*Macromolecules* **1999,** *32,* 315−321 **315**

# Syntheses of Semicrystalline Aromatic Poly(thioether thioether ketone)s (PTTK and PTBTK) and Their Copolymers with Ether Analogues

**Yong Ding,[†] Antisar R. Hlil, and Allan S. Hay***

*Department of Chemistry, McGill University, 801 Sherbrooke St. W., Montreal,*
*Quebec, H3A 2K6, Canada*

**Eishun Tsuchida and Kenji Miyatake**

*Department of Polymer Chemistry, Advanced Research Institute for Science and Engineering,*
*Waseda University, Tokyo 169-8555, Japan*

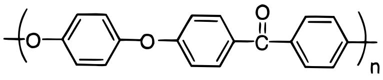
*Received June 29, 1998; Revised Manuscript Received November 17, 1998*

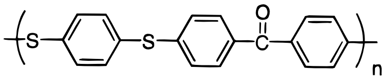
ABSTRACT: One-pot polymerization between bis(*N*,*N*′-dimethyl-*S*-carbamate)s and activated dihalo compounds was extended to the synthesis of semicrystalline poly(arylene thioether)s as well as their copolymers. Aromatic poly(thioether thioether ketone) (PTTK) and poly(thioether biphenyl thioether ketone) (PTBTK) were synthesized from 4,4′-difluorobenzophenone and bis(*N*,*N*′-dimethyl-*S*-carbamate)s prepared from hydroquinone and 4,4′-biphenol via the Newman−Kwart rearrangement reaction, respectively. Random copolymers were prepared by copolymerization of 4,4′-difluorobenzophenone with a mixture of bis(*N*,*N*′-dimethyl-*S*-carbamate)s or with a bis(*N*,*N*′-dimethyl-*S*-carbamate) and hydroquinone or 4,4′-biphenol. The reactions were carried out in benzophenone solution in the presence of a mixture of $Cs_2CO_3$ and $CaCO_3$ as the bases at polymerization temperatures ranging from 200 to 300 °C in order to keep the products in solution. All the polymers obtained were semicrystalline, as evidenced from the sharp melting points from the DSC scans for the polymers as prepared. However, the crystallization speeds for these polymers are very different depending on the compositions. The relationships between $T_g$, $T_m$, and structures are discussed. PTTK has a $T_g$ of 136 °C, $T_m$ of 304 °C, and an inherent viscosity of 0.32 dL/g in concentrated sulfuric acid, while PTBTK has a $T_g$ of 173 °C, $T_m$ of 351 °C, and an inherent viscosity of 0.46 dL/g.

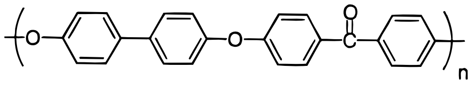
## Introduction

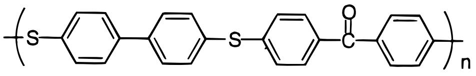
Aromatic poly(ether ketone)s are an important class of thermoplastic high-performance polymers possessing an excellent balance of mechanical properties and processability along with thermooxidative stability and chemical resistance. [1−3] The most well-known example is poly(ether ether ketone) (PEEK) which is a semicrystalline material and has a high sustained use temperature up to 280 °C. Poly(ether biphenyl ether ketone) (PEBEK), which has been prepared from 4,4′-biphenol and 4,4′-difluorobenzophenone and is also a highly crystalline polymer, has not yet gained any commercial value because of its extremely high melting point (395 °C) which places it beyond the temperature limits for melt processing of organic materials.[1,4]

The corresponding thioethers have received much less attention. Thiols are difficult to work with and to purify. Even at room temperature, oxidation of thiols occurs in the presence of base in DMF solution to give sulfonic acids. [5] In addition the lower molecular weight thiols, such as benzene-1,4-dithiol, are unpleasant to work with because of their odor. These problems can be avoided by the use of a one-pot polymerization that we have recently developed that utilizes bis(*N*,*N*′-dimethyl-*S*-carbamate)s as masked dithiols which can be converted in situ to the corresponding dithiols. [6−9] In contrast to the dithiols the carbamtes are easily purified, are odorless, and are readily available from the corresponding diols via the Newman−Kwart reaction.[10]


PEEK


PTTK


PEBEK


PTBTK

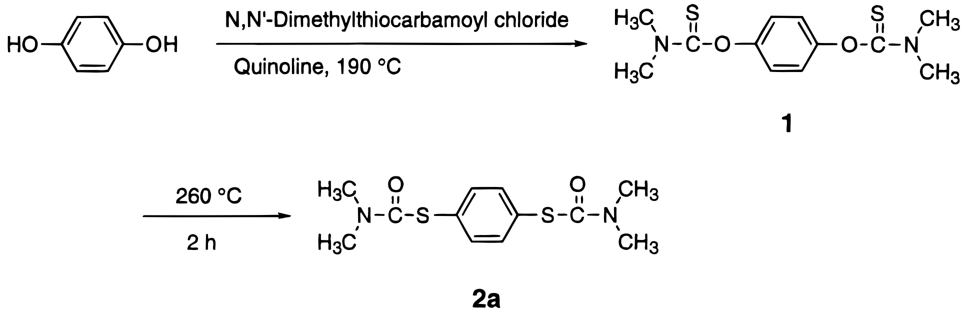
In a preliminary communication we recently reported our preliminary results on the synthesis of poly(thioether thioether ketone) (PTTK) starting from hydroquinone via a one-pot polymerization between a bis(*N*,*N*′-dimethyl-*S*-carbamate) and 4,4′-difluorobenzophenone in benzophenone in the presence of a mixture of $Cs_2CO_3$ and $CaCO_3$ as the bases[11] The resulting polymer has a combination of the properties of PEEK and poly(*p*-phenylene sulfide) (PPS), i.e., high crystallinity, higher $T_g$ than that of PPS and lower $T_g$ than that of PEEK, high thermal stability. The moderately high melting point facilitates processing while enabling the use of the material at elevated temperatures. One outstanding property of PTTK is its flame retardancy. [3,12] The limiting oxygen index (LOI) for PEEK is 35, while the LOI for PTTK is 49.[3] With the introduction

