

# On the synthesis of poly(*p*-benzamide) block copolymers by the phosphorylation reaction

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The multistep method suggested in the literature for the synthesis of poly(*p*-benzamide) (PBA) block copolymers has been critically re-examined. The reaction products after each step have been isolated and characterized, and the extent of competitive processes evaluated. Under the chosen experimental conditions, almost no PBA copolymer is formed in the presence of terephthalic acid and *p*-aminobenzhydrazide. The increase of the limiting viscosity number has been attributed to coupling reactions between PBA chains by the difunctional reagents used in steps 2 and 3.

(Keywords: block copolymers; poly(*p*-benzamide) copolymers; coupling)

## INTRODUCTION

The synthesis of block copolymers formed by a mesogenic and a flexible component can be considered a new research area of rapidly growing interest. For such materials several possibilities of application in various fields have been envisaged, with special emphasis on the polymer composites area. In this respect, block copolymers based on aromatic polyamides have been produced using various methods<sup>1-3</sup>. Great attention has been paid to the wholly aromatic amide-type copolymers, the synthesis and properties of which have been investigated by, among others, Preston *et al.*<sup>4,5</sup> using the phosphorylation reaction. This procedure, currently known as Yamazaki's method<sup>6,7</sup>, is based on the direct polycondensation of aromatic diacids and diamines, or of aromatic amino acids, in the presence of an aryl phosphite and an organic base<sup>1,3</sup>. At present, typical preparations involve the use of triphenyl or diphenyl phosphite, pyridine, and a reaction medium formed of *N*-methylpyrrolidone with added lithium and/or calcium chloride.

Block copolymers of *inter alia* poly(*p*-benzamide) (PBA) and poly(terephthalamide of *p*-aminobenzhydrazide) (PABH-T) have been prepared and characterized by Preston *et al.*<sup>5</sup> by sequential addition of the reactants, as in the so-called multistep method. Their procedure is based on the preliminary step of PBA synthesis, followed by direct addition of terephthalic acid to the reaction mixture, in order to have all PBA chains carboxy-terminated; *p*-aminobenzhydrazide is added at the final step. As alternative routes, both two-step and two-pot polycondensation reactions have been suggested<sup>5</sup>. In the first method both terephthalic acid and *p*-aminobenzhydrazide are simultaneously added to preformed PBA, whereas in the second procedure carboxy-terminated

PBA and amino-terminated PABH-T are mixed and left to react together. From the literature data<sup>4,5</sup> the multistep method seems to offer higher yields of block copolymer and better control of the copolymerization reaction.

The aim of our work is to investigate the validity and limitations of the multistep method in the synthesis of the above copolymers by careful characterization of the reaction products after each step. The range of reactant concentrations explored is very close to that quoted in the literature<sup>5</sup>.

## EXPERIMENTAL

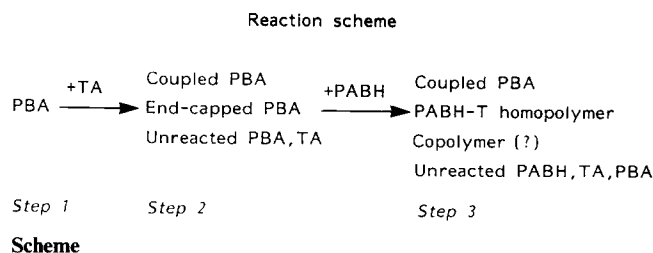
### Materials

*p*-Aminobenzoic acid (PABA) (Riedel, RG), terephthalic acid (TA) (Fluka, Purum) and *p*-aminobenzhydrazide (PABH) (Gallord-Schlesinger, Purum) were used as received. *N*-Methylpyrrolidone (NMP) (Janssen) was vacuum distilled and stored over Riedel type 4A molecular sieves; pyridine (Py) (C. Erba) was dried with NaOH pellets. Dimethylsulphoxide (DMSO) (Janssen) and triphenyl phosphite (TPP) (Janssen) were stored over molecular sieves. Lithium chloride (Riedel-de Haen, RG) was vacuum dried for 24 h at 200°C.

