitrile incorporating bis(arene)chromium[4] or bis(arene)vanadium compounds chemically bonded into the macrochains.

Novel bis(arene)chromium-containing polyacrylonitrile materials have been prepared by the reaction between acrylonitrile and the corresponding bis(arene)chromium complex (or mixture) in the absence of solvent under argon.[4] A cyanoethylation reaction mechanism (Scheme 1) was proposed by Domrachev and Razuvaev to account for

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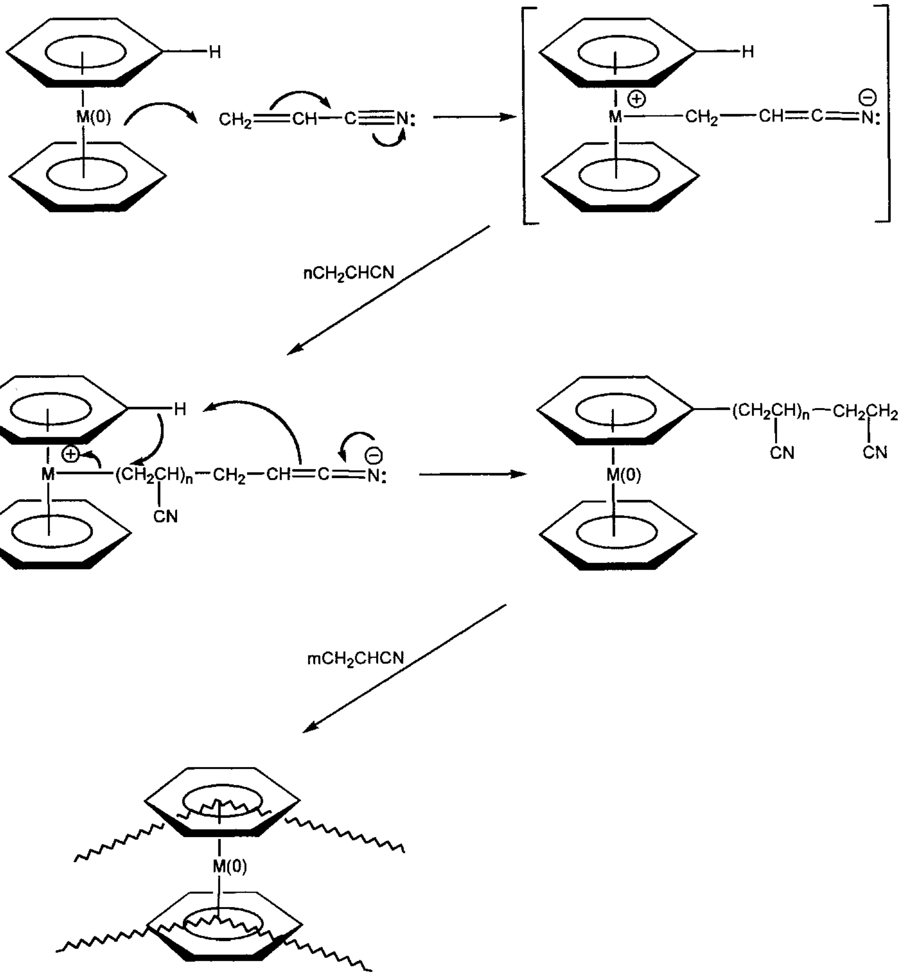

Scheme 1 Polycyanoethylation mechanism.

the bonding of the metal complex with polyacrylonitrile.[5] Acrylonitrile coordinative polymerization takes place at $(arene)_2M^0$, the chain termination step being transfer of an aromatic proton resulting in formation of a bond between the polyacrylonitrile chain and the arene ligand of the metal complex.

This reaction has now been extended to the polycyanoethylation of $(arene)_2M$, where M = Cr or V, and arene = PhH, $C_6H_4Et_2$ or mesitylene. The preparation of the Cr-containing polyacrylonitrile has been described previously.[4] The vanadium-containing material was synthesized in a similar fashion. Redistilled acrylonitrile and bis (benzene)vanadium were mixed under argon in the absence of solvent. The reaction mixture was cooled and stirred at room temperature for *ca* 20 min until the reaction product had hardened, giving the brown–black product in essentially quantitative yield. The resulting star-shaped molecules consist of a central $(arene)_2M$ species with up to four polyacrylonitrile arms covalently bonded to the arene ligands, all the materials being soluble in acetonitrile, DMF or DMSO. The ligand compositions of the starting $(Et_nC_6H_{6\text{-}n})_2M$ mixtures were determined by oxidizing the metal complexes with H_2O_2 followed by gas-liquid chromatography (GLC) analysis of the mixture of arenes thus afforded (Table 1). The ^1H NMR spectra of the products show the expected signals for protons of polyacrylonitrile and alkyl-substituted benzenes. In accordance with the mechanism

Table 1 Arene ligand compositions of $(Et_nC_6H_{6-n})_2M$

	Arene ligand (mol%)[a]			
M	C_6H_6	EtC_6H_5	$Et_2C_6H_4$	$Et_3C_6H_3$
Cr	$\ll 1$	35	35	30
V	$\ll 1$	4.5	61.4	34.1

[a] Arene ligand composition determined by GLC analysis following oxidation.

