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Synthesis of Poly(thioether thioether ketone) (PTTK) Starting from Hydroquinone

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Poly(ether ether ketone) (PEEK) is an important commercial high-performance polymer with outstanding heat resistance and solvent resistance.[1] It is manufactured from hydroquinone and 4,4′-difluorobenzophenone in the presence of potassium carbonate above 300 °C in diphenyl sulfone solvent.[2] Poly(thio-4-phenylene) (PPS) is another high-performance polymer possessing excellent mechanical properties, along with fire retardant properties, low moisture absorption, and good affinity for inorganic fillers.[3] Due to these excellent properties, PPS has been extensively studied and significant advances have been made in its synthesis in recent years.[4−16] Poly(thioether thioether ketone) (PTTK) is a hybrid of PEEK and PPS. One would expect that PTTK would have a much higher glass transition temperature than PPS while still possessing extremely high thermal stability, flame retardance, and excellent solvent resistance. PTTK has been synthesized from 4,4′-difluorobenzophenone and 1,4-phenylenedithiol by a nucleophilic substitution reaction.[17] However, 1,4-phenylenedithiol is oxidatively unstable and its purification is difficult and tedious. Herein, we report a novel process for the preparation of PTTK starting from hydroquinone based on a one-pot polymerization reaction between a bis(*N*,*N*-dimethyl-S-carbamate) and a fluoro compound in the presence of a mixture of cesium carbonate and calcium carbonate.[18−22] This process has the advantage of using an easily prepared and easily purified starting material, bis(*N*,*N*-dimethyl-S-carbamate) **3**, instead of using the oxidatively unstable 1,4-phenylenedithiol.

The procedure we previously used to synthesize bis(*N*,*N*-dimethylthiocarbamate)s[18−21] in KOH methanolic solution was not suitable for preparation of bis(*N*,*N*-dimethylthiocarbamate) **2**. A modified method was used to prepare this compound (Scheme 1). Typically, hydroquinone **1** (11.0 g, 0.1 mol) and a slight excess of *N*,*N*-dimethylthiocarbamyl chloride (27.2 g, 0.22 mol) was heated with quinoline (30 mL) at 190 °C under a nitrogen atmosphere for 45 min. The resulting solid was washed with concentrated HCl (20 mL), water (100 mL), and methanol (30 mL) and recrystallized from chloroform/methanol solution. A highly pure white solid was obtained in 70% yield. The bis(*N*,*N*-dimethylthiocarbamate) **2** was heated in the bulk at 260 °C under N_2 for 2 h to afford the desired bis(*N*,*N*-dimethyl-S-carbamate) **3** by the Newman−Kwart rearrangement reaction.[23] Pure monomer **3** (yield, 83%) was obtained by recrystallization from chloroform/methanol and further recrystallization from methyl ethyl ketone (MEK).

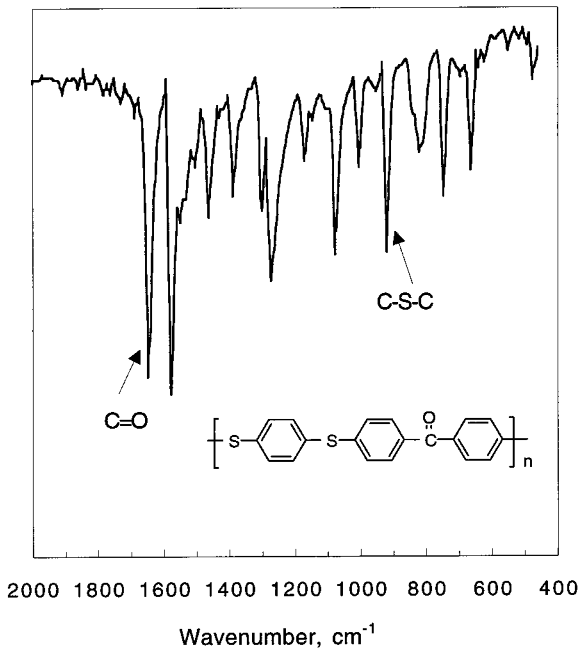

Figure 1.

