Attempted Polymerization of Benzimidazole via Reissert Reactions

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ABSTRACT: Benzimidazole is a potentially difunctional monomer; this paper describes our approaches to its polymerization using Reissert compound chemistry. Poly(benzimidazole Reissert compound)s (**25**) in which both nitrogen atoms are part of amide linkages and a cyano group is present at the 2-position of the benzimidazole ring were prepared from benzimidazole itself or bis(1-benzimidazyl)adipoyl (**24**) by reaction with diacid chlorides in the presence of trimethylsilyl cyanide; however, low molecular weights resulted under a variety of conditions. Attempts to synthesize polyethers by condensation of the new Reissert compound 1,3-bis(*p*-fluorobenzoyl)-2-cyano-2,3-dihydrobenzimidazole (**14b**) and Bisphenol A failed due to hydrolysis of **14b** under the reaction conditions. Surprisingly, 2-benzoylbenzimidazole (**16b**) was formed from the base-induced rearrangement of 1,3-dibenzoyl-2-cyano-2,3-dihydrobenzimidazole (**14a**); the presence of radical ion intermediates during the rearrangement reaction of **14a** with NaH/DMF was proven by CIDNP and ESR experiments.

Introduction

Polybenzimidazoles are well-known for their excellent mechanical properties, high-temperature stability, nonflammability, and high chemical resistance.[1-3] Thus, polybenzimidazoles have been extensively used for textiles (thermal and chemical protective clothing), in the replacement of asbestos in fire blocking, and also in film, foam, paper, adhesive, ion-exchange resins, etc.

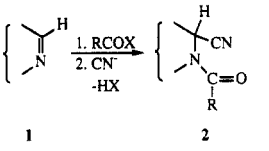
Because their properties are not found in other synthetic fibers, polybenzimidazoles have been extensively investigated.[1-3] Traditionally, polybenzimidazoles have been prepared by the reaction of aromatic tetraamines with dicarboxylic acids and their derivatives.[4,5] Thus, the benzimidazole ring is formed in the polymerization process and the product polymer must be processed from the reaction mixture, typically poly(phosphoric acid).

The low cost of benzimidazole and the high performance of polybenzimidazoles led us to look into new synthetic approaches to polybenzimidazoles starting from benzimidazole.

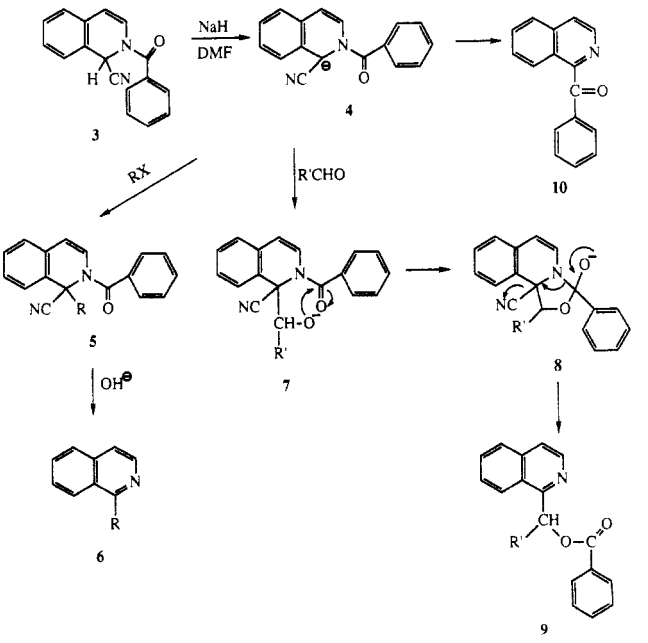
The *Reissert reaction* consists of the net addition of an acyl cyanide across a C=N bond (**1**; Scheme 1).[6-8] The resultant Reissert compounds (**2**) have an acidic proton α to the cyano group; the conjugate bases react with a number of electrophiles.[6-8] For example, reaction of 2-benzoyl-1-cyano-1,2-dihydroisoquinoline (**3**) via its anion **4** with alkyl halides produces the alkylated derivative **5** which by alkaline hydrolysis is converted to the rearomatized alkylated isoquinoline **6**. Similarly, condensation with aldehydes via the intermediate alkoxide **7** and cyclic alkoxide **8** produces the ester **9**. In the absence of an electrophile the Reissert anion rearomatizes by an intramolecular process with elimination of cyanide ion to produce the ketone **10** (Scheme 2).

