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NOTES

Novel Aromatic Polyamides Containing the 1,4-Phenylenetricarbonylchromium Structure

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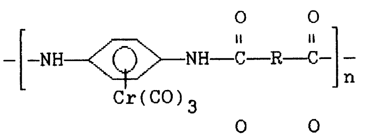
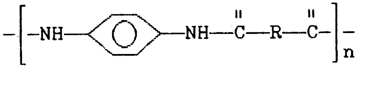
Aromatic polyamides are attracting much interest because of their excellent physical properties and commercial importance.[1-3] Poly(*p*-phenylene terephthalamide) and poly(*m*-phenylene terephthalamide) are two representative examples presently available on the market. The former is known to form a lyotropic liquid crystal in strong acids such as sulfuric acid, from which high strength and high modulus fibers can be spun. The use of strong acid, however, is a big drawback for such a fiber forming process.

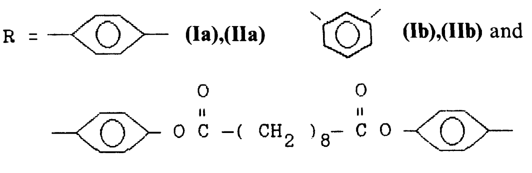
We have tried to synthesize organic soluble aromatic polyamides (**Ia**, **Ib**, and **Ic**) by complexing the *p*-phenylenediamine ring with tricarbonylchromium and preliminary results are discussed in this article. We believe that this is the first report describing the preparation of chromium complexed aromatic polyamides. For comparison, the corresponding uncomplexed polymers **IIa**, **IIb**, and **IIc** were also prepared:



(I)



(II)



(Ia),(IIa) **(Ib),(IIb)** and **(Ic),(IIc)**

EXPERIMENTAL

Synthesis of Polymers I

Since all the polymers **I** were prepared in the same manner, only one representative procedure is given. The two solutions of terephthaloyl chloride (0.426 g; 2.0 mmol) and *p*-phenylenediaminetricarbonylchromium (0.488 g; 2.0 mmol)[4] respectively dissolved in 10 ml of *N*,*N*-dimethylacetamide (DMA) were cooled in an ice–acetone bath. The terephthaloyl chloride solution was rapidly added to the *p*-phenylenediaminetricarbonylchromium solution with vigorous stirring and nitrogen gas bubbling. After the ice–acetone bath was removed, low vacuum (~50 mmHg) was applied to the system with continuous nitrogen gas bubbling, and the reaction was allowed to proceed for 30 minutes at room temperature. A transparent, very viscous solution was obtained. The reaction mixture was poured into ethanol. The precipitate was thoroughly washed with ethanol and then dried at 40°C in a vaccum oven for about 24 hours. The yield was 0.715 g (93%).

The dicarboxylic acid used for the synthesis of **Ic** was prepared from *p*-hydroxybenzoic acid and 1,10-decanedioic acid following a literature method.[5]

Synthesis of Polymers II

Polymers **II** were prepared by a similar procedure to that described above for the synthesis of polymers **I**. The only difference was that *p*-phenylenediamine (0.216 g; 2.0 mmol) was dissolved in 15 ml of 2 : 1 (v/v) DMA–pyridine mixture. The yield for **IIa** was 0.477 g (96%).

All of the polymers of series **II** either precipitated out or formed swollen gels when the reaction was over.

Characterization of Polymers

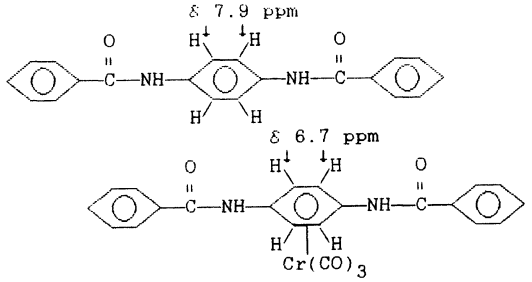
The structures of the polymers were confirmed by IR and NMR spectra. Differential scanning thermograms were obtained under a nitrogen atmosphere at a heating rate of 10°C min^{-1}. Solution viscosities were measured at 30°C using concentrated sulfuric acid or DMA containing 5 wt% LiCl as the solvent. The concentration of 0.2 g dl^{-1} was employed for viscosity measurement.

Synthesis of Model Compounds

The two model compounds, 1,4-phenylenedibenzamide, and 1,4-phenylenetricarbonylchromiumdibenzamide were synthesized and their H NMR spectra were used for the H NMR analysis of polymers. Since 1,4-phenylenetricarbonylchromiumdibenzamide has not yet been reported, its preparation method is given: Benzoyl chloride (0.282 g; 2.0 mmol) was dissolved in 5 ml of cold DMA. To this solution was dropwise added a solution of 1,4-phenylenediaminetricarbonylchromium (0.244 g; 1.0 mmol) dissolved in 10 ml of cold DMA. The solution was vigorously stirred under a reduced pressure (~50 mmHg) for one hour maintaining the temperature from 10 to 15°C. The mixture was poured into ethanol. The precipitate was thoroughly washed with ethanol and dried at 40°C in a vacuum oven. The product yield was 0.145 g (32%). The structure was confirmed by its IR and NMR spectra.

