Preparation of spherical polybenzimidazole particulates using a non-aqueous suspension methodology

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The successful preparation of spherical polybenzimidazole beads is reported. A non-aqueous suspension methodology is employed similar to that described in an earlier patent publication. A series of surface active agents, low molecular weight ones and polymeric dispersants, have been tested for their potential use in a high temperature suspension experiment. Polymeric dispersants proved most effective. Results on particulate formation as well as properties of the afforded polymer particles are discussed. A procedure for a successful non-aqueous suspension experiment is also given.

(Keywords: polybenzimidazole; particles; thermally stable polymers; non-aqueous suspension; polycondensation; polymeric surfactants)

Introduction

Since the early 1960s high performance products based on thermally stable polymers have become of major interest to scientists and industrial technologists[1]. Polybenzimidazoles form one class of such polymers. Their preparation[2] was first disclosed in the patent literature in 1959. High molecular weight polybenzimidazoles can be synthesized in a melt condensation process[3,4] as reported by Vogel and Marvel. This technique allows preparation of a multitude of fully aromatic polyheterocyclic macromolecules. The polycondensation involves the reaction between an aromatic bis(*o*-diamine) such as 1,2,4,5-tetraaminobenzene or 3,3′-diaminobenzidine with an ester of an aromatic dicarboxylic acid. Equimolar amounts of the monomers are usually heated up to 200–300°C under nitrogen[5]. The initially liquid monomers start to polymerize forming a poly(amino amide) a solid pre-polymer. This intermediate can subsequently be pulverized and post-heated for several hours at 350–400°C under a high vacuum. Under such conditions an almost quantitative conversion of the poly(amino amide) to the final polybenzimidazole can be achieved.

Melt condensation limits the use of monomers to those stable enough to resist the high temperatures required. Monomers with free carboxylic acid groups[4], e.g. 3,4-diaminobenzoic acid, undergo decarboxylation at elevated temperatures rather than forming a linear polymer chain.

For overcoming the drawbacks of the melt condensation process efforts have been directed towards the synthesis of polybenzimidazoles in solution[6]. Several solvents such as phenol, *N*,*N*′-dimethylaniline, *N*,*N*′-dimethylacetamide, etc. have been investigated for this purpose[7]. The results were unsatisfactory for various reasons. Phenolic solvents require heating in the solid state and thus purification of the resultant macromolecule becomes difficult. Solvents based on amines caused complications because of transamidation during polycondensation. On the other hand polyphosphoric acid[8] was found to be a most suitable reaction medium. A typical polycondensation in solution is performed by heating equimolar amounts of monomer in the acidic solvent for several hours at 180–200°C. The potent dehydration properties of polyphosphoric acid allow reaction to proceed at these lower temperatures.

A patent application[9] discloses the synthesis of polybenzimidazoles using non-aqueous suspension methodology. 3,4-Diaminobenzoic acid is suspended in an inert organic continuous phase, e.g. paraffin oil. Polyphosphoric acid is then added to the stirred mixture forming a suspension. The dispersed phase consists of the monomer dissolved in the acidic solvent and sodium dodecylbenzene sulphonate (SDBS) is claimed to serve as a surface active suspension stabilizer. Polycondensation is subsequently carried out by heating the reaction mixture to 200°C for several hours. The preparation of polybenzimidazole particulates in high yields and various particle sizes was reported.

A series of experiments carried out by the present authors have shown however that the suggested surfactant does not lend any stability to the above described non-aqueous suspension.

Therefore we report here on a systematic study, of the use of a range of surfactants, low molecular weight ones as well as polymeric stabilizers, culminating in the successful preparation of spherical polybenzimidazole particulates employing a non-aqueous suspension methodology.