---

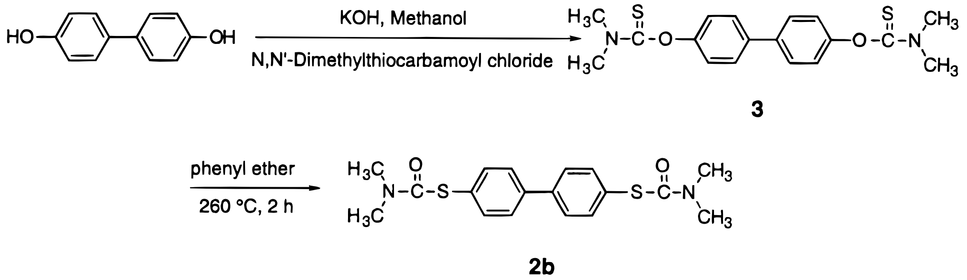
[†] Present address: Innovative Membrane Systems, Praxair Inc., 189 Dean Street, Norwood, MA 02062.

10.1021/ma9810060 CCC: $18.00

**Scheme 1**



**Scheme 2**



of the thioether linkage into the polymer chains, $T_g$s and $T_m$s of the resulting materials generally decrease without sacrificing the crystallinity which might allow the materials to be melt processed. Herein, we report the syntheses of PTTK, PTBTK and their random copolymers by the one-pot polymerization reaction we developed recently[6−9] along with a discussion of the structure−property relationships.

## Results and Discussion

**Monomer Syntheses.** Two bis(*N*,*N*′-dimethyl-*S*-carbamate) monomers were synthesized from hydroquinone and 4,4′-biphenol, respectively (Schemes 1 and 2). Compound **3** was synthesized by using methanol as the solvent and KOH as the base. However, the same synthetic method could not be applied to the synthesis of **1**. Extremely low yields were obtained in several attempts. In the literature,[10] even with the use of NaH in DMF as the base, only a very low yield was reported for the synthesis of **1**. We used a modified method to prepare this compound. Hydroquinone and excess amounts of *N*,*N*′-dimethylthiocarbamoyl chloride were mixed with quinoline and the mixture was heated at 190 °C for 45 min. The desired product **1** was obtained in 70% yield by this method. The rearrangement of **1** to **2a** was conducted in nitrogen atmosphere by simply heating **1** in bulk at 260 °C for 2 h. Small amounts of diphenyl ether were used as a solvent for the rearrangement of **3** to **2.** The $^1$H NMR spectra gave direct evidence for the rearrangement reactions. The sharp doublet corresponding to *N*,*N*′-dimethyl groups collapsed into one broad peak after the rearrangement in both cases. Monomers **2a** and **2b** are very stable compounds, easily purified, and almost odorless.

**PTTK and Its Random Copolymers.** The synthesis of PTTK was achieved by a one-pot polymerization of bis(*N*,*N*′-dimethyl-*S*-carbamate) **2a** with 4,4′-difluorobenzophenone in the presence of a mixture of cesium carbonate and calcium carbonate (Scheme 3). The optimum amount of $Cs_2CO_3$ was found to be 0.1−0.2 equiv.[11] Benzophenone was used as the reaction medium instead of diphenyl sulfone because of its greater stability in the polymerization reaction. Off-white powdery materials were obtained with inherent viscosities of 0.30−0.32 dL/g. The PTTK materials obtained could be molded into tough sheets. The glass transition temperature for PTTK is 136 °C.

A series of copolymers was prepared in a similar manner by the combination of **2a** with hydroquinone or 4,4′-biphenol (Scheme 3). The polymers obtained had inherent viscosities in the range of 0.30−1.11 dL/g measured in concentrated sulfuric acid. Poly(ether biphenyl ether ketone) (PEBEK) was not obtained due to the relative low boiling point of benzophenone and the insolubility of this polymer. Low molecular weight oligomers precipitated out before high molecular weight was achieved.

The thermal properties of copolymers **5** and **6** are listed in Tables 1 and 2. From DSC studies, it is apparent that all of the copolymers, **5** and **6,** are semicrystalline. $T_g$s were not observed in the first DSC heating scans for the polymer samples as prepared and only sharp melting points were found. When the polymer samples were quenched from the melt and then subjected to the second DSC scan, $T_g$s, crystallization temperatures, $T_c$, and melting points, $T_m$, were observed. The DSC charts for the copolymers **5** are shown in Figure 1. It is interesting to note that the introducion of thioether linkages into PEEK gives copolymer **5** which has a similar amount of crystallinity (thermodynamic). However, $T_m$s for copolymer **5** decrease as the content of thioether linkage increases. PEEK has a melting point of 326 °C, while PTTK has a $T_m$ of only 304 °C, which is 30 °C lower. Copolymer **6** (Table 2) are also semicrystalline polymers with thermal behavior similar to copolymer **5**. The melting points increase significantly with increasing PEBEK content and the homopolymer PEBEK could not be prepared because of its insolubility in the reaction mixture. All of the other copolymers except copolymer **6** with 20% PEBEK crystallize very rapidly from their amorphous states.