RESULTS AND DISCUSSION

All three complexed polyamides exhibited symmetric and asymmetric Cr–C–O stretching vibration absorption at 1900 and 1980 cm^{-1}, respectively, in their IR spectra. They also showed other expected absorptions such as amide carbonyl stretching absorption at 1680 cm^{-1} and amide N–H stretching absorption at 3380 cm^{-1}.



The H NMR spectra of the two model compounds provided a method of quantitatively analyzing the compositions of complexed polymers **I**. Knowing the relatively unstable nature of tricarbonylchromium complexes in solution,[6] we assumed that the complexed polymers may have undergone a certain degree of decomposition leading to copolymer structures consisting of both complexed and uncomplexed 1,4-phenylene moieties. The resonance peak of the protons in the 1,4-phenylene ring of 1,4-phenylenedibenzamide appeared at δ 7.9 ppm, while those in the complexed compound appeared at δ 6.7 ppm. The significant shift of the 1,4-phenylene ring protons to upfield by complexation appears to indicate that complexation reduces the aromaticity of the ring.[5] We observed a similar shift from δ 6.6 to 5.3 ppm for the ring protons of *p*-phenylenediamine. The resonance peak of the protons on the complexed or uncomplexed *p*-phenylenediamine moieties in the polymers appeared at the same positions as those of model compounds. The NMR spectra of polymers **I** were obtained directly using the reaction mixtures after the reactions were stopped. By comparing the resonance intensities at the two positions of δ 7.9 ppm and δ 6.7 ppm, we concluded all three complexed polymers to contain about, or more than 95% complexed 1,4-phenylenediamine moieties and those about or less than 5% uncomplexed. Elemental analysis of the complexed polymers provided erroneous results with very poor reproducibility. We believe that this is due to the relatively unstable nature of the complexes and that chromium forms various compounds during combustion of the samples.

The polymer yields and solution viscosities are tabulated in Table I. The solution viscosity numbers of polymers **I** are consistently higher than those of series II. We believe that this is due to the better solubility of polymers **I** which formed transparent, viscous solutions when polymerized in the manner described in Experimental, while the polymers **II** precipitated out during polymerization. The polymers **I**, however, became hard to dissolve in DMA once separated from the reaction mixture and dried. When the complex polymers dissolved in sulfuric acid were recovered by precipitation in methanol, they did not contain any $Cr(CO)_3$ structure as proved by IR spectra. This indicates that the complexes are destroyed in sulfuric acid. The complexed polymers also easily lost tricarbonylchromium by treating them with I_2 solution in DMA or ethanol at room temperature.[6] Decomposition of complexes could be easily confirmed by IR spectra. DSC thermograms (Figure 1) of polymers **I** revealed very broad endotherms starting at about 150°C and ending at about 260°C (**Ia**) or 300°C (**Ib** and **Ic**). These endotherms suggest gradual thermal decomposition of complexes. The second heating of the decomposed polymers did not show any endothermic reactions. Uncomplexed polymers **II** did not show any transitions or changes in this temperature range. Although data not included in this report, thermogravimetry also gave results consistent with DSC observations on the thermal decomposition of the polymers.

Table I. Yield and solution viscosities of polymers

Polymer	Yield wt%	η_{inh} $dl\,g^{-1}$
Ia	93	1.53[a]
Ib	82	0.72[a]
Ic	95	1.04[b]
IIa	96	0.43[a]
IIb	71	0.43[a]
IIc	96	0.62[b]

[a] Measured at 30°C on a $0.2\,g\,dl^{-1}$ solution in concentrated H_2SO_4.

[b] Measured at 30°C on a $0.2\,g\,dl^{-1}$ solution in 5 wt% LiCl–DMA.

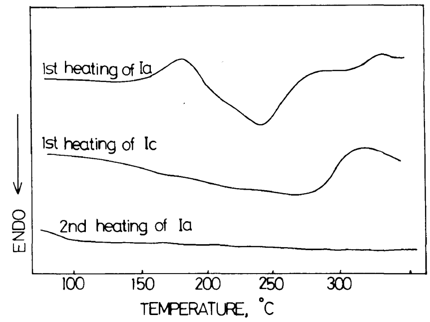


Figure 1. DSC thermograms of polymers **Ia** and **Ic**. Heating rate, $10^\circ C\,min^{-1}$.

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