Experimental

Materials. 3,4-Diaminobenzoic acid was used as supplied by the Aldrich Chemical Co. Ltd. Paraffin oil was used as supplied by A. J. Beveridge Ltd (grade: liquid paraffin 5LT). Polyphosphoric acid was prepared by dissolving P_2O_5 (Aldrich; 150 g) in concentrated orthophosphoric acid (Aldrich; 100 ml). 2-Dodecen-1-ylsuccinic anhydride and dodecylbenzenesulphonic acid sodium salt were used as supplied by the Aldrich Chemical Co. Ltd. Oleic acid dimer (hydrogenated,

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Pripol 1008) was used as supplied by Unichema International. Polybutadiene (carboxy terminated) was used as supplied by Shell Chemicals, grade Hycar 2000-165. Poly(butadiene-*co*-acrylonitrile, 10%) (carboxy terminated) was used as supplied by Shell Chemicals, grade Hycar 1300 × 15; Brookfield viscosity (cPs) at 27°C = 57 500 ± 17 500; bound acrylonitrile content = 10 ± 1%; carboxyl content, equivalent per hundred = 0.0535 ± 0.0035. Poly(butadiene-*co*-acrylonitrile, 25%) (carboxy terminated) was used as supplied by Shell Chemicals, grade Hycar 1300 × 13; Brookfield viscosity (cPs) at 27°C = 570 000 ± 160 000; bound acrylonitrile content = 25.5 ± 2.0%; carboxyl content, equivalent per hundred = 0.057 ± 0.007. Poly(ethylene-*co*-acrylic acid) (92:8) was used as supplied by Polyscience Ltd; ethylene content 92%; bound acrylic acid content 8%. Poly(butadiene-*b*-styrene) (methyl methacrylate terminated) was used as supplied by Exxon Chemicals Ltd; average molecular weight 2500–7500 g mol^{-1}. Polyisobutylene (carboxy terminated) was used as supplied by Exxon Chemicals Ltd; highly viscous liquid. Polyisobutylene (epoxide terminated) was used as supplied by Amoco Chemical Company, grade Actipol E23; highly viscous liquid, clear; average molecular weight 1433 g mol^{-1}; epoxide functionality only at one end of the polymer chain. Polyisobutylene (succinic anhydride terminated) was used as supplied by BP Chemicals Ltd; grade ADX 101B; solution in oil, industrial intermediate; average molecular weight 250–5800 g mol^{-1}; anhydride functionality at only one end of the polymer chain. Poly(maleic anhydride-*co*-octadec-1-ene) (1:1) was used as supplied by Polyscience Inc; copolymer composition 1:1 molar ratio. The ICI polymeric dispersant was a terpolymer of methyl methacrylate, glycidyl methacrylate and the condensation product of glycidyl methacrylate with an oligomer of 12-hydroxy-stearic acid. This was used as supplied by ICI, Paints Division; 50% solution in hexane; average molecular weight 30 000 g mol^{-1}. Poly(styrene-*co*-maleic anhydride) was used as supplied by the Aldrich Chemical Co. Ltd; average molecular weight 350 000 g mol^{-1}; styrene content 50%. Poly(styrene-*b*-hydrogenated butadiene-*b*-styrene) was used as supplied by Shell Chemical Co. Ltd; triblock copolymer; average molecular weight: first styrene block M_n = 30 000 g mol^{-1}; centre butadiene segment M_n = 115 000 g mol^{-1}; second styrene block M_n = 30 000 g mol^{-1}. Poly(vinylpyrrolidone-*co*-hexadec-1-ene) was used as supplied by GAF Co. Ltd, grade Antaron V-216; colourless liquid; average molecular weight 7300 g mol^{-1}. Poly(vinylpyrrolidone-*co*-eicos-1-ene) was used as supplied by GAF Co. Ltd, grade Antaron V-220; white to yellow waxy mass; average molecular weight 8600 g mol^{-1}. Sorbitan monooleate (Span 80) was used as supplied by the Sigma Chemical Co. Ltd.