Due to the reactivity of Reissert compounds, we have been interested in inserting them into the polymer backbone.[9,10] The reactive sites in such polymer backbones can be conveniently used to chemically modify the polymers. We have recently reported the synthesis of poly-

Scheme 1



Scheme 2



(isoquinoline) Reissert compound)s[10] and novel bis(benzoxazoles) and attempts to synthesize polymeric benzoxazole Reissert compounds.[11] In the present report we describe our attempts toward direct polymerization of benzimidazole under Reissert reaction conditions and some related chemistry of benzimidazole Reissert compounds.

Results and Discussion

One of the important requirements for step growth polymerization is the presence of difunctionality in the starting materials. Benzimidazole is difunctional in the sense that via Reissert compound formation two NCO

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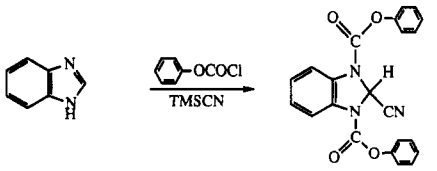
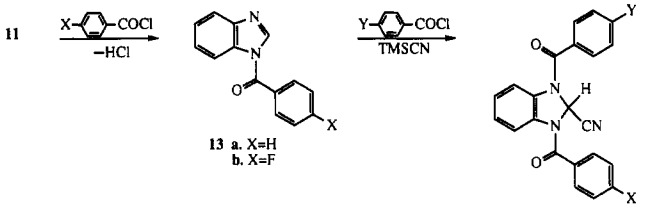
Scheme 3



11 12

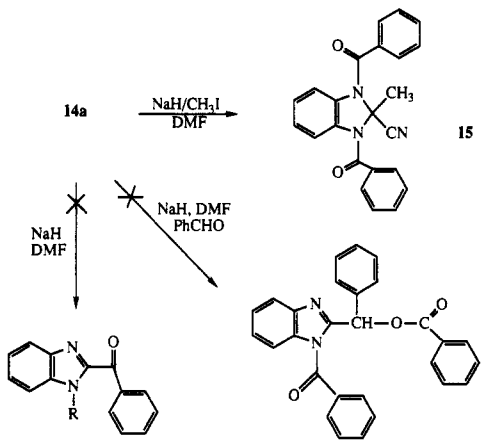
Scheme 4



13 a. X=H
b. X=F

14 a. X=Y=H
b. X=Y=F

Scheme 5



16a. R=COC_6H_5
16b. R=H

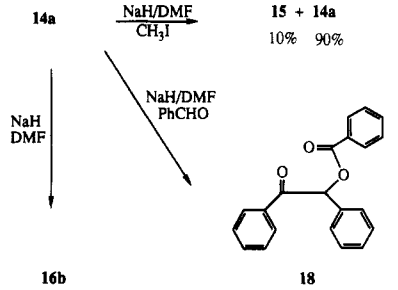
17

linkages can be formed. For example, Uff et al.[12] have performed the Reissert reaction on benzimidazole (11) with chloroformates using trimethylsilyl cyanide as a cyanide source and produced 1,3-bis(phenoxycarbonyl)-2-cyano-2,3-dihydrobenzimidazole (12); Scheme 3). However, our interest was to form amide linkages, rather than urethane moieties, so as to get higher performance materials.

I. Chemistry of the Model Benzimidazole Reissert Compound. We previously reported the synthesis of 1,3-dibenzoyl-2-cyano-2,3-dihydrobenzimidazole (**14a**) via a two-step process from benzimidazole via the intermediate 1-benzoylbenzimidazole (**13a**; Scheme 4).[13-15] One can vary the 1- and 3-substituents of **14** depending on the acid chlorides chosen in the two steps. Position 2 has a reactive cyano group and, most importantly, the hydrogen at C-2 is highly acidic. Thus, in principle, we have the ability to vary substituents on the N-1, C-2, and N-3 positions of the benzimidazole molecule, and this is not easily achievable with the routes available in the literature.[16]

On the basis of the well-documented chemistry of Reissert compounds,[6-8,17] we expected Reissert compound **14a** upon (a) methylation to give **15**, (b) treatment with NaH/DMF to form rearranged product **16**, and (c) benzaldehyde condensation to yield **17** (Scheme 5).[18] Interestingly, we obtained (a) a very low yield (10%) of methylated product **15**, (b) 2-benzoylbenzimidazole (**16b**), and (c) benzoin benzoate (**18**), respectively, in the above reactions (Scheme 6). Earlier, we proposed that these