**Scheme 3**

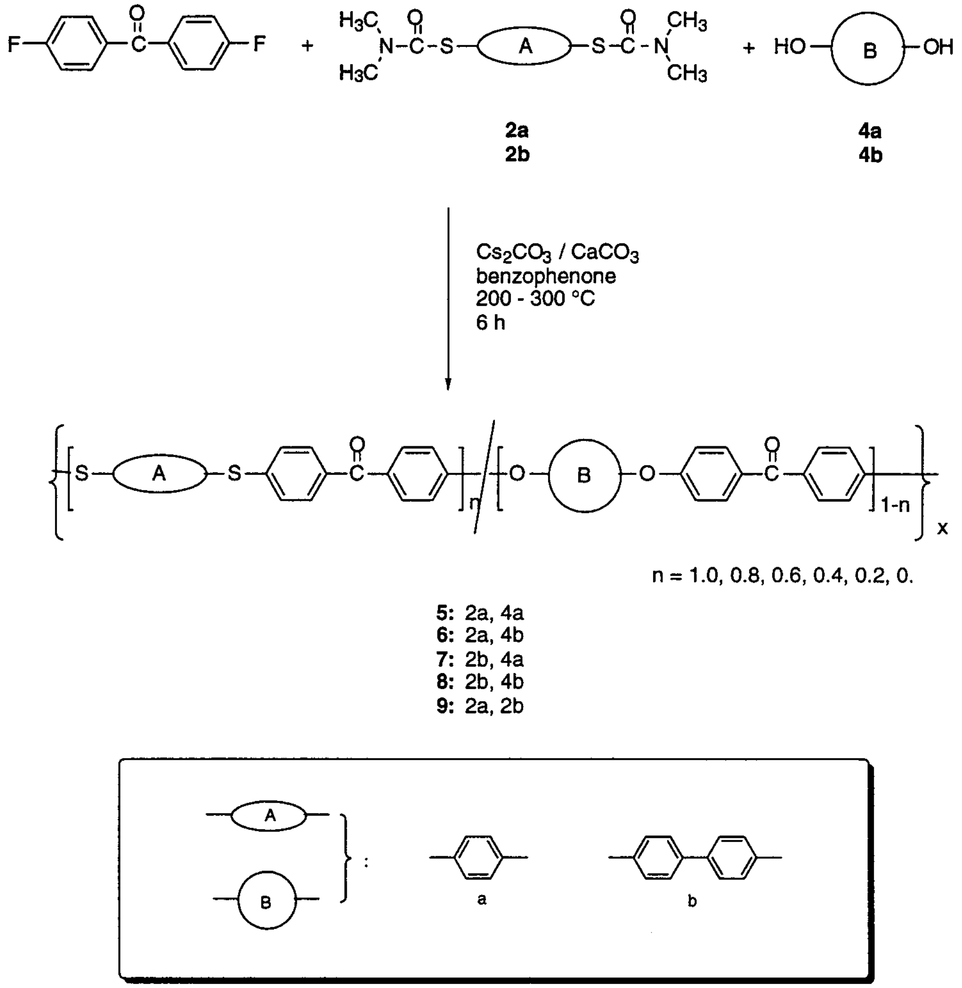
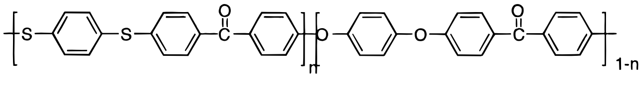


**Table 1. Properties of Copolymer 5**



5

| | | second DSC scan[b] | | | | | first DSC scan[b] | | |
|---|---|---|---|---|---|---|---|---|---|
| $n$ | $\eta_{inh}$[a] (dL/g) | $T_g$ (°C) | $T_c$ (°C) | $\Delta H_c$ (J/g) | $T_m'$ (°C) | $\Delta H_m'$ (J/g) | $T_m$ (°C) | $\Delta H_m$ (J/g) | TGA (°C)[c] |
| 1.0 | 0.32 | 136 | 183 | −21.1 | 296 | 26.4 | 304 | 41.4 | 510 |
| 0.8 | 0.30 | 136 | 197 | −27.8 | 296 | 30.4 | 301 | 42.0 | 520 |
| 0.6 | 0.37 | 137 | 193 | −27.3 | 301 | 31.2 | 302 | 44.2 | 516 |
| 0.4 | 0.42 | 139 | 192 | −28.6 | 309 | 35.0 | 309 | 49.4 | 514 |
| 0.2 | 0.58 | 142 | 190 | −25.6 | 324 | 30.9 | 324 | 44.4 | 550 |
| 0.0 | 1.11 | 148 | 188 | −19.0 | 326 | 21.1 | 337 | 49.2 | 556 |

[a] Measured in concentrated sulfuric acid with a concentration of 0.5 g/dL. [b] Heating rate at 20 °C/min under $N_2$. [c] 5% weight loss temperature under $N_2$.

