Polymers Containing Di(1*H*-benzo[*d*]imidazol-2-yl)arene Moieties: Polymerization via N−C Coupling Reactions

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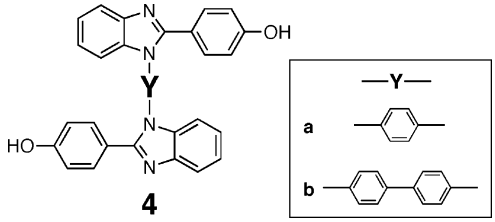
There has been a great deal of recent effort centered on Pd-catalyzed C−N coupling reactions of NH groups with unactivated halides[1,2] as well as methods to improve the standard copper-catalyzed Ullmann condensation reactions.[3−6] These reactions generally require the use of aryl bromides or iodides and quite high yields have been obtained, but in general, the yields are not high enough to consider their use in the formation of high molecular weight polymers.

In a series of papers and patents, Hergenrother and associates described the synthesis of poly(arylene ether benzimidazole)s by the reaction of bisphenols containing benzimidazole moieties **1** with activated halides **2** (Scheme 1).[7−13] The synthesis, properties, and potential applications of this class of polymers have been extensively reviewed.[14,15]

Poly(arylene ether)s containing *N*-arylenebenzimidazole groups were also prepared by the aromatic nucleophilic displacement reaction of bis(4-hydroxyphenyl-*N*-arylenebenzimidazole)s **4** with activated aromatic difluorides in sulfolane at 200 °C in the presence of anhydrous potassium carbonate.[8,9,16] The polymers exhibited glass transition temperatures (T_gs) ranging from 264 to 352 °C and inherent viscosities from 0.79 to 1.99 dL g^{-1} and had very good thermal stability.[7,17]



Polymers containing *N*-arylene moieties exhibited lower T_gs, tensile properties, and moisture uptake than the poly(arylene ether benzimidazole)s, presumably due to the lack of hydrogen bonding. The preparation of these polymers is a very lengthy and expensive process.[18] Poly(*N*-phenylbenzimidazole)s[18−20] have also been synthesized, and they are also more soluble and are reported to be more thermooxidatively stable than the parent polybenzimidazole (PBI) polymers since the NH groups have been replaced by *N*-phenyl groups.

In the preparation of poly(arylene ether benzimidazole)s and poly(*N*-arylenebenzimidazole)s[8,9] both NH and OH groups are present in the monomers, but only the OH groups are reported to react under the conditions used. Several years ago we found that high molecular weight polymers **6** could be prepared from 4-(4-hydroxyphenyl)phthalazin-1(2*H*)-one **5** by reaction with activated halides (Scheme 2).[21,22] The N−C coupling reaction was unexpected and indicated that the NH group behaved like a phenolic OH group in this reaction.