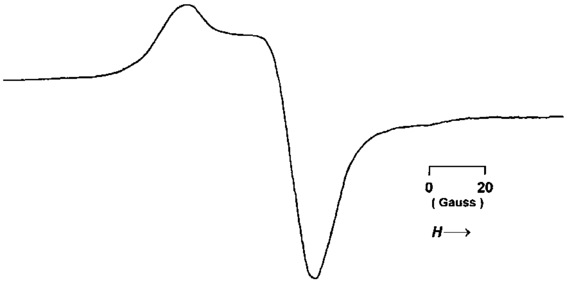

Figure 2 ESR spectrum of $(Et_nC_6H_{6-n})_2CrPAN$.

proposed by Domrachev and Razuvaev, the ratio of methyl to aromatic protons in the bis(arene)metal mixtures is found to increase during the polycyanoethylation reaction.

Consistent with some coordination of the CN groups with the metal atom, the IR spectra of the polymers show additional CN group absorption bands, apart from the one at 2220 cm^{-1}, typical for polyacrylonitrile (Fig. 1). The bands at 425 cm^{-1} (for the chromium-containing polymer) and 520 cm^{-1} (for the vanadium-containing polymer) are characteristic of a metal–arene bond and confirm the persistence of the sandwich structure. This is supported by the solid state ^{13}C NMR spectrum for the vanadium polymer, which shows a signal at 187 ppm in the region for bis(arene)complexes. A strong signal appears at 31 ppm (CH_2) and a less intense resonance at 123 ppm (CN). The relatively weak signal at 56 ppm most probably corresponds to the methylene groups of acrylonitrile units covalently bonded with arene ligands following the cyanoethylation reaction. The minor signal to high field (at *ca* 10 pm) results from CH_3 side groups in the polymer.

Pristine chromium-containing polyacrylonitrile is diamagnetic. However, the material becomes paramagnetic on exposure to air as a result of $(arene)_2Cr^0$ being oxidized to $Cr[arene_2]^+OH^-$. The EPR spectra of the oxidized chromium polymers (Fig. 2) show the typical anisotropic signal of paramagnetic chromium(I), with an additional and broader overlapping signal at the same field value arising from the majority of paramagnetic centres presumably in the form of clusters of chromium(I) species undergoing magnetic exchange interactions.

Low-temperature isothermal (4.2 K) magnetochemical investigations of the product of thermolysis at 160 °C chromium-containing polymer revealed in some cases remanent magnetization on returning the field to zero, indicating the presence of magnetic hysteresis.[4] The room-temperature magnetization plots for the product of thermolysis at 160 °C also showed some ferromagnetic component, with higher thermolysis temperatures resulting in a decreased ferromagnetic contribution. However, it should be noted that the formation of a ferromagnetic phase during the thermolysis process is not readily reproducible and it may be that some more controlled process (such as redox reactions leading to the magnetically ordered mixed-valence metal species) are required.

Thermolysis at temperatures above 200 °C is accompanied by the evolution of traces of cyanogen (gradually polymerizing to dark-brown paracyanogen) as well as ammonia. This process is accompanied by fundamental changes in the IR and ^{13}C NMR spectra of the solid residue. The appearance of a strong IR absorbance band at 1580 cm^{-1} indicates formation of conjugated ketoimine fragments and that at 800 cm^{-1} is consistent with the presence of a conjugated carbon backbone. The ^{13}C NMR spectra lend support to the presence of ketoimine fragments, the broad resonance at 152–156 ppm being assigned to the unsubstituted pyrrole sp^2 carbon atoms, and the 126–128 ppm resonance to substituted pyrrole sp^2 carbon atoms.[6]

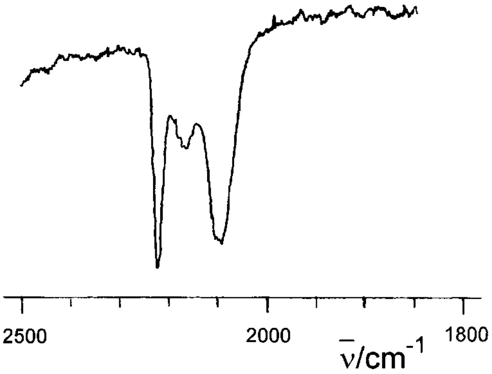

Figure 1 IR CN bands for $(Et_nC_6H_{6-n})_2MPAN$.

