

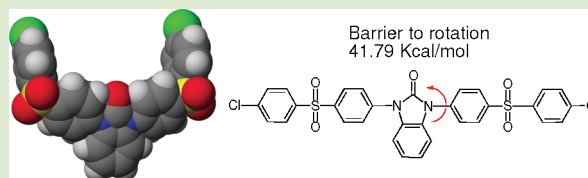
Synthesis and Properties of Polymers Containing 2*H*-Benzimidazol-2-one Moieties: Polymerization via N–C Coupling Reactions

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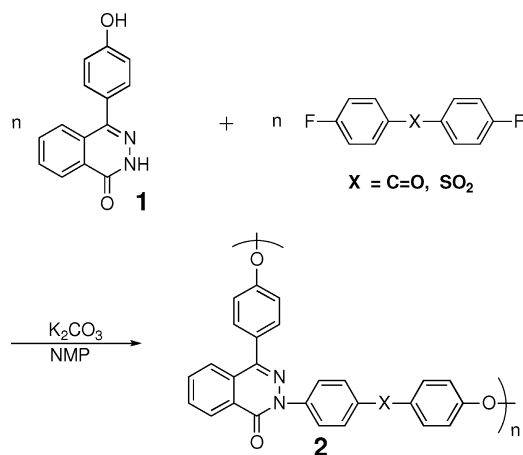
S Supporting Information

ABSTRACT: Novel homopolymers and copolymers containing 2*H*-benzimidazol-2-one units have been synthesized by N–C coupling reactions of 1*H*-benzo[*d*]imidazol-2(3*H*)-one and activated aromatic dihalides under conditions similar to those for the synthesis of poly(aryl ether)s and poly(benzimidazole sulfone)s. 1*H*-Benzo[*d*]imidazol-2(3*H*)-one behaved like a bisphenol in the polymerization reaction to afford, quantitatively, high molecular weight linear polymers with inherent viscosities (η_{inh}) ranging from 0.57 to 1.31 dL/g. The polymers were soluble in various organic solvents, and transparent, flexible, and creasable films were cast from its dichloromethane-solution. The homopolymer had a remarkably high glass transition temperature (T_g 348 °C) and good thermal stability. Only 30 mol % (8.9 wt %) of the 2*H*-benzimidazol-2-one unit for the copolymer with 4,4'-biphenol was required to raise the T_g of commercial poly(aryl ether), Radel R-5000 from 220 to 269 °C.



We previously found that high molecular weight polymers **2** could be synthesized from 4-(4-hydroxyphenyl)-phthalazin-1(2*H*)-one **1** by reaction with activated aromatic halides under conventional conditions for the synthesis of poly(aryl ether)s (Scheme 1).^{1,2} The N–C coupling reaction

Scheme 1. Synthesis of Phthalazinone-Containing Polymers

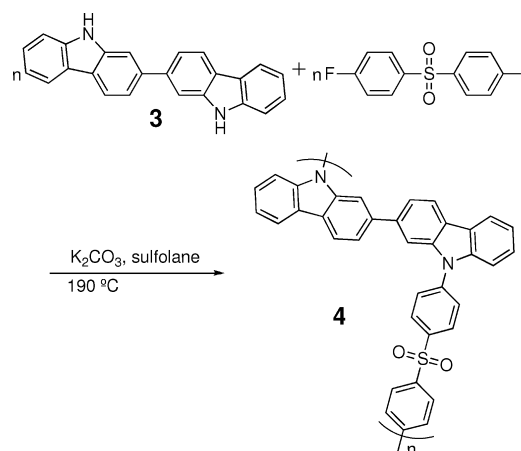


was unexpected and indicated that the NH group behaved like a phenolic OH group in this reaction. These polymers are excellent high temperature thermoplastics and are currently being commercialized. A series of polymers have also been synthesized by N–C coupling reactions from polyfluorinated phthalazinones³ and bisphthalazinones.^{4,5}

We have recently reported that, at elevated temperatures, bisbenzimidazoles **3** also reacted with activated aromatic halides to give high molecular weight polymer **4** that was thermally stable

(Scheme 2).⁶ The polymer **4** was highly fluorescent with emission in the blue region of the spectrum. The polymer **4** was