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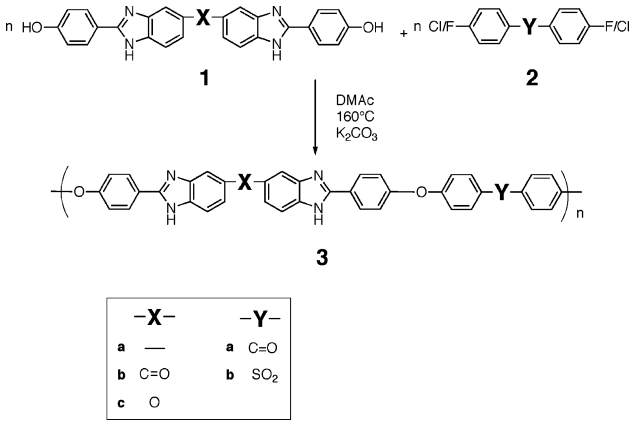
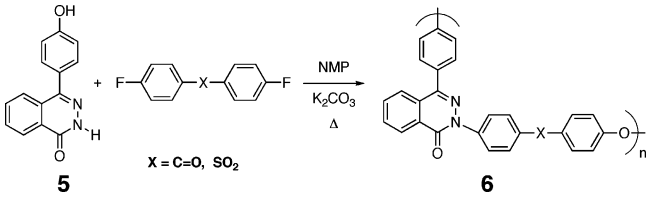
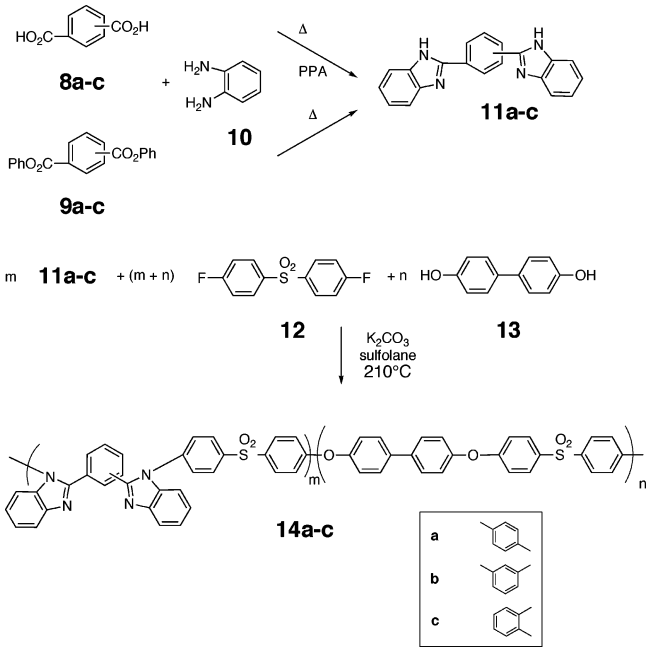
Scheme 1. Synthesis of Poly(arylene ether) Benzimidazoles



Scheme 2. Synthesis of Phthalazinone-Containing Polymers



Scheme 3. Synthesis of Poly(arylenebenzimidazole)s 14a−c (n = 0) and Copolymers with Bisphenols



The di(benzimidazolyl)benzenes **11a−c** are very readily available (Scheme 3) by, for example, reaction of the isomeric phthalic acids **8a−c**,[23] or the corresponding phenyl esters **9a−c**, with *o*-phenylenediamine **10**.[24] These materials were synthesized as model reactions for the synthesis of polybenzimidazoles from dibasic acids and, e.g., 3,3′,4,4′-tetraaminobiphenyl.[25]

Surprisingly, we have found that under similar conditions, but at higher temperatures than those used for the preparation of poly(arylene ether benzimidazole)s and poly(*N*-arylenebenzimidazole)s, the NH group in benzimidazoles will also undergo a C−N coupling reaction with activated halides, e.g., bis(4-fluorophenyl)sulfone, to give high molecular weight, linear

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Table 1. Properties of Copolymers

polymer	*m*	*n*	T_g[a] (°C)	$TGA_{-5\%}$[b] (°C)	η_{inh}[c] (dL/g)	λ_{UV}[d] (nm)	λ_{ex}[e] (nm)	λ_e[f] (nm)
14a	0.3	0.7	253	526	0.38	282, 342	350	406
14b	1	0	296	530	0.22			
	0.7	0.3	274	519	0.44	281	319	378
	0.5	0.5	260	533	0.34	282	278	379
	0.3	0.7	248	521	0.75	282	327	387
14c	0.3	0.7	245	542	0.39	279	314	401

[a] Obtained by DSC under N_2 with heating rate 20 °C/min. [b] 5% weight loss temperature. [c] 5 g/dL in $CHCl_3$ at 30 °C. [d] Maximum absorption wavenumber in UV−vis spectra. [e] Excitation wavenumber. [f] Fluorescence emission wavenumber.