The reaction conditions we used previously to prepare other poly(arylene thioether)s, which used a 0.5 equiv amount of cesium carbonate as the base (in the presence of excess of calcium carbonate) and diphenyl sulfone as the solvent failed to form any high molecular weight polymers.[18−20] Since the resulting PTTK is a semicrystalline polymer, a higher temperature is required to keep it in solution. However, once the temperature reached 270 °C, the reaction mixture became an intense red color, which is an indication of a redox reaction between the thiophenoxide anion and the sulfone group in diphenyl sulfone. Benzophenone was next used as the polymerization solvent (Scheme 2),[17,24] and it proved to be the solvent of choice for the present application. The amount of cesium carbonate used also had a profound influence on the polymerization. When 2 equiv of Cs_2CO_3 was used, only low molecular weight red PTTK oligomers were obtained. As the amount of Cs_2CO_3 used decreased, the color of the product became lighter and molecular weights increased. With 1 equiv of cesium carbonate, a relatively low molecular weight PTTK was obtained as a brown powder with an inherent viscosity of 0.24 dL/g in concentrated sulfuric acid. When 0.2 equiv of Cs_2CO_3 was used, an off-white podwer was obtained with an inherent viscosity of 0.32 dL/g. A PTTK was obtained with an inherent viscosity of 0.30 dL/g when 0.1 equiv of Cs_2CO_3 was used. With smaller amounts of Cs_2CO_3, the polymerization rate became very slow. Therefore, the optimum amount is 0.1−0.2 equiv of Cs_2CO_3 with an excess amount of calcium carbonate to prepare PTTK.[25]

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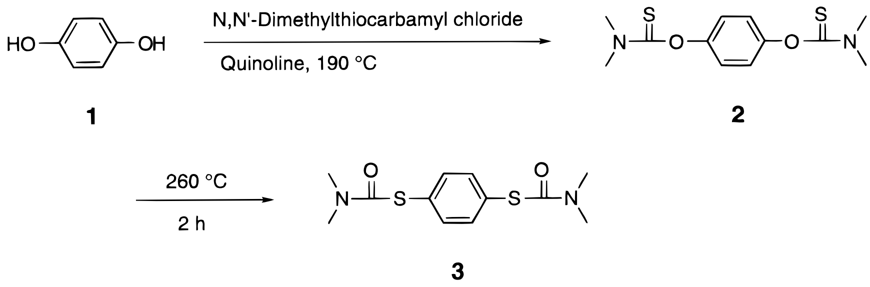
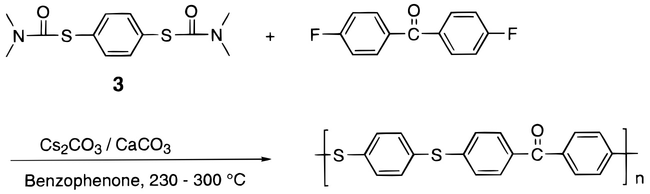
Scheme 1



Scheme 2



PTTK obtained by the present method is a semicrystalline material, which did not show any glass transition temperature (T_g) in the DSC in the first scan.[26] However, when quenched from 350 °C and subjected to DSC analysis, it showed a glass transition temperature (T_g), a crystallization temperature, and a melting point. The semicrystalline product, like PEEK, is very insoluble so that films cannot be cast from solution; however, when it is quenched from the melt, a tough flexible product is obtained. PTTK prepared using 0.2 equiv of Cs_2CO_3 has a T_g of 136 °C, which is the same as the reported value,[17] a T_c of 183 °C, and a T_m of 296 °C. The FT-IR spectrum of the PTTK is shown in Figure 1, which is identical to the literature spectrum.[17]

A proposed mechanism for the polymerization reaction is shown in Scheme 3. Cesium carbonate cleaves the S-carbamate to form a thiophenoxide anion. Calcium carbonate is an inert base when used alone. However, it reacts with the cesium fluoride formed from the nucleophilic substitution reaction to regenerate cesium carbonate. From the mechanism, one can expect that the mixture of cesium fluoride and calcium carbonate would also be a suitable base for the preparation of poly(arylene thioether)s starting from bis(*N*,*N*-dimethyl-S-carbamate)s and difluoro compounds. To verify this hypothesis, an experiment was carried out to prepare PTTK by using 0.2 equiv amounts of cesium fluoride (0.09 g, 0.6 mmol) instead of 0.2 equivalent amounts of cesium carbonate. As expected, PTTK was obtained with an inherent viscosity of 0.21 dL/g.