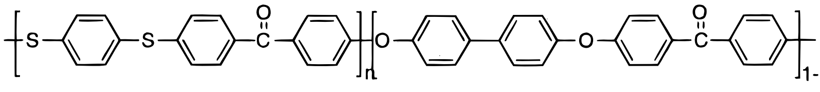
Generally, $T_g$ increases with the increase of ether linkages in the same series of polymers and also increases with the increasing content of biphenyl group. $T_g$s of copolymers can be calculated by the Fox equation:[13]

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \qquad (1)$$

The $T_g$ for PEEK is 148 °C and that for PTTK is 136 °C. The $T_g$ for PEBEK has been determined as 180 °C.[4] Generally, they are in good agreement, and the small discrepancies might be due to the effect of differences in molecular weights.

**PTBTK and Its Random Copolymers.** PTBTK and several copolymers were synthesized in the same manner as the synthesis of PTTK and its copolymers (Scheme 3). By the polymerization of **2b** with 4,4′-difluorobenzophenone, PTBTK was obtained as a light brown powder with an inherent viscosity of 0.45 dL/g as measured in concentrated sulfuric acid. Other copolymers were obtained by copolymerization of **2b** with either 4,4′-biphenol or hydroquinone or bis($N$,$N$′-dimethyl-$S$-carbamate) **2a**. All of these polymers are

**Table 2. Properties of Copolymer 6**



**6**

| $n$ | $\eta_{inh}$[a] (dL/g) | second DSC scan[b] | | | | | first DSC scan[b] | | TGA (°C)[c] |
|---|---|---|---|---|---|---|---|---|---|
| | | $T_g$ (°C) | $T_c$ (°C) | $\Delta H_c$ (J/g) | $T_m'$ (°C) | $\Delta H_m'$ (J/g) | $T_m$ (°C) | $\Delta H_m$ (J/g) | |
| 1.0 | 0.36 | 136 | 183 | −21.1 | 296 | 26.4 | 304 | 41.4 | 510 |
| 0.8 | 0.30 | 139 | 229 | −4.2 | 280 | 5.2 | 295 | 34.2 | 509 |
| 0.6 | 0.44 | 148 | 206 | −21.3 | 289 | 16.3 | 286 | 31.6 | 539 |
| 0.4 | 0.57 | 155 | 205 | −22.8 | 343 | 25.6 | 345 | 38.2 | 528 |
| 0.2 | 0.79 | 165 | 203 | −20.1 | 389 | 28.3 | 388 | 37.8 | 542 |

[a] Measured in concentrated sulfuric acid with a concentration of 0.5 g/dL. [b] Heating rate at 20 °C/min under $N_2$. [c] 5% weight loss temperature under $N_2$.