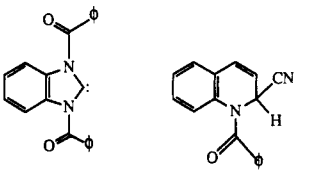
Scheme 6



16b 18

unusual reactions arise due to a highly delocalized, very stable carbanion (as indicated by the deep blue color formation) with many resonance structures.[18]

Interestingly, even after the addition of a few drops of water to the solution of the anion of **14a**, the blue color persisted. The possibility of formation of carbene **19** as



19 20

in the case of imidazole[19] was thus envisioned, but such intermediates were ruled out by carrying out the NaH/DMF reactions under anhydrous conditions and monitoring them at regular intervals by NMR. Generation of carbenes was ruled out by chemically induced dynamic nuclear polarization (CIDNP) (by both ^1H and ^{13}C NMR) and also FTIR experiments.

Finally, the electron spin resonance (ESR) spectrum of NaH/DMF reaction intermediates (Figure 1) clearly showed the presence of radical ions, hitherto not noticed in Reissert chemistry. However, the nature of the radical ion changed with time, as can be seen from Figure 1. Similar base-catalyzed (NaH/DMF) rearrangements of isoquinoline Reissert compound **3** and quinoline Reissert compound **20** did not show radical ion intermediate formation.

II. Benzimidazole-Based Monomers. Reaction of benzimidazole (11) with *p*-fluorobenzoyl chloride in the presence of a base, triethylamine, in DMF afforded a quantitative yield of 1-(*p*-fluorobenzoyl)benzimidazole (**13b**; Scheme 4). **13b** was then subjected to the Reissert reaction with *p*-fluorobenzoyl chloride and trimethylsilyl cyanide (TMSCN) in the presence of a catalytic amount of $AlCl_3$ in dichloromethane. A quantitative yield of Reissert compound monomer **14b** was obtained.

We attempted to synthesize the reactive acryloylbenzimidazole Reissert compound **22** in two steps. A complex mixture of products was obtained when benzimidazole was reacted wtih acryloyl chloride in the presence of triethylamine or pyridine as a base in DMF or chloroform as the solvent (Scheme 7). However, when benzimidazole itself was used as the base, that is, taking 2 equiv of benzimidazole per 1 equiv of acryloyl chloride, a new product was isolated, the dimer 1,3-bis(1-benzimidazyl)-1-propanone (**23**). Compound **23** probably formed via the intermediacy of **21**, followed by the Michael addition of another benzimidazole moiety.

Bis(benzimidazole) **24** was prepared by reacting 2 equiv of benzimidazole with the diacid chloride in DMF in the presence of a base, triethylamine (Scheme 8).[20,21]

III. Poly(benzimidazole Reissert compound)s. We subjected benzimidazole (11) to Reissert reactions with adipoyl chloride or 4,4'-oxybis(benzoyl chloride) using

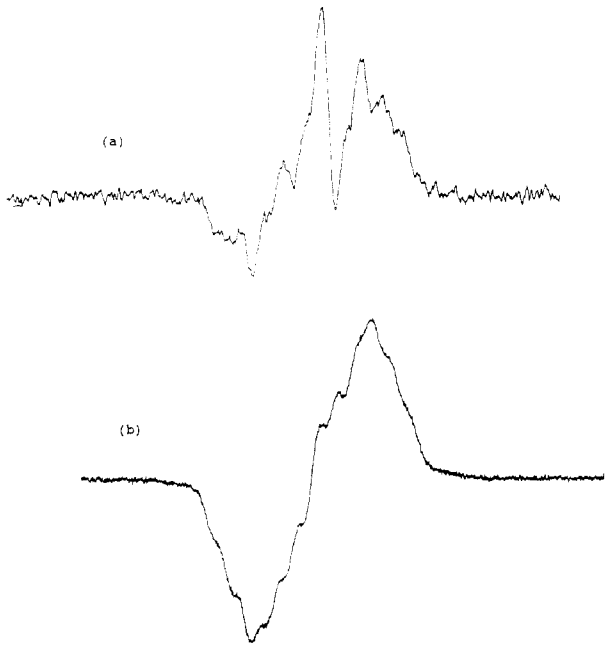
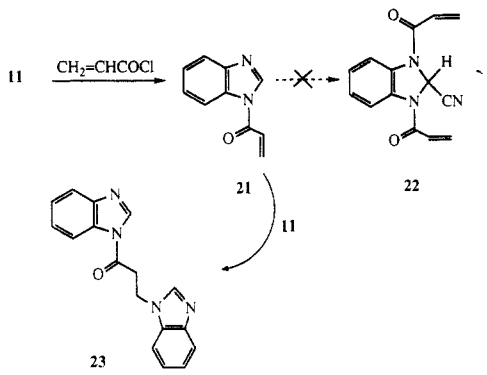
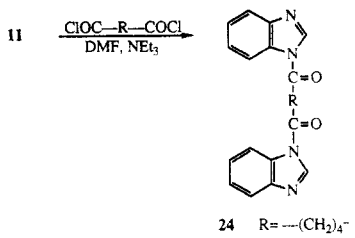