Suspension experiments. The following general experimental set-up was used for the preparation of polybenzimidazoles in suspension. A 250 ml three-necked round-bottomed flask equipped with an overhead stirrer having a D-shaped Teflon paddle, was thoroughly swept with nitrogen. Paraffin oil (100 ml), containing the desired amount and type of suspension stabilizer, was placed into the flask and purged for 30–45 min with nitrogen under continuous stirring. After the addition of 3,4-diaminobenzoic acid (6.5 g; 4.58 × 10^{-2} mol) purging was continued for 15 min before polyphosphoric acid (28 g; 10.8 ml) was slowly added to the reactants. An incremental temperature increase (1°C every 3 min) up to 160–170°C induced the first step of the polycondensation. The reaction mixture was kept at 170°C for 16 h. Cyclization was completed during an additional 4 h at 220–230°C. The suspension was then allowed to cool down under continuous agitation. The loose solid particulate product was collected by filtration and washed with water and neutralized by dispersing it in a saturated aqueous sodium bicarbonate solution for 2 days. The polybenzimidazole was again collected by filtration and washed with water until neutral. Finally the polymer was washed free of any remaining paraffin oil in a Soxhlet apparatus for 16 h using dichloromethane as solvent. The particulates were dried in a vacuum oven at 70°C for 16 h.

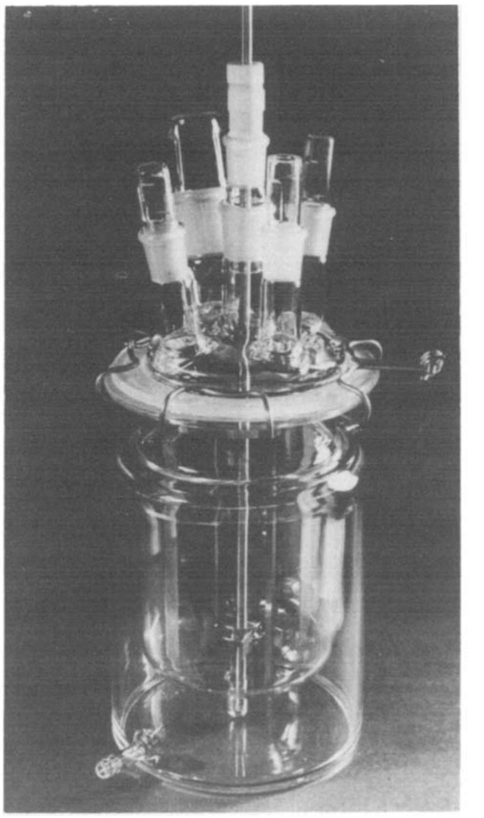

Figure 1 Photograph of the polymerization reactor used for the second set of suspension experiments

The various suspension stabilizers listed above have been examined for the bead polymerization of polybenzimidazoles. In a second set of experiments a different flask design has been used. This polymerization reactor possessed characteristics which are known to benefit the process of a suspension polymerization (*Figure 1*).

Results and discussion

Characterization of poly(2,5-yl-benzimidazole). The synthesis of polybenzimidazole (*Figure 2*) using a non-aqueous suspension methodology yielded typically 90–100% conversion of monomer to polymer. Most losses occurred during the initial dispersion polymerization process with residues left in the flask and on the stirrer. The final polymer was characterized by a yellow to brown colour. Poly(2,5-yl-benzimidazole) showed characteristic i.r. absorption bands in the region of 1625 cm^{-1} (heterocyclic ring vibration), 1547 cm^{-1}