Scheme 2. Synthesis of Carbazole-Containing Polymers



a rigid structure with little flexibility. We have recently reported more flexible bisbenzimidazoles that yielded soluble polymers after a N–C coupling polymerization reaction.⁷

Surprisingly, we have also found the NH group in benzimidazoles will also undergo a N–C coupling reaction with activated aromatic halides, for example, bis(4-fluorophenyl)sulfone.^{8,9} High molecular weight, linear polymers (e.g., **6**) were formed from bisbenzimidazoles (e.g., **1,3**-

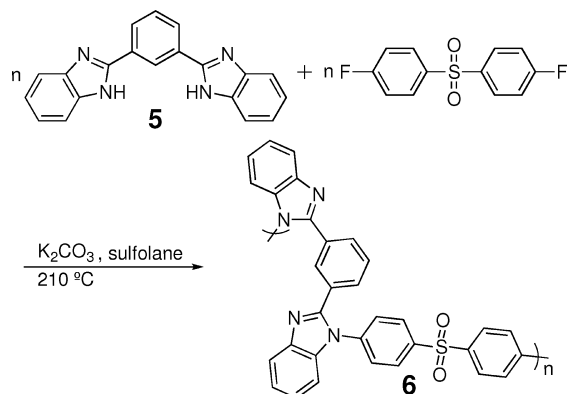
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bis(1*H*-benzo[*d*]imidazol-2-yl)benzene **5**; Scheme 3). The homopolymers and copolymers with 4,4'-biphenol had very

Scheme 3. Synthesis of Poly(benzimidazole sulfone)s

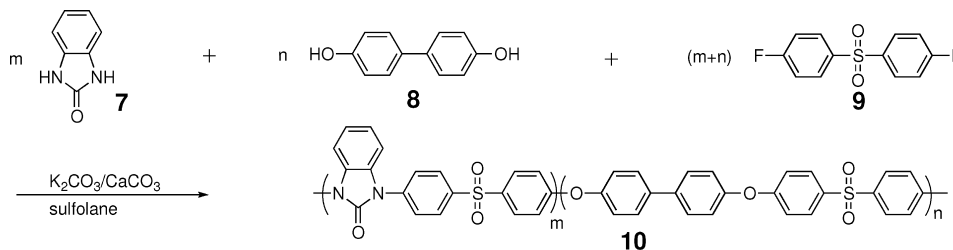


high glass transition temperatures (T_g) ranging between 220 °C (poly(aryl ether)) and 296 °C depending on the concentration of the 4,4'-biphenol. Further, all these polymers had good thermal stability.

1*H*-Benzo[*d*]imidazol-2(3*H*)-one **7** is very readily available by the reaction of urea with *o*-phenylenediamine.^{10,11} Compound **7** has been reported to be stable toward acid or base hydrolysis under normal conditions.¹² The alkylation of **7** has been described in a number of papers.^{13–15} The reaction of **7** with unactivated aromatic bromide (e.g., 4-bromoanisole) with a CuI catalyst in toluene at reflux for 24 h gave an 82% yield of the diaryl-substituted product.¹⁶ Since almost quantitative yields are required to synthesize high molecular weight linear polymers, the yields are well short of the yields that would be required to give a high molecular weight polymer using appropriately disubstituted bromo-compounds. Only one patent has so far dealt with the polycondensation with **7** as monomer.¹⁷ The reactions of **7** with aromatic diacid chlorides, aliphatic dichlorides, and bis(halomethyl)benzene were described. However, in most cases, the yields of polymers were quite low, and no information on molecular weights was provided. The reaction of **7** with isophthaloyl dichloride in 1,2-dichlorobenzene in the presence of magnesium, for example, was reported to give a polymer in only 47% yield with a melt temperature of 300 °C. A polymer from 1,5-dichloropentane was also synthesized, but no properties were given.

Herein, we report the first examples of well-characterized and high molecular weight all-aromatic poly(benzimidazolone sulfone)s by a novel N–C coupling polycondensation reaction of 1*H*-benzo[*d*]imidazol-2(3*H*)-one **7** with activated aromatic dihalide **9**. Copolymerization of **7** and **9** with 4,4'-biphenol **8** is also described.