Figure 1. ESR spectra of NaH/DMF reaction intermediates from **14a**: (a) 300 s, after addition of NaH; (b) after a 1-h reaction period.

Scheme 7



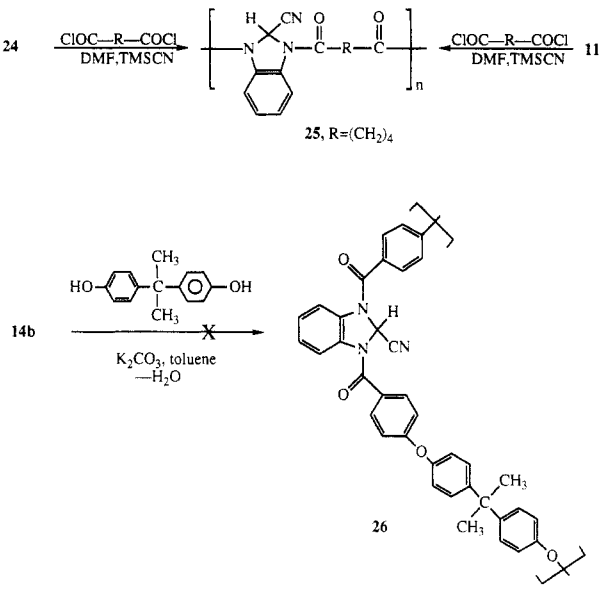
Scheme 8



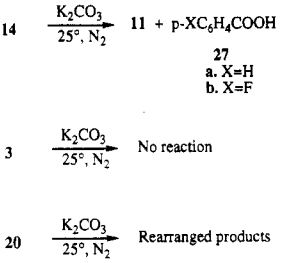
TMSCN (Scheme 9). Several anhydrous, polar solvents (DMF, NMP, dioxane) were examined, along with two different bases (triethylamine or pyridine, 2 equiv), for various reaction periods (24–96 h). These reactions led to either very low molecular weight polymer **25** as judged by low intrinsic viscosities ([η] ≤ 0.1 dL/g) or the corresponding bis(benzimidazole) **24**.

A two-step approach to poly(benzimidazole Reissert compound)s was then explored. The first step involved forming the bis(benzimidazole), followed by a second step involving acylation in the presence of trimethylsilyl cyanide, i.e., the Reissert reaction. Thus, bis(benzimidazole) **24** was reacted with adipoyl chloride in the presence of TMSCN to form **25** (Scheme 9).[22] Again, only low-viscosity products were obtained. For a sample of **25**, [η] = 0.1 dL/g, by thermogravimmetric analysis (TGA) in air 10% weight loss was observed at 220 °C; no glass transition

Scheme 9



Scheme 10



(T_g) or melting (T_m) was observed by differential scanning calorimetry in either the first or second heating up to 150 °C.

As an alternative means of incorporating the benzimidazole Reissert compound structure into polymer backbones, we attempted to polymerize Reissert compound monomer **14b** with isopropylidenebisphenol (Bisphenol A) under standard polyetherification reaction conditions (K_2CO_3/DMAc). A gummy, low molecular weight material was obtained, instead of the expected polyether **26** (Scheme 9). Interestingly, we had observed at this point a mild hydrolysis of Reissert compounds, hitherto not observed.

IV. Mild Hydrolysis of Benzimidazole Reissert Compounds. Hydrolysis of Reissert compounds to the parent heterocycle using common reagents under ambient conditions is highly desirable in the multistep synthesis of important heterocycles. Thus, the accidental finding of hydrolysis of an amide bond of a benzimidazole Reissert compound at room temperature was further explored. When **14a** was reacted with K_2CO_3/DMAc at 25 °C, benzimidazole (**11**; 100%) and benzoic acid (**27a**; 88%) were obtained (Scheme 10). Similar results were obtained when the solvent was changed to DMF. The fluorobenzoyl analog **14b** also behaved in the same manner as shown in Table 1 (Scheme 10).

