polymer communications

Direct synthesis of aromatic polyamides using the imidazole–triphenylphosphite system

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(*Received 24 March 1992*)

The possibility of using imidazole as a catalytic component in the direct synthesis of poly(*p*-phenyleneterephthalamide) and poly(*p*-benzamide) by phosphorylation with triphenylphosphite was investigated. In the presence of imidazole it was possible to perform the whole synthesis in a homogeneous solution, thus avoiding the formation of a precipitate or a swollen gel, as usually described in literature, particularly for poly(*p*-phenyleneterephthalamide). Higher molecular weights were obtained in our systems, as compared to typical values from the direct synthesis method.

(Keywords: synthesis; aromatic polyamides; imidazole)

Introduction

In 1980, Higashi *et al.*[1] reported that, by using triphenylphosphite in *N*-methylpyrrolidone (NMP) containing 4 wt% LiCl, it was possible to obtain poly(*p*-phenyleneterephthalamide) (PPDT) with an inherent viscosity (in concentrated sulphuric acid) of 0.53, which was an improvement of their previous results (inherent viscosity 0.19) obtained in the presence of pyridine[2]. In the same paper[2], the authors pointed out the impossibility of recovering any polymer if imidazole was used instead of pyridine in the synthesis of poly(*p*-benzamide) (PBA). In contrast, our preliminary results show a positive role for imidazole in the synthesis of both PPDT and PBA.

Experimental

Materials. NMP (Aldrich) was distilled over calcium hydride. Imidazole (Aldrich) was distilled at reduced pressure. Triphenylphosphite (Aldrich) was purified by fractional distillation at reduced pressure. *p*-Phenylenediamine (Aldrich) was purified by sublimation in the presence of silica gel. Terephthalic acid (Aldrich) was used without further purification. LiCl and $CaCl_2$ (Aldrich) were dried for 24 h at 300°C.

Polymerizations. A 250 ml three-necked round bottom flask, fitted with a mechanical stirrer and an inlet and outlet for argon, was placed in a thermostatically controlled oil bath. For a typical run, in the reaction vessel were successively added the solvent medium consisting of 50 ml NMP, $CaCl_2$ (3 g) and LiCl (1 g), 0.01 mol (0.681 g) imidazole, 0.01 mol (3.10 g) triphenylphosphite, 0.005 mol (0.831 g) terephthalic acid and 0.005 mol (0.541 g) *p*-phenylenediamine [or 0.01 mol (1.371 g) *p*-aminobenzoic acid]. The reaction mixture was stirred for 2.5 h and then poured into methanol. The precipitated polymer was washed in boiling methanol and dried in a vacuum oven for 18 h at 70°C.

Results and discussion

Preliminary data from our syntheses are reported in *Table 1*. It can be seen that our results are in good agreement with literature values in the case of PPDT synthesized in NMP–LiCl solution both in the presence and in the absence of pyridine. When we performed the same reaction in the presence of imidazole, we obtained an increase in the molecular weight of PPDT (inherent viscosity 0.75). Moreover, we obtained PBA with a relatively high inherent viscosity (1.03) by carrying out its synthesis in the presence of imidazole, as described in Experimental.

These encouraging results persuaded us to evaluate the role of imidazole under the optimum conditions for the synthesis of higher molecular weight PPDT.

It is well known that Krigbaum *et al.*[3] obtained PPDT characterized by an inherent viscosity as high as 6.2 by using a reaction medium consisting of NMP, pyridine and a mixture of LiCl and $CaCl_2$. Our data for the synthesis of PPDT in the presence of imidazole are reported in *Tables 2* and *3*. Krigbaum *et al.*[3,4] reported that the best reaction conditions, when pyridine is used, are a temperature of 115°C and an overall concentration of reactants equal to 0.083 mol l^{-1}. In our experimental conditions the best reaction temperature was found to be 115°C, but we obtained better results when working

Table 1 Inherent viscosities (dl g^{-1}) of PPDT synthesized in various reaction media

NMP + pyridine[a]	NMP[b]	NMP + imidazole[c]
0.22 (0.19)	0.47 (0.53)	0.75

[a] Synthesis performed after ref. 2 (4 wt% LiCl added to the solvent)
[b] Synthesis performed after ref. 1 (4 wt% LiCl added to the solvent)
[c] Synthesis performed after ref. 1 but in the presence of imidazole (equimolar content as referred to the overall concentration of reactants)
Literature data are reported in parentheses
Inherent viscosities were measured at 30°C, using 0.1 dl g^{-1} solutions in 96% sulphuric acid

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0032-3861/92/194197-02

Table 2 Effect of reaction temperature on the direct polycondensation reaction of PPDT[a]

T (°C)	η_{inh} (dl g^{-1})	State
100	1.27	Solution
107	1.44	Solution
115	2.11	Solution
125	1.80	Solution and precipitate

[a] Syntheses performed as described in Experimental

Table 3 Influence of the overall concentration of reactants on the direct polycondensation reaction of PPDT[a]

Concentration (mol l^{-1})	η_{inh} (dl g^{-1})	State
0.083	1.13	Solution
0.100	2.11	Solution
0.125	1.63	Precipitate

[a] Syntheses performed as described in Experimental

at higher reactant concentration, i.e. 0.100 mol l^{-1} (at lower concentrations the polymer inherent viscosity drastically decreases). In our system, we obtained PPDT with a maximum inherent viscosity of 2.11.

It is important to underline that, in contrast to what is reported in the literature for other methods, the presence of imidazole in the reaction medium makes the direct synthesis of PPDT possible in fully homogeneous conditions because of the increased solubility of the polymer. In our opinion, this aspect could have relevant scientific and technological implications, especially if it is possible to increase the molecular weight of the produced polymer. Further studies are in progress.

References

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