Scheme 4. Synthesis of Poly(benzimidazolone sulfone)s and Copolymers with 4,4'-Biphenol



The N–C coupling reaction of **7** and **9** was carried out under conditions similar to those used to synthesize poly(aryl ether)s and poly(benzimidazole sulfone)s by an aromatic nucleophilic substitution⁹ (Scheme 4). Desired high molecular weight (M_n 16000, M_w 35000, and MWD 2.1) poly(benzimidazolone sulfone) **10** ($m = 1$) was successfully obtained in 93% yield as a white fiber (Table 1).¹⁸ High molecular weight (M_w up to

Table 1. Properties of Poly(benzimidazolone sulfone)s and Copolymers with 4,4'-Biphenol

m	n	T_g^a (°C)	T_{ds}^b (°C)	η_{inh}^c (dL/g)	M_n^d	M_w^d	MWD ^d
1	0	348	487	0.57	16000 ^e	35000 ^e	2.1 ^e
0.7	0.3	315	465	1.31	68000	130000	1.9
0.5	0.5	290	506	1.14	60000	120000	2.0
0.3	0.7	269	514	1.31	32000	54000	1.6
0	1	220 ^f	550 ^f	g	g	g	g

^aObtained by DSC in N₂ at a heating rate of 20 °C/min. ^b5% weight loss temperature, measured by TGA in N₂ at a heating rate of 20 °C/min. ^c0.5 g/dL in NMP at 30 °C. ^dDetermined by GPC in CHCl₃ at 1.0 mL/min at rt calibrated with polystyrene standards. ^eDetermined by GPC in DMF at 1.0 mL/min at 30 °C calibrated with polyethylene glycol standards. ^fRadel R-5000. ^gNot determined.

130000) copolymers **10** ($m = 0.7–0.3$) with 4,4'-biphenol were readily obtained in high yield (>91%) under similar conditions. These results demonstrated that 1*H*-benzo[*d*]imidazol-2(3*H*)-one **7** behaved like a bisphenol to afford high yields of linear, high molecular weight polymers **10** ($m = 1–0.3$) under conditions similar to those for the synthesis of poly(aryl ether)s and poly(benzimidazole sulfone)s. The homopolymer **10** ($m = 1$) was soluble in various polar solvents such as 1-methyl-2-pyrrolidinone (NMP), while the copolymers **10** ($m = 0.7–0.3$) with 4,4'-biphenol were soluble in various common organic solvents such as dichloromethane and NMP. Transparent, flexible, and creasable films of homopolymer **10** ($m = 1$) and copolymers **10** ($m = 0.7–0.3$) were cast from its dichloromethane solution.

All the poly(benzimidazolone sulfone)s **10** ($m = 1–0.3$) showed very high thermal stability (T_{ds} up to 514 °C). The homopolymer **10** ($m = 1$) showed a remarkably high T_g (348 °C) because of the introduction of the rigid 2*H*-benzimidazol-2-one unit into the polymer backbones. This will be further discussed in the next section. The T_g of the copolymers **10** ($m = 0.7–0$) ranged between 220 °C for the commercially available homopolymer (poly(aryl ether) **10** ($m = 0$)¹⁹ and 315 °C, depending on the concentration of the 4,4'-biphenol. Because of the very high T_g of the homopolymer **10** ($m = 1$; 348 °C), only small amounts of **7** need to be added to raise the T_g of the resulting copolymer to much higher temperatures to open up new potential applications for engineering thermoplastics.²⁰ For

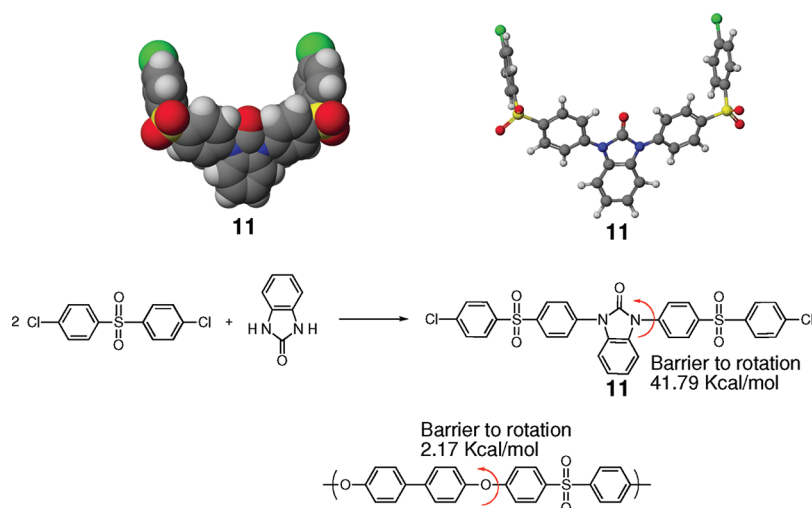


Figure 1. Barrier to rotation of C–O–C and C–N–C bonds generated by a molecular mechanics calculation using the Fujitsu CAChe 4.5 program.