From these reaction conditions the isoquinoline Reissert compound **3** was recovered quantitatively (Scheme 10). However, when the quinoline Reissert compound, 1-benzoyl-2-cyano-1,2-dihydroquinoline (**20**), was treated wtih (a) K_2CO_3/DMAc or (b) PhCHO/K_2CO_3/DMAc, the anion of this Reissert compound was evidenced by the formation of a deep pinkish coloration. Upon workup both reactions yielded a major and two minor products, which were not identified (Scheme 10).

Table 1. Mild Hydrolysis of Reissert Compounds

cpd	reaction conditions	products (% yield)
14a	K_2CO_3, DMAc, 25 °C, N_2, 3 days	11 (100) + 27a (88)
14a	K_2CO_3, DMF, 25 °C, N_2, 3 days	11 (92) + 27a (52)
14b	K_2CO_3, DMAc, 25 °C, N_2, 3 days	11 (100) + 27b (100)
3	K_2CO_3, DMAc, 25 °C, N_2, 3 days	no reaction
20	K_2CO_3, DMAc 25 °C, N_2, 2 days *or* K_2CO_3, DMF, 25 °C, N_2, 3 h *or* K_2CO_3, DMAc, PhCHO, 25 °C, N_2, 2 days	20 & minor amounts of several rearranged products

Conclusions

Polymerizations of benzimidazole and 1,1-coupled bis(benzimidazole)s have been carried out by reaction with diacid chlorides in the presence of trimethylsilyl cyanide (the Reissert reaction); however, under a variety of conditions only low molecular weight products resulted. Attempts to synthesize polyethers by condensation of the new Reissert compound 1,3-bis(*p*-fluorobenzoyl)-2-cyano-2,3-dihydrobenzimidazole (**14b**) and Bisphenol A failed due to hydrolysis of **14b** under the reaction conditions. Benzimidazole Reissert compounds display unusual chemistry such as hydrolysis to the parent heterocycle under very mild conditions and generation of radical ion intermediates in the presence of base.

Experimental Section

Melting points were determined on a Haake-Buchler melting point apparatus and are corrected. Proton nuclear magnetic resonance (NMR, DMSO-d_6) spectra were recorded on a Bruker 270-mHz instrument and a Hewlett Packard 7550A graphics plotter. A Varian 400-mHz instrument was used for the ^{13}C NMR spectra (DMSO-d_6) and CIDNP experiments. Fourier transform infrared (FTIR, KBr) spectra were recorded on a Nicolet MX-1. Elemental analyses were performed by Atlantic Microlab (Norcross, GA). ESR experiments were carried out in a Bruker instrument with a 200-s sweep time. Thermogravimetric analysis (TGA) was carried out on a DuPont 951 TGA coupled to a DuPont instruments thermal analyst 2100. Transition temperatures were determined by a dual-cell DuPont instrument 912 differential scanning calorimeter (DSC) coupled to the same data station as in TGA at a heating rate of 10 °C min^{-1}.

1-(*p*-Fluorobenzoyl)benzimidazole (13b). To a well-stirred solution of benzimidazole (200 mmol, 23.6 g) and triethylamine (220 mmol, 22.36 g or 31 mL) in DMF (200 mL) cooled in an ice-water bath under dry conditions (N_2) was added benzoyl chloride (220 mmol, 30.92 g or 26 mL) during a 30-min period. Stirring was continued for 2 days at 25 °C. The reaction mixture was poured into water (3 L) and stirred for 6 h. The solid obtained was stirred in water (4 L) for 1 h, filtered, and dried. The product obtained was treated once with Norit and recrystallized from ethyl acetate and hexane, 48.20 g (100%). Mp: 140–141 °C. FTIR: 3123, 3080 (C–H), 1707 (C=O), 1601, 1507 (aromatic), 1476, 1448, 1408, 1400, 1369, 1341, 1306, 1290, 1241, 1224, 1206 cm^{-1}. ^1H NMR: δ 8.48 (s, 1H, H_2), 8.3–7.78 (m, 4H, H_4–H_7), 7.7–7.4 (m, 4H, *p*-fluorobenzoyl H). Anal. Calcd for $C_{14}H_9N_2OF$: C, 69.99; H, 3.78; N, 11.66. Found: C, 69.82; H, 3.83; N, 11.63.