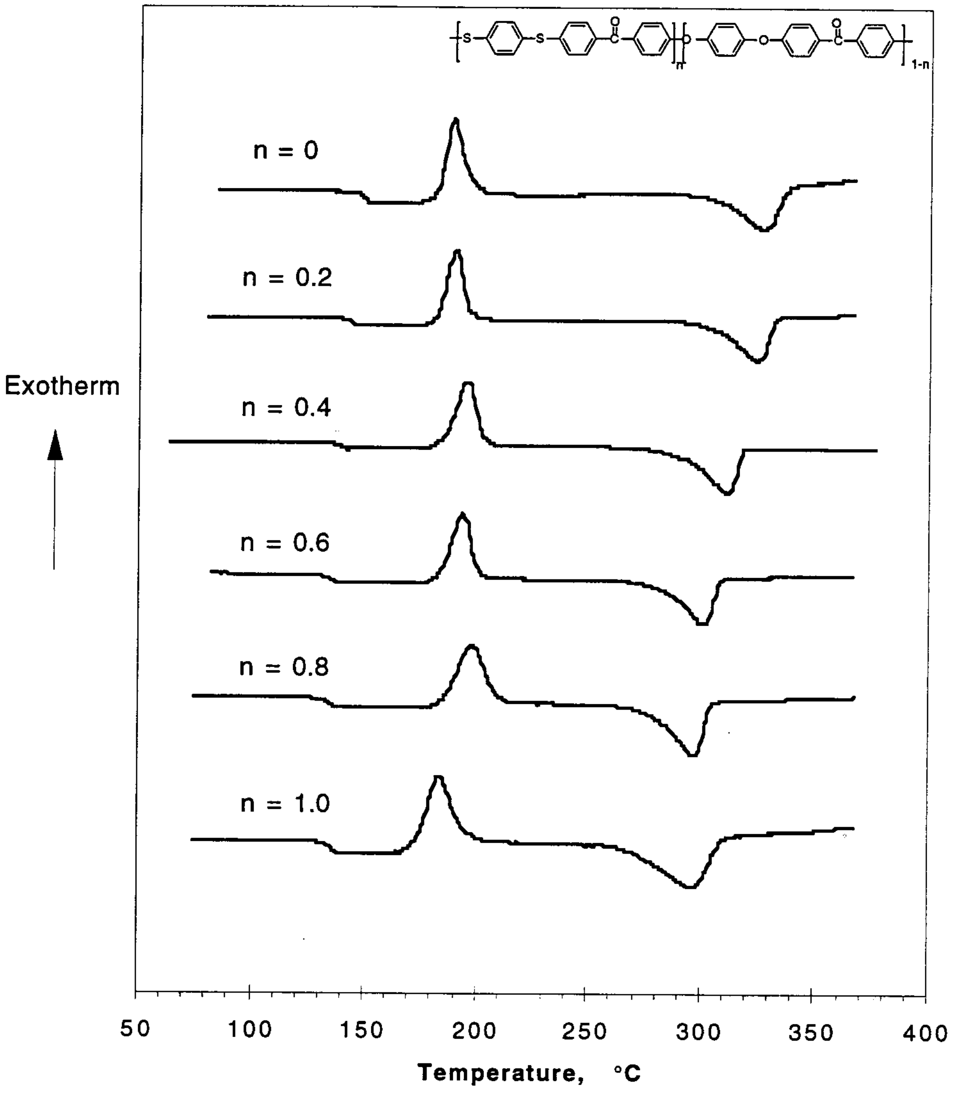


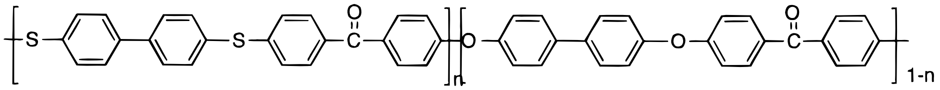
**Figure 1.** DSC scans for PTTK and PEEK copolymers.

insoluble in common organic solvents at room temperature and are soluble in concentrated sulfuric acid.

Thermal properties of three series of copolymers **5**−**7** are listed in Tables 1−3. Similar to PTTK copolymers, PTBTK copolymers do not show $T_g$s in the first heating scans for the polymer samples as prepared. Only sharp melting points were observed. Poly(ether biphenyl ether ketone) has an extremely high melting point (395 °C) [4] which places it beyond the limit for processing of organic materials. However, PTBTK has a moderate melting point of 351 °C, which is only 14 °C higher than PEEK and in the range of processable temperatures. The $T_g$ of PTBTK is 173 °C, which is 25 °C higher than PEEK. Combined with its potential advantages of better flame retardance, PTBTK could be a very good candidate for commercialization providing that an economical synthesis was available.

Judging from the melt enthalpy changes from the DSC studies, the introduction of the thioether linkage into PEBEK polymer does not significantly change the

**Table 3. Properties of Copolymer 7**

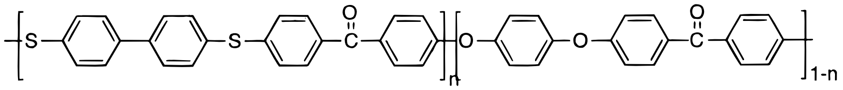


**7**

| | | second DSC scan$^b$ | | | | | first DSC scan$^b$ | | |
|---|---|---|---|---|---|---|---|---|---|
| $n$ | $\eta_{inh}$$^a$ (dL/g) | $T_g$ (°C) | $T_c$ (°C) | $\Delta H_c$ (J/g) | $T_m'$ (°C) | $\Delta H_m'$ (J/g) | $T_m$ (°C) | $\Delta H_m$ (J/g) | TGA (°C)$^c$ |
| 1.0 | 0.46 | 173 | | | 345$^d$ | 0.4$^d$ | 351 | 34.1 | 537 |
| 0.8 | 0.43 | 171 | 220 | −23.0 | 342 | 24.0 | 358 | 43.1 | 531 |
| 0.6 | 0.47 | 171 | 207 | −15.7 | 361 | 20.7 | 365 | 36.2 | 533 |
| 0.4 | 0.86 | 177 | 217 | −19.8 | 382 | 25.5 | 385 | 46.8 | 550 |
| 0.2 | 0.46 | 177 | 246 | −3.3 | 357 | 6.5 | 387 | 38.8 | 547 |

$^a$ Measured in concentrated sulfuric acid with a concentration of 0.5 g/dL. $^b$ Heating rate at 20 °C/min under $N_2$. $^c$ 5% weight loss temperature under $N_2$. $^d$ Annealed at 310 °C for 1 h.

**Table 4. Properties of Copolymer 8**

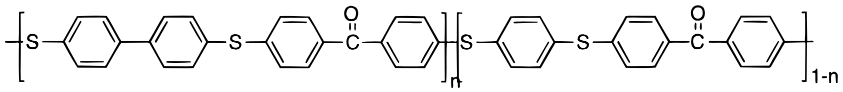


**8**

| | | second DSC scan$^b$ | | | | | first DSC scan$^b$ | | |
|---|---|---|---|---|---|---|---|---|---|
| $n$ | $\eta_{inh}$$^a$ (dL/g) | $T_g$ (°C) | $T_c$ (°C) | $\Delta H_c$ (J/g) | $T_m'$ (°C) | $\Delta H_m'$ (J/g) | $T_m$ (°C) | $\Delta H_m$ (J/g) | TGA (°C)$^c$ |
| 1.0 | 0.46 | 173,176$^d$ | | | 332,$^c$ 345$^d$ | | 351 | 34.1 | 537 |
| 0.8 | 0.35 | 170 | 234$^f$ | | 303.5$^f$ | | 320 | 23.3 | 529 |
| 0.6 | 0.18 | 158 | 229 | −19.2 | 308 | 13.9 | 285 | 34.8 | 524 |
| 0.4 | 0.27 | 157 | | | | | 280 | 10.3 | 524 |
| 0.2 | 0.47 | 150 | 212 | −24.2 | 300 | 22.8 | 304 | 42.5 | 549 |
| 0.0 | 1.11 | 148 | 188 | −19.0 | 326 | 21.1 | 337 | 49.2 | 556 |

$^a$ Measured in concentrated sulfuric acid with a concentration of 0.5 g/dL. $^b$ Heating rate at 20 °C/min under $N_2$. $^c$ 5% weight loss temperature under $N_2$. $^d$ Annealed at 310 °C for 1 h. $^e$ Annealed at 330 °C for 30 min. $^f$ Annealed at 300 °C for 30 min.