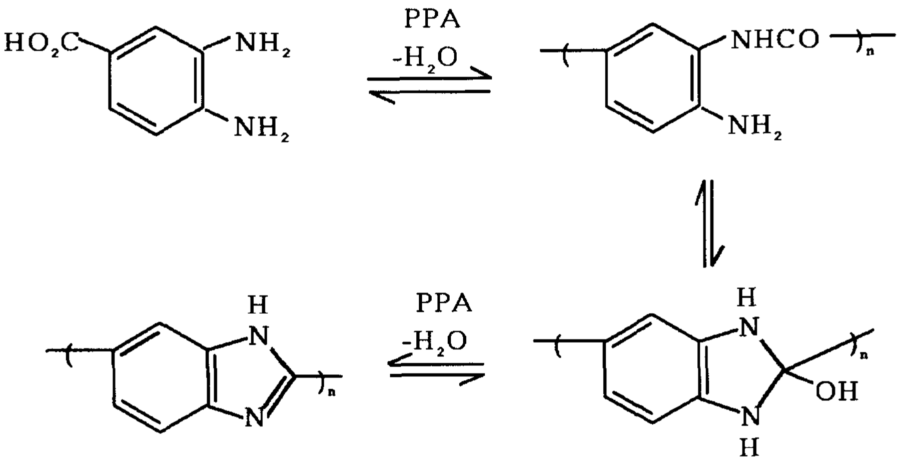

Figure 2 Schematic representation of the synthetic pathway to fully aromatic polybenzimidazoles in polyphosphoric acid (PPA)

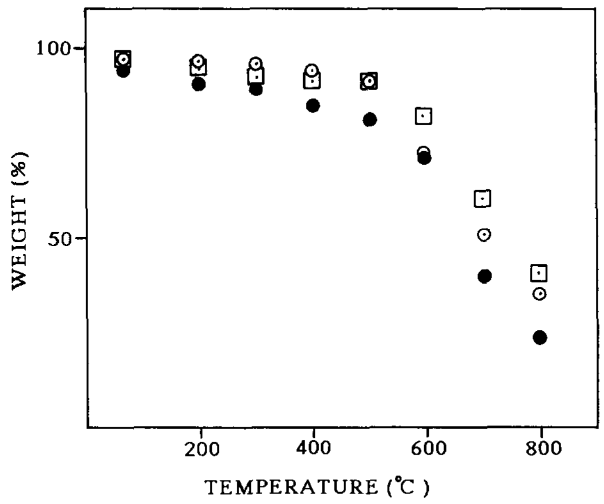

Figure 3 T.g.a. curves from polybenzimidazole samples prepared in suspension using various amounts of poly(maleic anhydride-*co*-octadec-1-ene) as the stabilizer; (☐) reference polymer; (○) 0.3 wt% stabilizer; (●) 0.2 wt% stabilizer; heating rate 10°C min^{-1} in air

(combined C=C, C=N vibration), 1431 cm^{-1} (heterocyclic ring in plane vibration), 1286 cm^{-1} (C–N stretch vibration) and 814 cm^{-1} (N–H out of plane vibration). An important band which is absent is a sharp feature at ~1670 cm^{-1}. This corresponds to a carbonyl absorption of an aromatic amide group and its absence confirms that efficient cyclization of the intermediate amino-amide pre-polymer to benzimidazole has occurred during polycondensation. This bond is clearly seen in the i.r. spectrum of poly(amide-*co*-benzimidazole) compounds[10].

The elemental nitrogen microanalytical figure for poly(5-yl-benzimidazole) was found to be 21.2%, which compares with a calculated value of 24.1%. In comparison with low molecular weight organic molecules the agreement between theoretical and experimental N% is rather poor. On the other hand it is known that efficient combustion of these fully aromatic main chain polymers can be very difficult and the results obtained are, in fact, not unreasonable. Nevertheless the data suggest that impurities may be absorbed in the polymer matrix. Solid ash residues were left after burning the sample in oxygen. Most probably these consist of iron compounds from the stirrer, and silica compounds originating from the flask, generated by the highly corrosive nature of polyphosphoric acid.

Poly(2,5-yl-benzimidazole) was found to be stable up to 400°C in the presence of air and thereafter progressive oxidative degradation took place (*Figure 3*). Such high thermal stability is consistent with results reported in the literature[11,12].

Reference suspension polymerization. In the patent literature[9] SDBS was suggested as a suitable surfactant for the preparation of polybenzimidazole using a non-aqueous suspension methodology. This suspension stabilizer was employed in a reference procedure for the production of poly(2,5-yl-benzimidazole) particulates. A high molecular weight polymer was obtained with an inherent viscosity corresponding to $\eta_{\text{inh.}} = 1.49\ \text{cm}^3\ \text{g}^{-1}$. This dispersion technique however proved to be entirely unsatisfactory with at best a broad range of particle size and shape arising in the product. There was also considerable particle aggregation, along with polymer deposition on the stirrer as well as on the flask wall. This process was difficult to control, highly irreproducible and often suspension polycondensation could not be maintained due to polymer deposition on the equipment.