### Multistep procedure

In the first step PBA was synthesized following Yamazaki's method<sup>5-7</sup> (0.4 mol l<sup>-1</sup> of PABA in NMP-Py 3:2 v/v solution containing 4 wt% of LiCl; 1 mol of TPP per mole of PABA; *T* = 100°C; *t* = 2.5 h). In the second step, after further dilution of the reactants with the solvent mixture up to 1.5 times the original volume, *T* was raised to 110°C and TA introduced (from 0.14 to 6.93 mol per equivalent of PBA terminal amino groups, as calculated from  $\bar{M}_n$ ); a small amount of TPP (half of TA moles present) was also added. After 3 h, the third step started, with the introduction of PABH in equimolar amounts

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as referred to initial TA content. The reaction was carried out for an additional 15 h at the same temperature.

Parallel runs to isolate and fully characterize the reaction products after steps 1 and 2 were also performed.

#### Product purification and characterization

Precipitation of the polymer from the reaction mixture was accomplished by methanol addition under vigorous stirring, followed by filtration, cold-washing with methanol and ethanol, reflux washing with methanol for 3 h, and vacuum drying at 60°C for 24 h. After step 3, the products were also treated with DMSO, a solvent of the PABH-T homopolymer, in order to isolate unreacted PBA and the block copolymer.

$\bar{M}_n$  values of PBA were evaluated by carboxyl end-group titration as suggested, with minor modifications, in the literature<sup>8,9</sup>, using dimethylacetamide (DMAc)+3% LiCl as solvent and calomel (K901 Radiometer)/platinum electrodes. The potentiometric titration was performed with 0.1 N alcoholic NaOH (methanol:benzyl alcohol, 1:9 v/v).

Limiting viscosity numbers for PBA after steps 1 and 2 ( $[\eta]_1$  and  $[\eta]_2$ ) were evaluated both in 96% H<sub>2</sub>SO<sub>4</sub> and DMAc+3% LiCl at 25°C. Only the latter solvent was used for the viscosity measurements of the reaction products after step 3 ( $[\eta]_3$ ), in order to avoid degradation of PABH-T sequences supposedly present in the copolymer by sulphuric acid<sup>10</sup>. The double extrapolations of  $\eta_{sp}/c$  and  $(\ln \eta_{rel}/c)$  to zero concentration were linear for all samples in the adopted concentration range and yielded coincident intercepts.

A good linear correlation between the logarithms of PBA limiting viscosity values in H<sub>2</sub>SO<sub>4</sub> and DMAc+3% LiCl was found, without any evidence of aggregation phenomena in the latter solvent. It is now generally accepted<sup>11</sup> that such aggregation of PBA chains becomes relevant only at moderate concentration.

## RESULTS AND DISCUSSION

End-group titration of PBA, prepared in step 1 as described in the 'Experimental' section, gives a  $\bar{M}_n$  value of ~7500. The limiting viscosity number in H<sub>2</sub>SO<sub>4</sub> is 1.73 dl g<sup>-1</sup>; by using the  $[\eta]$  versus  $\bar{M}_w$  relationship found by Shaefgen *et al.*<sup>12</sup>, a  $\bar{M}_w$  value of ~12 000 is calculated, which gives a polydispersity index  $Q$  of 1.6–1.7. The corresponding  $[\eta]_1$  value in DMAc+3% LiCl at 25°C is 2.28 dl g<sup>-1</sup>.

With reference to the latter value, our data on the limiting viscosity numbers  $[\eta]_2$  of PBA samples treated with various amounts of TA are shown in Figure 1. As already mentioned, these samples have been isolated from the reaction medium after step 2 of the multistep polycondensation procedure.

The abscissa values represent the ratios between the

moles of TA and the equivalents of terminal amino groups in PBA,  $[-NH_2]_1$ , calculated from  $\bar{M}_n$ , i.e. the number of TA molecules per PBA chain formed in step 1. The experimental points are well aligned on a bell-shaped curve with a maximum that is very close to the origin, followed by a regular decrease for higher TA content in the reaction medium.

It is worth considering that the value (2.28 dl g<sup>-1</sup>) for the limiting viscosity number of the PBA sample prepared by addition of 6.9 mol of TA per equivalent of  $-NH_2$  is coincident with the value of neat PBA as prepared in step 1, thus indicating that, for these high  $[TA]/[-NH_2]_1$  ratios, TA either remains unreacted in the medium or is only involved as end-capping agent of PBA. On the contrary, in order to interpret the marked increase of  $[\eta]_2$  for lower TA concentrations, a coupling effect of TA on two PBA molecules should also be envisaged in this composition range. The maximum of the viscosity curve, very close to a 1:2 ratio between TA molecules and PBA chains, might support this correlation.