**Table 5. Properties of Copolymer 9**



**9**

| | | second DSC scan$^b$ | | | | | first DSC scan$^b$ | | |
|---|---|---|---|---|---|---|---|---|---|
| $n$ | $\eta_{inh}$$^a$ (dL/g) | $T_g$ (°C) | $T_c$ (°C) | $\Delta H_c$ (J/g) | $T_m'$ (°C) | $\Delta H_m'$ (J/g) | $T_m$ (°C) | $\Delta H_m$ (J/g) | TGA (°C)$^c$ |
| 1.0 | 0.46 | 173,.176$^d$ | | | 332,$^c$ 345$^d$ | 0.4$^d$ | 351 | 34.1 | 537 |
| 0.8 | 0.35 | 169 | | | | | 322 | 39.2 | 533 |
| 0.6 | 0.25 | 164 | | | | | 279 | 27.8 | 536 |
| 0.4 | 0.18 | 152 | | | | | 232 | 32.8 | 524 |
| 0.2 | 0.19 | 148 | | | | | 265 | 20.2 | 525 |
| 0.0 | 0.36 | 136 | 183 | −21.1 | 296 | 26.4 | 304 | 41.4 | 510 |

$^a$ Measured in concentrated sulfuric acid with a concentration of 0.5 g/dL. $^b$ Heating rate at 20 °C/min under $N_2$. $^c$ 5% weight loss temperature under $N_2$. $^d$ Annealed at 310 °C for 1 h. $^e$ Annealed at 330 °C for 30 min.

crystallinity. However, the crystallization rates are very different. PTBTK did not show any crystallization during the second DSC heating scan when the sample was quenched from the melt (380 °C). A melting point was also not observed. These experiments were repeated several times with the same result. When the sample was held at 200 °C for one-half hour and then subjected to DSC analysis, a melting point was then observed. The introduction of the hydroquinone moiety into PTBTK (Table 4) affected the crystallinity. Crystallization was observed in the quenched samples for PTBTK copolymers **8** with 40% and 80% of PEEK contents whereas, with 60% PEEK content, no $T_c$ or $T_m$ was observed. The copolymers **9** prepared from monomers **2a** and **2b** are all semicrystalline polymers (Table 5). However, their melting points are quite low. Crystallization was not observed for any of the copolymers **9** in the second DSC heating scan for the samples quenched from the melt (350 °C), indicating that these copolymers have relatively slow crystallization rates. None of these copolymers crystallized when annealed at various temperatures and times.

The sulfur-containing copolymers all crystallized with difficulty, or not at all, from the melt. The calculated $T_g$s for these PTBTK copolymers are generally in good agreement with the observed results and the small discrepancies may due to the effect of differing molecular weights of the polymer samples.

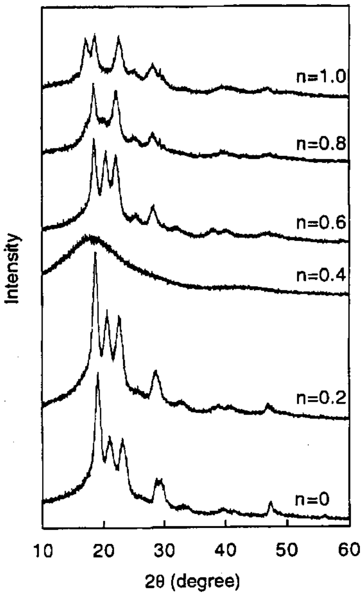


**Figure 2.** X-ray diffraction patterns of copolymer **5**.

Wide-angle X-ray diffraction measurements were carried out for the pristine copolymers **5** (Figure 2). PEEK shows a sharp and strong diffraction pattern peaked at 19.08, 21.06, 23.16, 29.50, 38.94, and 47.38° of 2Φ. The crystal system of PEEK is orthorhombic and the lattice parameters are determined to be: $a = 7.67$ Å, $b = 5.84$ Å, and $c = 10.0$ Å. These values are in good agreement with the previously reported ones ($a = 7.75$ Å, $b = 5.86$ Å, $c = 10.00$ Å).[14] The diffraction intensity decreases as the content of thioether linkages increases. The copolymer containing 40 mol % TTK units is less crystalline than the others and shows the only amorphous halo. At higher content of TTK units than 80 mol %, the peak at 21.06° disappears and a new peak appears at 17.20°. In the diffraction pattern of PTTK, all the recorded reflections could be satisfactorily indexed by assuming an orthorhombic unit cell of dimensions: $a = 7.84$ Å, $b = 5.99$ Å, $c = 10.30$ Å. The systematic absence of the reflections $hk0$ with $(h + k)$ odd, $0kl$ with k odd and $h0l$ with $l$ odd led us to the space group $Pbcn$-$D_{2h}$,[15] similar to those of PEEK[15] and PPS.[16] The $c$ dimension of 10.30 Å corresponds to the distance between sulfur and carbonyl groups (10.22 Å) of 4-(4-phenylthio)phenylthiobenzophenone as a model compound optimized by PM3 calculations (Figure 3). It can be concluded that the thioether and carbonyl units are equivalent in the crystal plane. However, since the standard C−S bond (1.74 Å) is longer than the C−C (1.50 Å) and the C−O (1.36 Å) bonds. PTTK has slightly less crystallinity compared with PEEK, which is consistent with the enthalpy changes measured from DSC.

