Chemical Synthesis of Polyphenylene in an Ionic Liquid: the Possibility of Relative Molecular Mass Regulation

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An ionic liquid based on aluminum chloride and butylpyridinium chloride has been used as the solvent for the chemical synthesis of poly(p-phenylene).

A large number of publications have been devoted to the synthesis and investigation of poly(p-phenylene) (PpP) (see, for example, recent reviews[1,2]).

Ionic liquids are convenient electrolytes for electrochemical synthesis.[3] In the present work such a liquid was first used for the oxidative dehydropolycondensation of benzene.

The synthesis of Bu^{n}PyCl and the ionic liquid was performed according to the procedure described in ref.[4] The mole ratio was $AlCl_3 : Bu^nPyCl = 2 : 1$. The $CuCl_2$ concentration in all experiments was constant and equal to the concentration of the saturated solution at room temperature.

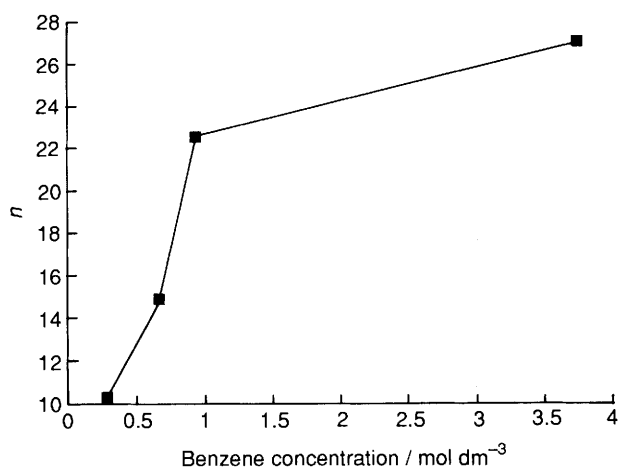A typical procedure for PpP synthesis was as follows. To 2

Fig. 1 Dependence of the degree of polymerisation of PpP ($n = 2I_{807}/I_{690} + 2$) on the concentration of benzene

the M_r of the polymer depends on the benzene concentration (Fig. 1).

$$n = 2I_{807}/I_{690} + 2 \qquad (1)$$

We also found that a two-stage synthesis is more suitable for this system. In the first step, a small quantity of benzene is added, which leads to the formation of stable cation-radicals. In the second step, an excess of benzene is added. Such a method gives PpP with an M_r of up to 38 phenyl nuclei. This is more than twice that obtained using the Kovacic method for PpP synthesis.[1]

These results allow us to suggest a hypothesis that the M_r of PpP (and other polymers that are synthesized by the oxidative dehydropolycondensation method) depends on the rate of formation of a solid state. The solubility of PpP in an ionic liquid is greater than that in the usual solvents. This circumstance, combined with a sufficient amount of the oxidizing agent,[8] gives a positive result.

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ml of an ionic liquid was added 0.1 g of anhydrous $CuCl_2$ and the mixture heated at 60–70 °C for 4–5 min in a water bath to dissolve the oxidizing agent. After cooling to room temperature, the necessary amount of benzene was added and the mixture left covered for a day. Then the reaction mixture was poured into water, filtered and treated with HCl (1 : 1). After that the polymer was washed with water and dried.

It is known from the literature that there are at least three ways of estimating the relative molecular mass (M_r) of PpP from IR spectroscopic data.[5–7] These are all based on the calculation of the ratio between the intensities of the bands characteristic for the protons of the terminal phenyl nuclei (760 and 690 cm^{-1}) and the intensity of the 807 cm^{-1} band for 1,4-disubstituted phenyl rings. For our calculations a formula [see eqn. (1)] from ref. 5 was used, where n is the degree of polymerisation and I is the band intensity. It was shown that

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