The proposal that SDBS could be a valuable suspension stabilizer for a polyphosphoric acid solution of monomer dispersed in oil is surprising. SDBS is an ionic surfactant of high hydrophilic–lipophilic balance (HLB) and is soluble only in water and aqueous alcohols. Complete insolubility in oil makes it totally unsuitable for polar dispersions in oil, and in this polymerization it almost certainly becomes located uselessly within the polyphosphoric acid droplets. Any successful surfactant is likely to be of low HLB, and at the very least soluble in the continuous oil phase.

Surfactants investigated in the non-aqueous suspension methodology. A broad range of different compounds were investigated as potential suspension stabilizers in various concentrations. Right at the outset it was felt that polymeric stabilizers capable of providing some degree of steric stabilization probably offered the best prospect for a robust dispersion system. A few low molecular weight species were also investigated.

Low molecular weight surfactants as potential stabilizers. Using Span 80 (sorbitan monooleate) a low HLB nonionic surfactant as a suspension stabilizer, a relatively low molecular weight polymer was obtained. The inherent viscosity was determined as 0.53 $cm^3 g^{-1}$ compared to 1.49 $cm^3 g^{-1}$ measured for the reference polymer. The i.r. spectrum of the polybenzimidazole showed the presence of aliphatic hydrocarbon structures. Absorption bands were found in the region of 2925 and 2853 cm^{-1}. This also suggests that the low molecular weight stabilizer reacts via its ester groups with a growing polymer chain, thus acting as a chain terminator during pre-polymer formation. The main problem encountered however with this short chain surfactant lies in its low efficiency in dispersing the reactants and products. The polymer formed tended to adhere firmly to the reactor wall and stirrer. Only a minor percentage of the product stayed in controlled suspension. As a result polybenzimidazoles were obtained as lumps and agglomerates of irregular size and shape.

Other low molecular weight stabilizers examined were 2-dodecen-1-ylsuccinic anhydride, dodecylbenzene sulphonic acid sodium salt and oleic acid dimer. These yielded similar products. It seems, therefore that although these surfactants might be adsorbed onto or become chemically bonded to the surface of the dispersed droplets, penetration into the continuous phase is restricted and hence steric stabilization is weak.

Polymers as potential suspension stabilizers. In general it was found that polymeric surfactants performed more satisfactorily as dispersion stabilizers. During polycondensation the reactants initially sedimented at slightly elevated temperatures (~40–60°C) but under continuous agitation re-dispersion was observed in the temperature range of ~80–110°C. At this stage the flask wall was almost free of intermediate products. All reactants became visibly dispersed in a clear continuous oil phase as spherical and distorted droplets. Paraffin oil changes to a fluid of lower viscosity above 140°C. At this stage droplet reformation might occur as a result of a new flow pattern arising from the altered physical shear and turbulence parameters. However, this was not observed.

It is believed that pre-polymer formation takes place mainly in the temperature range 100–160°C whilst conversion of the poly(amino amide) to the final polybenzimidazole structure is completed at higher temperatures (180–220°C). It was predominantly during the last heating cycle that agglomeration and polymer settlement was found likely to occur. Polymeric stabilizers carrying functional acid on ester moieties either along the polymer backbone or as terminal groups gave rise to the formation of stable particulate polybenzimidazoles. It is believed that these dispersants become chemically bound to the growing polybenzimidazole macromolecules. I.r. analysis of polymer products prepared in the presence of such stabilizers revealed characteristic absorption bands for aliphatic hydrocarbons at 2925 and 2853 cm^{-1}. Resonance peaks typical for aliphatic carbon atoms were also detected using solid-state ^{13}C n.m.r. spectroscopy (30–10 ppm). Surfactants, particularly polymeric ones, chemically bound to the dispersed phase can give rise to more efficient steric stabilization. Desorption of dispersant molecules upon droplet collision or during high temperature polycondensation becomes almost eliminated. As a consequence the yield of particulate poly(2,5-ylbenzimidazole) was high (90–100%) when using this type of surfactant. Only a relatively small percentage of polymer product was found adhering either to the flask wall or the stirrer. Unfortunately the shape and size of polymer particulates varied quite a lot.