2-Cyano-1,3-bis(*p*-fluorobenzoyl)-2,3-dihydrobenzimidazole (14b). p-Fluorobenzoyl chloride (50.0 mmol, 7.93 g or 5.91 mL) and TMSCN (52 mmol, 7.4 mL) were added to a well-stirred solution of **13b** (50.0 mmol, 12.05 g) and $AlCl_3$ (200 mg) in CH_2Cl_2 (100 mL). The resulting solution was stirred at 25 °C for 36 h, and CH_2Cl_2 was removed by rotary evaporation. Water (300 mL) was added to the reaction mixture, which was then stirred for 5 h. The pale yellow solid obtained was filtered and dried (19.5 g, 100%). The crude product was treated with activated carbon (Norit brand) and recrystallized from ethyl acetate and hexane. Mp: 145.7–146.5 °C. FTIR: 3077, 2675 (C–H), 1681 (N–CO), 1606, 1510 (aromatic), 1490, 1410, 1387, 1373, 1367, 1351, 1278 cm^{-1}. ^1H NMR: δ 7.85–7.75 (m, 4H, Ar–H), 7.50–7.40 (m, 4H, Ar–H), 7.03–6.92 (m, 3H, H_2, H_5, H_6) and 6.65–6.45 (bs, 2H, H_4, H_7). Anal. Calcd for $C_{22}H_{13}N_3O_2F_2$: C, 67.86; H, 3.37; N, 10.80. Found: C, 67.78; H, 3.43: N, 10.75.

Attempted Methylation of 14a. To a well-stirred solution of **14a** (0.423 g, 1.20 mmol) and methyl iodide (0.43 g, 3.0 mmol) in dry DMF (10 mL) in a nitrogen atmosphere was added NaH (0.048 g of 60% dispersion in oil, 1.2 mmol). After stirring 24 h at 25 °C, the reaction was quenched by pouring into water (200 mL). It was extracted with dichloromethane (3 × 75 mL). Organic layers were pooled and washed with water (3 × 75 mL), dried over magnesium sulfate, concentrated, and dried to get a crude product, 0.33 g (75%). Proton NMR of this product showed <10% desired product **15** and the rest to be the starting material.

2-Benzoylbenzimidazole (16b) from 14a. To a well-stirred solution of **14a** (0.707 g, 2.00 mmol) in dry DMF (10 mL) in a nitrogen atmosphere was added in hexane (2 mL) NaH (0.096 g of 60% dispersion in oil, washed with hexane, 2.4 mmol). After stirring 24 h at 25 °C, the deep green solution was quenched by pouring into water (200 mL). The color of the solution turned to pale yellow. It was extracted with ethyl acetate (3 × 75 mL). Organic layers were pooled and washed with water (3 × 75 mL), dried over magnesium sulfate, treated once with Norit, concentrated, and dried to get crude product, 0.36 g (81%). **16b** was purified by recrystallization from ethyl acetate. Mp: 210–211 °C (lit.[23,24] mp 209–210 °C). FTIR: 3100–2300 (NH), 1657 (C=O), 1598, 1515 (aromatic), 1483, 1436 cm^{-1}. MS (EI): *m/e* 222 (M^+). MS (CI): *m/e* 223 [$(M + 1)^+$]. ^{13}C NMR (DMSO-d_6): δ 184.1 (–CO–), 148.2 and 135.9 (quaternary), 134.1, 131.2, 128.8, 124.9 (Ar–CH). ^1H NMR: δ 13.65–13.35 (bs, D_2O exchangeable, 1H), 8.61 and 8.58 (d or two s, 2H), 7.85–7.60 (m, 5H), 7.5–7.3 (m, 2H). Anal. Calcd for $C_{14}H_{10}N_2O$: C, 75.65; H, 4.54; N, 12.61. Found: C, 75.23; H, 4.71; N, 12.85.