Although the possibility of direct coupling between two PBA chains cannot be completely disregarded, being the regradation reaction possibly favoured by both TPP addition and temperature increase (see 'Experimental'), the blank runs in the same conditions without added TA show only a very slight increase of  $[\eta]$  (from 1.73 to 1.75 dl g<sup>-1</sup> in sulphuric acid). Moreover, the same  $[\eta]$  values for both neat PBA and the sample prepared in the presence of a large excess of TA further support the scarce relevance of this contribution.

The coupling of two PBA chains by TA and the consequent insertion of a TA-derived CRU (constitutional repeat unit) only causes inversions between carbonyl and amino groups in the sequence of amide bonds along the chain. Therefore the hydrodynamic behaviour of PBA cannot be appreciably altered and the following relationship should hold:

$$w_2 = \left( \frac{1}{2^a - 1} \right) \left( \frac{[\eta]_2 - [\eta]_1}{[\eta]_1} \right) \quad (1)$$

$w_2$  is the weight fraction of coupled PBA chains and  $[\eta]_1$  and  $[\eta]_2$ , as indicated previously, are the limiting viscosity numbers of PBA samples in DMAc+3% LiCl after steps 1 and 2, respectively. Thus,  $w_2$  can be evaluated from the fractional increment of the viscosity, provided

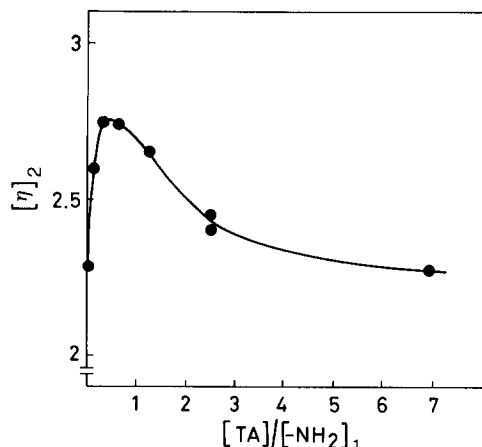


Figure 1  $[\eta]_2$  values of PBA (after step 2) as a function of  $[TA]/[-NH_2]_1$  ratio

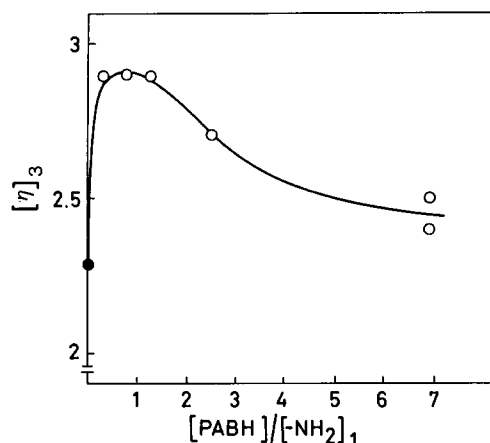


Figure 2  $[\eta]_3$  values (after step 3) as a function of  $[PABH]/[-NH_2]_1$  ratio

that  $a$ , the exponent of the Mark-Houwink equation, is known.

The good linear correlation found between the logarithms of  $[\eta]$  values of PBA in 96%  $H_2SO_4$  and  $DMAc + 3\% LiCl$ , together with the known  $[\eta]$  versus  $\bar{M}_w$  relationship<sup>12</sup> in  $H_2SO_4$ , allows an estimate of the exponent  $a$  close to 1.44 in the amide solvent and in the range of explored molecular masses. On these grounds it can be evaluated that about 12 wt% of PBA chains are coupled at the curve maximum and this percentage decreases regularly as TA content increases.

Therefore, in the reactant concentration range under examination, a complex mixture of coupled and uncoupled PBA chains (in part TA-terminated) plus some free TA is present at the end of step 2. Their relative amounts depend on the specific  $[TA]/[-NH_2]_1$  ratio under consideration.