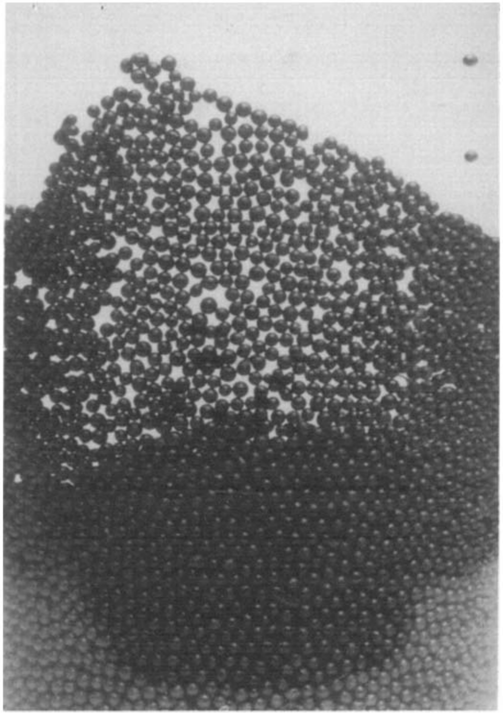

Figure 4 Photograph showing polybenzimidazole beads with an average particle size of 106 μm. Prepared using a non-aqueous suspension methodology and carboxy-terminated polyisobutylene as surfactant

Even though chemically grafted the suspension stabilizer does not have a major impact on the thermostability of the final polybenzimidazole. T.g.a. traces showed little weight loss at temperatures below 400°C in air (*Figure 3*).

The best suspension results were obtained when using a 250 ml round-bottomed flask and carboxy-terminated polyisobutylene as a stabilizer. The macromolecular product consisted of almost 100% of spherical beads with a fairly narrow particle size distribution. The average diameter of these particulates, as shown in *Figure 4*, was determined as 106 μm. No polymeric material was found in the flask after reaction was complete. Unfortunately this system did not prove to be particularly robust. Repetitive experiments afforded only products consisting of a mixture of spherical beads (~40–70%) and deformed particles (60–30%). During all these repeat preparations a little polymer did become stuck to the surface of the equipment but most product was particulate in nature.

An analysis of the particulates using the scanning electron microscope revealed that the surface contained holes, probably formed by the reaction solvent (polyphosphoric acid) acting as a porogen. Tiny rims also occur around the holes and are probably caused by local heat released during neutralization of the polyphosphoric acid after completion of polycondensation. The surface area of these particulates was rather low (1.8 $m^2 g^{-1}$) as determined by nitrogen adsorption. Also, the accessible pore volume was rather limited (0.16 ml Hg g^{-1}; from mercury intrusion).

None of the other polymeric surfactants listed in the Experimental section with a functional group capable of anchoring to the polybenzimidazole yielded spherical polymer beads in as high a proportion of the total product. Mainly irregular-shaped particulates like drums, sticks, bent pipes or other deformed droplets were found. The product was however obtained as discrete loose particles leaving almost no polymer layer behind on the reactor and stirrer. Using polymeric stabilizers carrying more than one functional ester or acid group can lead to crosslinked polybenzimidazoles as shown by their insolubility in concentrated sulphuric acid.

Dispersants without chemical anchoring groups, e.g. poly(styrene-*b*-hydrogenated-*b*-styrene), were also employed as the surface active agent. The dispersion of the reactants was quite successful up to 160°C. When the temperature was further increased severe particle agglomeration took place. The product contained large lumps and no beads and it seems likely that the surfactant becomes desorbed from the dispersed phase at elevated temperatures leading to destabilization of the droplets.