These fragments are also present in the conjugated naphthyridine-type polymers formed on thermolysis of polyacrylonitrile itself.[7–9] However, unlike the thermolysis products of pure acrylonitrile, the polymeric solid residues obtained by thermolysis at 320–350 °C of metal-containing acrylonitrile are soluble in sulfuric acid giving intensely red–brown solutions. The properties of the materials are consistent with the formation of conjugated naphthyridine-type structures.[4] Elemental analysis gives the empirical formulae $CrC_{12.6}H_{12.4}N_{2.9}O_{1.4}$ (for the product from the oxidized form of the precursor) and $VC_{16.2}H_{16.9}N_{3.6}$. All the thermolysis products are X-ray amorphous.

The presence of extensive electron conjugation is confirmed by the extraordinarily high nonlinear-optical properties of CrPAN thermolysed at 350 °C as measured by the degenerate four-wave mixing (DFWM) and Z-scan techniques. DFWM experiments were made with a Q-switched single-mode Nd:YAG laser-oscillator at 1064 nm and both co- and cross-polarized pumps, the pulse duration being 6 ns. The pulse energy of each pumping wave was up to 10 mJ. It can be shown that for both experimental arrangements thermal grating effects may be neglected. We made two series of measurements. In the first the probe wave was orthogonally polarized to both pumping waves. So the grating, which was written by probe beam and pumps, could not be thermal. In the second case the probe wave was co-polarized with the co-running pump and orthogonally polarized to the near backward pump. The interference field of the near running waves wrote the grating with period $\Lambda \approx 200\ \mu m$ with a delay time for isobar formation of about $\tau_s = 2\pi/\Lambda c_s = 34\ ns \gg 6\ ns$ (the speed of sound in the solvent is *ca* $c_s = 10^5\ cm\ sec^{-1}$).[10] Thus, in the case of the co-polarized probe wave and the co-running pump the fast grating (due to Kerr-like nonlinearities) is estimated to predominate over the thermally induced grating (the absorbance of the solution was found to be negligible ($<0.05\ cm^{-1}$)) if the nonlinear susceptibility $\chi^{(3)}$ is greater than 2.4×10^{-13} esu (as is so for the present polymer).[10] In addition to the DFWM experiment, Z-scan measurements at 1064 nm with a 6 ns pulse were also made. For the Z-scan experiment we used a lens with a focal distance of 60 cm. The beam diameter in the focal plane was about 200 μm, so the thermal contribution was negligible. The values of $|n_2|$ for the solutions were measured using pure chloroform as reference ($|n_2| = 3 \times 10^{-15}\ cm^2\ W^{-1}$).[11]

By comparison of the results for the two series of DFWM experiments and the Z-scan measurements the electronic contribution, nuclear (orientational) contribution and contribution due to two-photon absorption to the fast nonlinearity can be separated.[10,12] The electronic contribution was found to be greater than the nuclear one by a factor of seven. The value of the electronic $|n_2|$ determined by DFWM measurements for CrPAN for a very dilute solution in conc. H_2SO_4 ($1\ g\ l^{-1}$) was found to be $0.8 \times 10^{-13}\ cm^2\ W^{-1}$ (corresponding to $|Re\chi^{(3)}| = 0.4 \times 10^{-11}$ esu). The Z-scan measurements showed a negative value for the electronic contribution to n_2 that was only 10% less than that measured by the DFWM technique. It should be noted that the Z-scan did not show any two-photon absorption for beam intensities up to $0.3\ GW\ cm^{-2}$.

Based on number density considerations (~ 0.1 wt.% polymer in the solution), the value of n_2 might be expected to be greater by three orders of magnitude for the neat polymer suggesting $\chi^{(3)}$ activity exceeding even that for poly(1,4-vinylene-phenylene) and its derivatives.[13] The metal-containing polymers form transparent films on casting from acetonitrile solution and it should, therefore, be possible to obtain films of the pyrolysed materials with extremely high third-order nonlinear optical properties.

In conclusion, the novel metal-containing polyacrylonitrile materials described here exhibit not only interesting magnetic but also promising optical properties, in particular the outstanding nonlinear refractive index.

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