When step 2 is immediately followed by step 3, the data shown in Figures 2 and 3 are obtained. The  $[\eta]_3$  values of Figure 2, plotted as functions of PABH molecules per PBA chain, pertain to polymer samples free of PABH-T homopolymer removed by exhaustive washing with DMSO. Therefore, they should be considered as only related to a mixture of neat PBA (coupled or uncoupled) and the copolymer between PBA and PABH-T, as suggested in ref. 5. On these grounds the increase of the limiting viscosity number after step 3 has been assumed by Preston *et al.*<sup>5</sup> as the main experimental evidence in favour of copolymer formation. However, a comparison with the very similar trend shown by the data of Figure 1 may provide complementary or alternative explanations for this viscosity increase, presumably due to an analogous PBA coupling by PABH.

Further evidence against copolymer formation is given by the data of Figure 3, where the percentage yield of DMSO extractables referred to the total of TA and PABH moles introduced (lower curve) is plotted as a function of the reactant molar ratio. From these data it is evident that a large fraction of PABH-T homopolymer is formed in the chosen experimental conditions for molar ratios higher than 1. Obviously, no homopolymer is formed for ratios below 1. The decrease of PABH-T homopolymer yield at high TA and PABH content seems to be the result of several effects, such as the production of very low-molecular-mass products (PABH-T oligomers), which do not precipitate from the reaction medium by methanol treatment, or an adverse influence of the PBA

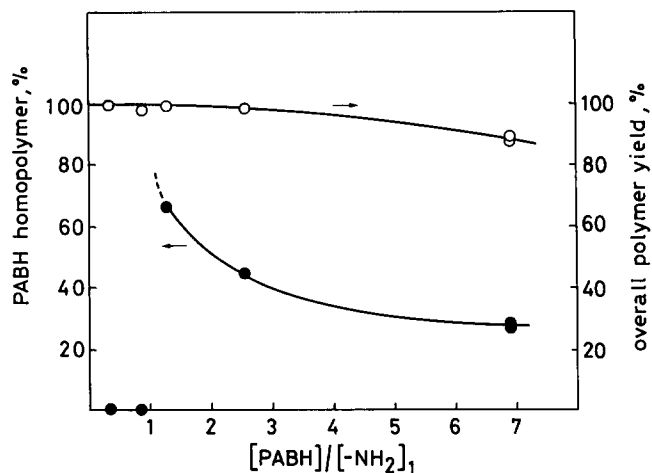


Figure 3 Overall high polymer yield (○) and percentage yield of PABH-T homopolymer (●) (both after step 3) as functions of  $[PABH]/[-NH_2]_1$  ratio

matrix on the condensation reaction of TA and PABH. It should also be recognized that optimum yields of PABH-T are obtained only when DPP instead of TPP is used<sup>4</sup>.

Furthermore, the overall high polymer yield (upper curve) does not remain constant at 100%, as claimed in ref. 5, but shows a relevant decrease at high TA (and PABH) content. Subtracting the moles of TA and PABH, which do not participate in the reaction with preformed PBA, from the total it can easily be seen that there are not enough remaining moles to start a PABH-T chain of length comparable to that of preformed PBA. Even at the highest TA and PABH content, only very few CRU units of PBA-T per PBA chain could be formed. Therefore, in our opinion, it is hard to attribute the increase of viscosity after step 3 merely to copolymer formation, disregarding the more relevant contribution arising from the coupling reaction by PABH.

The viscosity increments of step 3 referred to step 2 show that the maximum value is about 12%, corresponding to a nominal molar ratio of 2:2:1 for PABH/TA/PBA chain. The insertion of a (relatively) flexible CRU unit derived from the reaction between PABH and two PBA chains prevents the extension of equation (1) to this case, in order to evaluate the extent of the coupling reaction and more precise refinements.

From our data it can be inferred that: (a) the viscosity increase, as such, cannot be assumed as a measure of the extent of copolymer formation; and (b) the suggested procedure does not allow a clean synthesis of block copolymers in the whole range of adopted reactant concentrations, as summarized in the reaction scheme. Very recently, a similar criticism has been expressed also by Preston *et al.*<sup>13</sup>, who have proposed an alternative way to synthesize block copolymers based on poly(*p*-phenylene terephthalamide) (PPD-T). At present we are successfully experimenting on a new route of synthesis for PBA-based copolymers, using a two-pot procedure. Detailed results will be given in the near future<sup>14</sup>.

#### ACKNOWLEDGEMENTS

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