In conclusion, we have established a new method for the preparation of PTTK, which has the combined properties of PEEK and PPS. An easily prepared and purified material, bis(*N*,*N*-dimethyl-S-carbamate) **3**, was used as the starting material. Currently, we are applying the new methodology to synthesize a new polymer, poly(thioether biphenylene thioether ketone) (PTBTK), and to synthesize random copolymers of PEEK, PEBEK, PTTK, and PTBTK with modified properties. The results will be reported in due course.

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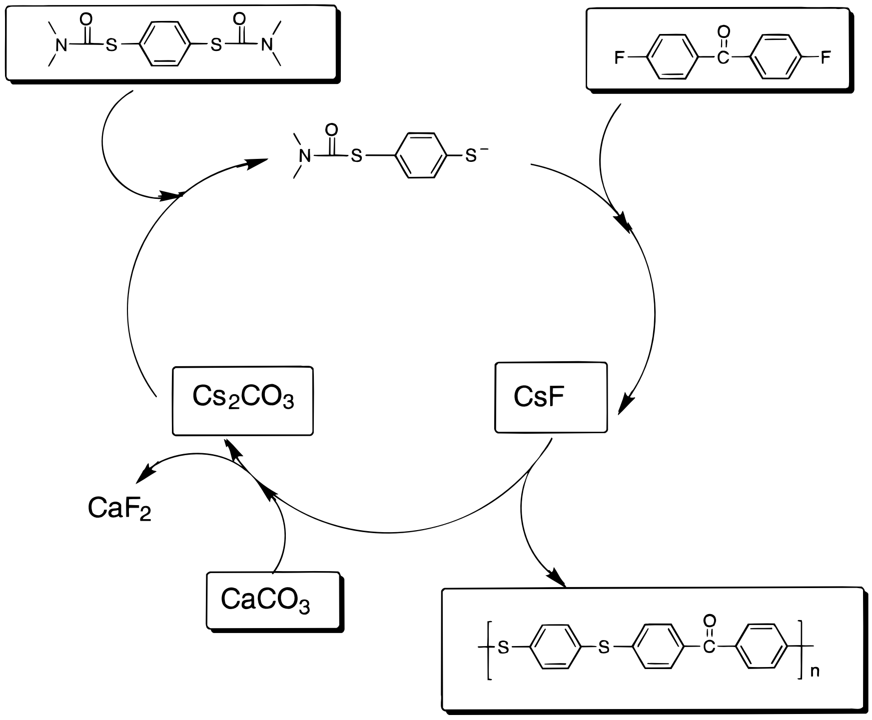
Scheme 3



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(25) Typical experimental procedure: Into a 50 mL three neck round-bottom flask equipped with a nitrogen inlet, a magnetic stirrer, a Dean−Stark trap and a condenser were charged 4, 4′-difluorobenzophenone (0.6546 g, 3.00 mmol), **3** (0.8532 g, 3.00 mmol), benzophenone (8.0 g), cesium carbonate (0.10 g, 0.3 mmol), and calcium carbonate (0.90 g, 9.0 mmol). The mixture was heated at 200 °C for 1 h, and then it was raised to 250 °C for another 1 h. Finally, the temperature was raised to 300 °C to keep the polymer in solution and kept at that temperature for 4 h. The mixture was cooled, washed consecutively with 100 mL of hot acetone, 100 mL of 5% aqueous HCl, 200 mL of water, and 100 mL of hot acetone. After drying at 100 °C in vacuo for 24 h, a quantative yield of an off-white powder polymer was obtained.

(26) DSC analysis was carried out on a Seiko 220 DSC instrument at a heating rate of 20 °C/min under N_2.

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