Benzoylbenzoin (18) from 14a. To a well-stirred solution of **14a** (0.707 g, 2.00 mmol) and benzaldehyde (0.212 g, 2.00 mmol) in dry DMF (10 mL) in a nitrogen atomosphere was added in hexane (2 mL) NaH (0.096 g of 60% dispersion in oil, 2.4 mmol, washed with hexane). After stirring 24 h at 25 °C, the deep green solution was quenched by pouring into water (200 mL). The color of the solution turned to pale yellow. It was extracted with ethyl acetate (3 × 75 mL). Organic layers were pooled and washed with brine (3 × 75 mL), dried over sodium sulfate, treated once with Norit, concentrated, and dried to get crude product, 0.85 g (100%). **18** was purified by recrystallization from ethyl acetate. Mp: 124–125 °C (lit.[25–28] mp 124–125 °C). FTIR: 3070 (Ar–H), 2960 (CH), 1713, 1696 (C=O), 1649, 1599, 1589, 1583 and 1500 cm^{-1}. ^{13}C NMR: 193.58 and 165.06 (–CO–), 141.76, 135–133 (5 peaks, aromatic CH), 125.7 (quaternary), 121.6 and 77.4 (CH). ^1H NMR: δ 8.3–8.0 (m, 4H), 7.8–7.35 (m, 10H), 7.25–7.15 (m, 2H). Anal. Calcd for $C_{21}H_{16}O_3$: C, 79.73; H, 5.10. Found: C, 79.72; H, 5.03.

1,3-Bis(1-benzimidazyl)-1-propanone (23). To a well-stirred solution of benzimidazole (23.6 g, 200 mmol) in dry chloroform (200 mL) was added drop by drop at 0 °C acryloyl chloride (9.995 g, 110 mmol), and stirring was continued for 24 h. The reaction mixture was poured into water (1.5 L) and left overnight. The chloroform layer was separated, and the aqueous layer was extracted with chloroform (200 mL). The chloroform layers were pooled, washed consecutively with aqueous 8% HCl (2 × 100 mL), aqueous saturated $NaHCO_3$ (2 × 100 mL), and water (3 × 100 mL), dried over Na_2SO_4, and concentrated, to get product **23**, 3.34 g (12%, not optimized). Mp: 137–138 °C. FTIR: 3400–2960, 1676, 1647, 1539, 1495, 1450, 746 cm^{-1}. ^1H NMR: δ 9.26 (s, 1H, H_2), 8.2 (s, 1H, $H_{2'}$), 7.64 (t, J = 6.6 Hz, 2H, Ar–H), 7.44–7.40 (m, 1H, Ar–H), 7.29–7.09 (m, 3H, Ar–H), 3.34 (t, J = 6.1 Hz, 2H, $COCH_2$), 2.86 (t, J = 6.4 Hz, 2H, $N–CH_2$).

Bis(1-benzimidazyl)-1,6-dicarbonylhexane (24). To a well-stirred solution of benzimidazole (22 mmol, 2.6 g) and triethylamine (11 mmol, 1.1 g) in DMF (10 mL) was added adipoyl chloride (10.0 mmol, 1.83 g) in dichloromethane (10 mL). The resulting reaction medium was stirred at 25 °C for 24 h. The reaction mixture was poured into water and stirred for 3 h. An essentially quantitative yield of the product was obtained by filtering the solid. The solid was washed with water, ethanol (2 × 10 mL), and ether (2 × 25 mL) and dried. The crude product was taken up in hot DMF (35 mL) and precipitated into water (250 mL), filtered, crystallized from tetrahydrofuran, and dried.

The yield was 3.2 g (93%). Mp: 250–252 °C (dec). FTIR: 3150–2900 (C–H), 1721 (N–CO), 1680, 1677, 1610, 1507 (aromatic), 1477, 1451, 1419, 1387, 1348, 1335, 1309, 1284, 1235, 1204, 1165 cm^{-1}. ^1H NMR: δ 8.96 (s, 2H, H_2), 8.25–8.15 (m, 2H, Ar–H), 7.78–7.74 (m, 2H, Ar–H), 7.45–7.35 (m, 4H, Ar–H), 3.3–3.2 (s, 4H, $COCH_2$) 1.95–1.80 (s, 4H, CH_2CH_2). Anal. Calcd for $C_{20}H_{18}N_4O_2 \cdot 0.25H_2O$: C, 68.46; H, 5.32; N, 15.97. Found: C, 68.53; H, 5.24; N, 16.02.