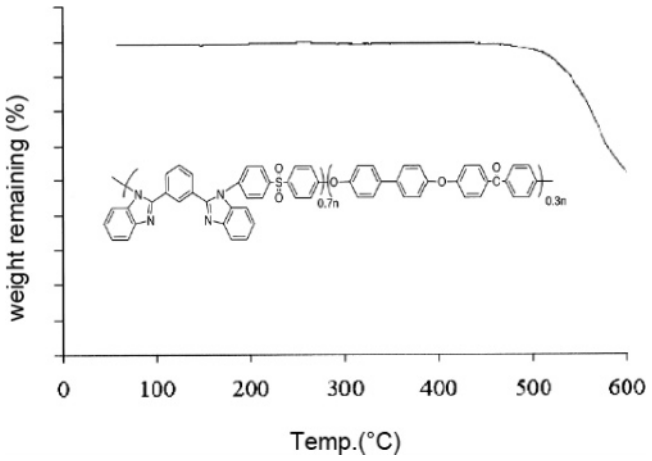

Figure 1. TGA analysis of **14b**.

polymers **14a**−**c** ($n = 0$), as illustrated in Scheme 3. We have also synthesized high molecular weight copolymers by copolymerization of the bisbenzimidazoles **11a**−**c** with 4,4′-biphenol **13** (Scheme 3).

As would be expected, since they are also poly(arylene ether) benzimidazoles, the properties of the copolymers are similar to those of the polymers prepared by Hergenrother et al.[7,8] The homopolymers and copolymers have very high T_gs, and they are very thermally stable. The $T_{d-5\%}$ (5% weight loss in N_2) for the homopolymers and copolymers **14b** ranges between 519 and 533 °C (Table 1). A typical TGA curve for **14b** is shown in Figure 1.

The following example for the synthesis of the copolymer **14b** ($m = 0.7$; $n = 0.3$) is typical of the procedure used. To a 25 mL three-necked round-bottom flask equipped with a Dean−Stark trap, water condenser, magnetic stirrer, and nitrogen inlet was added 4,4′-biphenol **13** (0.056 g 0.30 mmol), 1,3-(dibenzimidazolyl)benzene **11b** (0.22 g, 0.70 mmol), bis(4-fluorophenyl)sulfone **12** (0.25 g, 1.0 mmol), $CaCO_3$(0.15 g, 1.5 mmol), and anhydrous K_2CO_3 (0.28 g, 2.00 mmol) in 2 mL of sulfolane and 3 mL of chlorobenzene. The reaction mixture was heated to azeotrope off the resulting water with the chlorobenzene. The chlorobenzene was then removed, and the reaction mixture was brought up to 180−210 °C for 1−2 h. When the reaction mixture became too viscous to be stirred, an additional 2 mL of sulfolane was added to dilute the solution, and it was kept at 210 °C for 20 min until the viscosity increased significantly. The reaction mixture was cooled down and diluted with dichloromethane, and the solution was poured into 200 mL of methanol and 2 mL of acetic acid to precipitate out the polymer. The resulting polymer was redissolved in chloroform, the chloroform solution was filtered through a thin layer of celite to remove inorganic materials, and the polymer was isolated by precipitation into methanol. The polymer was collected by filtration and dried in vacuo at 80 °C for 24 h (yield 97%).

We previously reported that in the preparation of high molecular weight poly(aryl ether) dendrimers the fluoride ion released in the reaction promoted equilibration reactions as a result of chain cleavage reactions.[26] In those reactions, and in the present case, it was necessary to add $CaCO_3$ to remove the fluoride ion formed as insoluble CaF_2 so that high molecular weight polymer could be produced.

The polymers and copolymers derived from the isomeric di(benzimidazolyl)benzenes all absorb UV light and are strongly fluorescent in the blue region with fluorescence maxima ranging from 378 to 406 nm (Table 1).

In conclusion, we have reported a new synthesis of poly(arylenebenzimidazole)s, and copolymers with bisphenols, by a N−C coupling reaction from readily available bisbenzimidazole monomers. The polymers are high-performance engineering thermoplastics. The scope of this new polymerization reaction is under study.

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