## Conclusions

We have demonstrated here that the one-pot polymerization between bis($N,N'$-dimethyl-$S$-carbamate)s and activated dihalo compounds can be used to synthesize semicrystalline poly(arylene thioether)s as well as their copolymers. This process offers an excellent method for the modification of poly(arylene ether)s by introducing thioether linkages into polymer chains. Several series of semicrystalline polymers have been prepared by copolymerization of 4,4′-difluorobenzophenone with two bis($N,N'$-dimethyl-$S$-carbamate) monomers, **2a** and **2b**, combining with either hydroquinone or 4,4′-biphenol in the presence of a cesium carbonate and calcium carbonate mixture. Benzophenone was used as the polymerization medium. The structure−property relationships are discussed. The melting points of PTTK and PTBTK are significant lower than their ether analogues. This feature is significant in that processable semicrystalline polymers might be produced by replacing ether linkage in the polymer chains with thioether linkage.

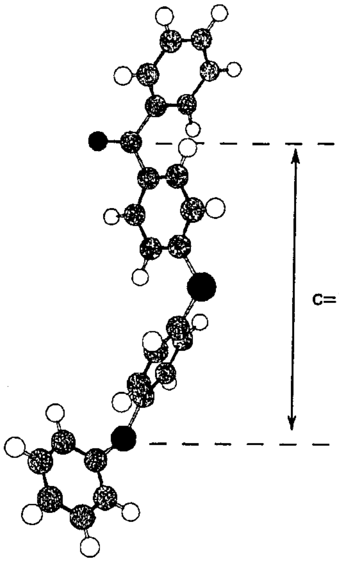


**Figure 3.** Stereoscopic illustration of 4-(4-phenylthio)-phenylthiobenzophenone showing the c dimension as a model for PTTK.

## Experimental Section

**Materials and Instrumentation.** Hydroquinone, 4,4′-difluorobenzophenone, $N,N'$-dimethylthiocarbamoyl chloride, diphenyl ether, and benzophenone were purchased from Aldrich Chemical Co., Inc., and used as received. Fine grade anhydrous cesium carbonate and calcium carbonate were purchased from CM Chemical Products, Inc., and ACP Chemicals, Inc., respectively. Quinoline was distilled prior to use, and 4,4′-biphenol was purified by recrystallization with anhydrous ethanol. Proton NMR spectra, reported in ppm, were recorded on a Varian UNITY 500 spectrometer using $CDCl_3$ as the solvent with tetramethylsilane as the internal reference. Differential scanning calorimetric (DSC) analyses were performed on a Seiko 220 DSC instrument at a heating rate of 20 °C/min under nitrogen atmosphere (flow rate of 200 mL/min), and $T_g$s were reported as temperatures at the middle of the thermal transitions. Thermogravimetric analyses (TGA) were performed on a Seiko 220 TGA instrument at a heating rate of 20 °C/min under $N_2$ (flow rate) and were reported as temperatures at which 5% weight losses were observed. Both of the above instruments were calibrated with an indium standard. The inherent viscosities were measured with a Ubbelohde viscometer at 25 °C in concentrated $H_2SO_4$ solution at a concentration of 0.5 g/dL.

Wide-angle X-ray scattering (WAXS) patterns were obtained on a powder sample employing a Rigaku RAD-C diffractometer with a curved crystal, graphite monochromator and counting equipment. Measurements were made bwith Ni-filtered Cu Kα radiation. With the goniometer operated at 30 kV and 15 mA, the intensities of 1-s counts were taken every 0.02° (2Φ) over the angular range 10−60° and were recorded. The equilibrium geometry of 4-(4-phenylthio)phenylthiobenzophenone was optimized using the PM3/RF semiempirical [17,18] mode as implemented in the MOPAC-93.00 system of programs.[19]

**Bis($N,N'$-dimethylthiocarbamate) 1.** Hydroquinone (11.0 g, 0.1 mol), quinoline (30 mL), and a slight excess of $N,N'$-dimethylthiocarbamoyl chloride (27.2 g, 0.22 mol) were charged into a 100 mL three-neck round-bottom flask and heated at

190 °C under 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 white solid was obtained in 70% yield. Mp: 210−214 °C (lit.[10] 214−216 °C).

**Bis(*N*,*N*′-dimethyl-*S*-carbamate) 2a.** The bis(*N*,*N*′-dimethylthiocarbamate) **1** (10.0 g, 0.035 mol) was heated in the bulk at 260 °C under $N_2$ for 2 h to afford the desired bis(*N*,*N*′-dimethyl-*S*-carbamate) **2a** by the Newman−Kwart rearrangement reaction. Pure monomer **2a** (8.3 g, yield, 83%) was obtained by recrystallization from chloroform/methanol and further recrystallization from methyl ethyl ketone (MEK). Mp: 201−203 °C (lit.[10] 200−202 °C).