Conclusions

Poly(2,5-yl-benzimidazole) can be prepared as spherical beads in high yield using a non-aqueous suspension methodology with an appropriate surfactant. Polymeric suspension stabilizers containing reactive functional groups are more efficient than low molecular weight species and in the present work carboxy-terminated polyisobutylene was particularly effective. The surfactant appears to become chemically grafted to the growing polymer chains. Thus displacement of the surface active agents during polycondensation is reduced and as a consequence steric stabilization enhanced. Even when deformed particulates were obtained little polymer residue was found sticking to the apparatus. This can be regarded as an important improvement to the original process outlined in the patent literature. Low molecular weight stabilizers carrying a functional ester or acid group can act as chain termination agents during polycondensation, thus affording polybenzimidazoles of lower molecular weight. In contrast polymeric stabilizers with multiple pendant functional groups can cause crosslinking in the final product. Finally even though the surfactant becomes chemically bonded to the particulates the original thermostability of the polybenzimidazole remains essentially unchanged.

A number of problems remain which prevent the suspension methodology from being robust.

The viscosity of the continuous phase (paraffin oil) falls during the heating cycle which is necessary to complete polycondensation. This creates a change in the flow pattern and the shear rate which disturbs particle stability. Replacing paraffin oil by Santotherm 66, a hydrogenated terphenyl based oil, as a continuous phase gave no better results. Polyphosphoric acid, a high viscosity solvent/dehydrating agent, can age upon storage. Organic reactions employing polyphosphoric acid are known to yield inconsistent results. Replacing this with methane sulphonic acid containing 10 wt% phosphorus pentoxide did not however improve the yield of spherical particulates of polybenzimidazole. In addition changing the ratio of polyphosphoric acid did not improve particulate formation. Polyphosphoric acid is also used commercially as a plasticizer for polybenzimidazoles. When the polymer particulates were first collected they were rather soft. It is possible therefore that some particle deformation or agglomeration occurs during the work-up steps. Only after the removal of the acid were the polybenzimidazole particulates converted into extremely hard particles.

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References

1 Cassidy, P. E. 'Thermally Stable Polymers, Synthesis and Properties', 1st Edn, Marcell Dekker, New York, 1980, p. 163
2 Brinker, K. C. and Robinson, I. V. *US Pat. 2895948*, 1959
3 Vogel, H. and Marvel, C. S. *J. Polym. Sci.* 1961, **50**, 511; *J. Polym. Sci., Polym. Chem. Edn.* 1963, **1**, 1531
4 Buckley, A., Stuetz, D. E. and Serad, G. A. 'Encyclopaedia of Polymer Science and Engineering' (Eds. H. F. Mark, N. M. Bikales, C. C. Overberger, G. Menges and J. I. Kroschwitz), J. Wiley and Sons, New York, 1988, Vol. 11, p. 522
5 Neuse, E. W. *Adv. Polym. Sci.* 1982, **47**, 1
6 Levine, H. H. 'Encyclopaedia of Polymer Science and Technology', 1st Edn, Vol. II, Interscience Publishers, New York, 1973, p. 121
7 Plummer, L. and Marvel, C. S. *J. Polym. Sci., Polym. Chem. Edn.* 1963, **A1**, 1531
8 Iwakura, Y., Uno, K. and Imai, Y. *J. Polym. Sci., Polym. Chem. Edn.* 1964, **A2**, 2605
9 Milford, G. N. *US Pat. 4394500*, 1983
10 Brock, T., Sherrington, D. C. and Tang, H. G. *Polymer* 1991, **32**, 353
11 Varma, I. K. and Veena. *J. Polym. Sci., Polym. Chem. Edn.* 1976, **14**, 973
12 Breed, L. W. and Wiley Jr, J. C. *J. Polym. Sci., Polym. Chem. Edn.* 1976, **14**, 83