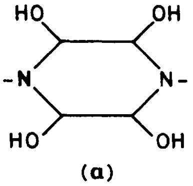
A New Dopable Soluble Electrically Conducting Polyazine Polymer

Yong Cao* and Suzhen Li
Institute of Chemistry, Academia Sinica, Beijing, China

The synthesis and initial characterization of a new soluble and dopable electrically conducting polyazine polymer [$(CH{=}N{-}N{=}CH)_n$] are reported.

There has been much recent interest in electrically conducting polymers, spurred by the discovery of dopable films of polyacetylene.[1] The complete insolubility and poor tractability of conventional conducting polymers have so far prevented a good understanding of their electrical and electronic properties and their technical applications. Much recent research has been directed towards the synthesis of soluble conducting polymers.[2—4] We now report the synthesis and preliminary characterization of a new soluble and dopable conducting polymer based on conjugated carbon–nitrogen chains.

The polyazine was prepared by condensation of trimeric glyoxal dihydrate and hydrazine in dimethylformamide (DMF) as solvent. Anhydrous hydrazine was slowly added to a solution of trimeric glyoxal dihydrate at 0 °C. Polycondensation was completed by raising the temperature to 80—100 °C. Filtration and evaporation afforded two polyazine fractions: DMF-soluble and DMF-insoluble. The yield of the soluble fraction was 20—80% of the total, depending on the temperature and duration of heating. The soluble fraction dissolved readily in dimethyl sulphoxide and slightly in acetone and chloroform. The DMF-insoluble fraction did not



(a)

dissolve in common organic solvents, but could be dissolved in concentrated acids such as H_2SO_4, $HClO_4$, and $HOSO_2Cl$.

The i.r. spectrum showed peaks at 1632 and 1590 cm^{-1} originating from conjugated -CH=N-N=CH- chains, and a peak at 1310 cm^{-1} derived from -CH= out-of-plane deformation. A peak at 3300 cm^{-1} attributable to OH vibration and a weak peak at 2936 cm^{-1} originating from C–H vibration presumably indicated the existence of the fragment (**a**) as a defect in the polymer chain. The extent of this defect could be estimated as less 5 mol% per CH=N-N=CH unit from the oxygen content derived by elemental analysis. The soluble and insoluble polyazine fractions exhibited similar i.r. features except that peaks at 1632 and 1590 cm^{-1} were shifted to lower frequency (1611 and 1549 cm^{-1}) in the insoluble fraction. This indicates that the latter is more extensively conjugated. This is supported by the Raman shifts of the symmetric C=N stretching absorptions measured with excitation at 4880 Å. These bands were found at 1475 cm^{-1} for the soluble fraction and 1463 cm^{-1} for the insoluble one.

The soluble polyazine is reddish brown, and its u.v.–visible spectrum shows a maximum absorption band at 420 nm with a long tail extending to *ca.* 600 nm, indicating that the π-electrons are extensively delocalised along the polymer chain. *X*-Ray diffraction studies indicated that both soluble and insoluble polyazines are totally amorphous, in contrast with polyacetylene, which possesses some degree of crystallinity.[5] Differential scanning calorimetry (DSC) showed sharp endothermic peaks at 70.0 °C for the soluble fraction and 73.6 °C for the insoluble one. The nature of this phase transition is unclear at present. The polyazine obtained was stable in air. In fact, the neutral polyazine showed no weight gain after exposure to dry air at room temperature for several months.

The electrical conductivity of a cast film of the soluble polyazine and of a compacted pellet of the isoluble one is *ca.* 10^{-11} S cm^{-1} (*cf. ca.* 10^{-9} S cm^{-1} for *cis*-polyacetylene). The polyazine has a high affinity for iodine. The largest proportion of iodine vapour absorbed by the soluble polymer was *ca.* 220 wt.% (*ca.* one mole per CH=N–N=CH unit) at room temperature. The highest measured electrical conductivity of iodine-doped polyazine at room temperature was 1×10^{-2} S cm^{-1}. This result is consistent with the presence of extensively delocalised π-electrons along the polyazine chain.

In summary, we have obtained the first example of a dopable polyazine which is stable in air and soluble in common organic solvents.

We thank the Chinese Science Fund for partial support of this work.

Received, 8th February 1988; Com. 8/00450A

References

1 H. Shirakawa, E. J. Louis, A. G. MacDiarmid, C. K. Chiang, and A. J. Heeger, *J. Chem. Soc., Chem. Commun.*, 1977, 578.
2 M. Aldissi, *Synth. Met.*, 1980, **13**, 87.
3 M. Sato, S. Taanaka, and K. Kaeriyama, *J. Chem. Soc., Chem. Commun.*, 1985, 713.
4 S. Li, Y. Cao, and Z. Xue, *Synth. Met.*, 1987, **19**, 1072.
5 T. Ito, H. Shirakawa, and S. Ikeda, *J. Polym. Sci.*, 1974, **12**, 1.