example, only 30 mol %, that is, 8.9 wt % of the 2*H*-benzimidazol-2-one unit is required to raise the T_g of commercially available poly(aryl ether), Radel R-5000 from 220 to 269 °C, as prepared from 4,4'-biphenol and bis(4-chlorophenyl) sulfone.

Examination of molecular models of the intermediate **11** obtained by reaction of 1*H*-benzo[*d*]imidazol-2(3*H*)-one **7** provides an explanation of the remarkably high T_g for poly(benzimidazolone sulfone)s **10** (Figure 1). The barrier to rotation of the very flexible C–O–C bond in the poly(aryl ether) is only 2.17 kcal/mol, whereas the barrier to rotation of the C–N–C bond is calculated to be 41.79 kcal/mol, so that the products, poly(benzimidazolone sulfone)s **10**, containing the rigid structures as in **11**, which raise the T_g s, are formed. The space-filling model further illustrates the steric hindrance in the rigid structural unit produced that would dramatically increase the T_g s of the copolymers produced.

The following example for the synthesis of the copolymer **10** ($m = 0.3$) is typical of the procedure used. To a 25 mL three-necked, round-bottom flask equipped with a Dean–Stark trap, a condenser, a magnetic stirrer, and an argon inlet were added 1*H*-benzo[*d*]imidazol-2(3*H*)-one **7** (0.080 g, 0.60 mmol), 4,4'-biphenol **8** (0.26 g, 1.4 mmol), bis(4-fluorophenyl)sulfone **9** (0.51 g, 2.0 mmol), CaCO₃ (0.20 g, 2.0 mmol), anhydrous K₂CO₃ (0.28 g, 2.0 mmol), sulfolane (1.6 g), and chlorobenzene (3 mL). The mixture was heated to azeotrope off the resulting water with chlorobenzene. The chlorobenzene was then removed, and the resulting mixture was heated at 180–200 °C for 1–2 h. When the reaction system became too viscous to be stirred, an additional 2 g of sulfolane was added to dilute the solution, and the mixture was kept at 200 °C for an additional 30 min until the viscosity significantly increased. The reaction mixture was cooled down and diluted with dichloromethane. The solution was poured into 100 mL of methanol containing 1 mL of acetic acid to precipitate out the resulting polymer. The precipitated polymer was collected by filtration and redissolved in dichloromethane. The dichloromethane solution was filtered through a thin layer of Celite to remove inorganic materials. The polymer was further purified by reprecipitation from dichloromethane solution into methanol. The polymer collected by filtration was dried in vacuo at 80 °C for 24 h (yield 91%). High molecular weight copolymers can

also be synthesized using the less expensive bis(4-chlorophenyl)sulfone instead of bis(4-fluorophenyl)sulfone.

We previously reported that in the preparation of high molecular weight poly(aryl ether) dendrimers the fluoride ion released in the reaction cleaved ether linkages in the dendrimers.²¹ In those reactions, and in the present case, it was necessary to add CaCO₃ to remove the fluoride ion formed as insoluble CaF₂ so that the high molecular weight polymer could be obtained.

In conclusion, we have described the successful synthesis of the first examples of high molecular weight all-aromatic poly(benzimidazolone sulfone)s and copolymers with bisphenols by a novel N–C coupling reactions from readily available 1*H*-benzo[*d*]imidazol-2(3*H*)-one monomer. A new family of engineering thermoplastics with a range of higher use temperatures is now possible where the T_g of the copolymers can be tailored to the needs of the potential application. Further investigations on this new polymerization are ongoing in our laboratory.

■ ASSOCIATED CONTENT

📄 Supporting Information

Characterization (MALDI-TOF mass and ¹H NMR spectra) of poly(benzimidazolone sulfone) **10** ($m = 1$). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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