**Bis(*N*,*N*′-dimethyl-*S*-carbamate) 2b.** The mixture of **3** (10.0 g, 0.028 mol) and diphenyl ether (5.0 g) was placed in a salt bath preheated to 260 °C for 2 h under nitrogen atmosphere. After cooling, the solid was first washed with 50 mL of methanol and then recrystallized from MEK. Pale yellow crystals of **2b** (8.1 g, yield 81%) were obtained. Mp: 198−200 °C. $^1$H NMR ($CDCl_3$): $\delta$ (ppm) 7.59 (d, 4H, $J = 8.1$ Hz), 7.56 (d, 4H, $J = 8.1$ Hz), 3.07 (s, 12 H, $-CH_3$). $^{13}$C NMR ($CDCl_3$): $\delta$ (ppm) 166.7, 141.2, 136.0, 128.1, 127.7, 36.9. MS: $m/z$ 360 ($M^+$, 100), 288 (7), 72 (54). HRMS: found, 360.09630; calcd for $C_{18}H_{20}N_2O_2S_2$, 360.09662.

**Bis(*N*,*N*′-dimethylthiocarbamate) 3.** The starting material 4,4′-biphenol (10.6 g, 0.057 mol) was added to 300 mL of ice-cold methanolic solution which contained 7.3 g (0.13 mol) of potassium hydroxide. The mixture was stirred at 0 °C for 1.0 h, and then *N*,*N*′-dimethylthiocarbamoyl chloride (13.53 g, 0.11 mol) was added. After the reaction was stirred for another 2 h, the precipitate was collected by filtration and washed with cold methanol−water (200 mL). Pure white solid **3** (11.2 g, yield 55%) was obtained after recrystallization from DMF. Mp: 260−262 °C. $^1$H NMR ($CDCl_3$): $\delta$ (ppm) 7.59 (d, 4H, $J = 8.5$ Hz), 7.13 (d, 4H, $J = 8.5$ Hz), 3.47 (s, 6H, $-CH_3$), 3.35 (s, 6H, $-CH_3$). $^{13}$C NMR ($CDCl_3$): $\delta$ (ppm) 187.5, 153.3, 138.0, 127.8, 122.9, 43.2, 38.7. MS: $m/z$ 360 ($M^+$, 100), 273 (33), 88 (54), 72 (22). HRMS: found, 360.09690; calcd for $C_{18}H_{20}N_2O_2S_2$, 360.09662.

**Polymerizations.** An example of the preparation of one random copolymer follows. Into a 50 mL three neck round-bottom flask equipped with a nitrogen inlet, a magnetic stirrer, a Dean−Stark trap and a condenser, 4,4′-difluorobenzophenone (0.6546 g, 3.00 mmol), **2a** (0.5119 g, 1.80 mmol), hydroquinone (0.1321 g, 1.20 mmol), benzophenone (8.0 g), cesium carbonate (0.10 g, 0.3 mmol), and calcium carbonate (0.90 g, 9.0 mmol) were charged. The mixture was heated at 200 °C for 1 h and then 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 vaccuo for 24 h, high yields (95−99%) of off-white powder polymers were obtained. Inherent viscosity (5% concentrated $H_2SO_4$), 0.37 dL/g.

**Acknowledgment.** We appreciate the financial support provided by the Natural Sciences and Engineering Research Council of Canada.

## References and Notes

(1) Attwood, T. E.; Dawson, P. C.; Freeman, J. L.; Hoy, L. R. J.; Rose, J. B.; Staniland, P. A. *Polymer* **1981**, *22*, 1096−1103.
(2) Wolf, P. In *Polymeric Materials Encyclopedia*; Salamone, J. C., Ed.; CRC Press: New York, 1996; Vol. 7, p 5544.
(3) Yoneda, H.; Fukawa, I. In *Polymeric Materials Encyclopedia*; Salamone, J. C., Ed.; CRC Press: New York, 1996; Vol. 7, p 5550.
(4) Lindfors, B. E.; Mani, R. S.; McGrath, J. E.; Mohanty, D. K. *Makromol. Chem., Rapid Commun.* **1991**, *12*, 337−345.
(5) Wallace, T. J.; Schriesheim, A. *Tetrahedron Lett.* **1963**, *17*, 1131−1136.
(6) Ding, Y.; Hay, A. S. *Polym. Prepr.* **1997**, *38* (2), 269−270.
(7) Ding, Y.; Hay, A. S. *Tetrahedron* **1997**, 15237−15246.
(8) Ding, Y.; Hlil, A.; Hay, A. S. *Polym. Prepr.* **1997**, *38* (2), 187−188.
(9) Ding, Y.; Hlil, A. R.; Hay, A. S. *J. Pol. Sci. Chem.* **1998**, *36*, 1201−1208.
(10) Newman, M. S.; Karnes, H. A. *Journal of Organic Chemistry* **1966**, *31*, 3980−3984.
(11) Ding, Y.; Hay, A. S. *Macromolecules* **1998**, *31*, 2690.
(12) Fukawa, I.; Yoneda, H.; Sakurai, H., U.S. Patent 4,772,679, 1988, assigned to Asahi Kase Kogyo Kabushiki Kaisha.
(13) Fox, T. G. *Bull. Am. Phys. Soc.* **1956**, *1*, 123.
(14) Dawson, P. C.; Blundell, D. J. *Polymer* **1980**, *21*, 577.
(15) Hay, J. N.; Kemmish, D. J.; Langford, J. I.; Rae, A. I. M. *Polymer* **1984**, *25*, 175.
(16) Tabor, B. J.; Magre, E. P.; Boon, J. *Eur. Pol. J.* **1971**, *7*, 1127.
(17) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209.
(18) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 221.
(19) Stewart, J. J. P. MoPAC-93.00, Fujitsu Limited: Tokyo, Japan, 1993.

MA9810060