Poly(benzimidazole Reissert compound)s 25 (Representative Procedure). To a well-stirred suspension of **24** (10.0 mmol, 3.46 g) in *N*-methylpyrrolidinone (35 mL) was added adipoyl chloride (10.0 mmol, 1.83 g). The clear solution obtained after the addition of trimethylsilyl cyanide (22 mmol, 5.0 mL) was stirred at 25 °C for 24 h. The reaction mixture was quenched by pouring into water (600 mL). The precipitate obtained was treated with 8% aqueous HCl and then thoroughly washed with water, ethanol, and ether and dried (90 °C, 0.8 Torr, overnight). The crude product weighed 4.9 g. $[\eta]$ = 0.1 dL/g (NMP, 25 °C). TGA (in air): 10% weight loss at 220 °C. DSC: no glass transition (T_g) or melting (T_m) observed in either the first or second heating up to 150 °C. FTIR: 3125–2910 (C–H), 1721, 1680, 1677 (C=O), 1607, 1507, 1477, 1451, 1419, 1387, 1348 cm^{-1}. ^1H NMR: δ 8.3–6.7 (m, 5H, Ar–H), 3.2–2.2 (m, 4H, $COCH_2$), 2.0–1.4 (m, 4H, CH_2-CH_2). The above workup was repeated, and it was found that the polymer was degrading during the viscosity measurements ($[\eta]$ = 0.03 dL/g, NMP, 25 °C).

Hydrolysis of 14a with K_2CO_3. A mixture of **14a** (2.00 mmol, 0.707 g) and K_2CO_3 (2.20 mmol, 0.304 g) in DMAc (10 mL, dry) was stirred for 3 days at 25 °C under dry conditions. It was then poured into water (500 mL), stirred overnight, and extracted with ethyl acetate (3 × 100 mL). Organic layers were pooled, washed with water (4 × 100 mL), dried over Na_2SO_4, and concentrated to get crude benzimidazole (0.24 g, 100%). It was then purified by recrystallization from ethyl acetate. Mp and ^1H NMR matched those of benzimidazole. The aqueous layer was acidified (to pH 2) and extracted with ethyl acetate (3 × 100 mL). The organic layer was washed with water (3 × 100 mL), dried over Na_2SO_4, and concentrated to get benzoic acid, 0.43 g (88%).

Hydrolysis of 14b with K_2CO_3. A mixture of **14b** (2.0 mmol, 0.78 g) and K_2CO_3 (2.2 mmol, 0.31 g) in DMAc (10 mL, dry) was stirred for 3 days at 25 °C under dry conditions. It was then poured into water (500 mL), stirred overnight, and extracted with ethyl acetate (3 × 100 mL). Organic layers were pooled, washed with water (4 × 100 mL), dried over Na_2SO_4 and concentrated to get crude benzimidazole, 0.24 g (100%). It was then purified by recrystallization from ethyl acetate. Mp and ^1H NMR matched those of an authentic sample of benzimidazole. Anal. Calcd for $C_7H_6N_2$: C, 71.16; H, 5.12; N, 23.72. Found: C, 71.55; H, 5.31; N, 23.56. The aqueous layer was acidified (to pH 2) and extracted with ethyl acetate (3 × 100 mL). The organic layer was washed with water (3 × 100 mL), dried over Na_2SO_4, and concentrated to get *p*-fluorobenzoic acid, 0.564 g (100%).

Hydrolysis of 3 with K_2CO_3. A mixture of **3** (2.0 mmol, 0.52 g) and K_2CO_3 (2.2 mmol, 0.304 g) in DMAc (10 mL, dry) was stirred for 3 days at 25 °C under dry conditions. It was then poured into water (500 mL) and stirred overnight. The solid obtained was filtered, washed with excess water and hexanes (100 mL), and dried (0.5 g, 96%). Mp and ^1H NMR matched those of the starting material.

Hydrolysis of 20 with K_2CO_3. A mixture of **20** (2.0 mmol, 0.52 g) and K_2CO_3 (2.2 mmol, 0.304 g) in DMAc (10 mL, dry) was stirred for 3 days at 25 °C under dry conditions. It was then poured into water (500 mL) and stirred overnight. The solid obtained was filtered, washed with excess water and hexanes (100 mL), and dried (0.42 g). The crude product contained at least three products, purification of which by flash column (silica) chromatography was unsuccessful.

Reaction of 20 with K_2CO_3 in the Presence of PhCHO. A mixture of **20** (2.0 mmol, 0.52 g), K_2CO_3 (2.2 mmol, 0.304 g), and PhCHO (2.2 mmol, 0.23 mL) in DMAc (10 mL, dry) was stirred for 2 days at 25 °C under dry conditions. It was then poured into water (500 mL) and stirred overnight. The solid obtained was filtered, washed with excess water and hexanes (100 mL), and dried (0.71 g). The crude product contained at least three products, purification of which by flash column (silica) chromatography was unsuccessful.

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