

## Synthesis and Properties of Wholly Aromatic Poly(thioether-ketone)s Bearing 2,6-Dimethyl-1,5-naphthylene Unit

Sumiko MATSUMURA, Nobuhiro KIHARA, and Toshikazu TAKATA

Department of Applied Chemistry, Osaka Prefecture University, Gakuen-cho,  
Sakai-shi, Osaka 599-8531, Japan

Tel 072-254-9290, Fax 072-254-9910, takata@chem.osakafu-u.ac.jp

Poly(ether-ketone) (PEK), *e.g.* poly(ether-ether-ketone) (PEEK), is one of the most important high-performance engineering plastics displaying excellent physical properties such as high thermostability and chemical resistance. However, PEEK has low solubility, and high  $T_m$  around 340 °C, that is, low processability, probably due to the rigid and planar wholly aromatic structure. In addition, PEEK has relatively low  $T_g$  (143 °C), while the dimensional stability is relatively low because it is semicrystalline. Although high thermostability is normally in contradiction with processability, many studies have recently been carried out to develop novel PEKs endowed with both high processability and high thermostability. We have previously developed novel PEK **1** having the 2,6-dimethyl-1,5-naphthylene unit, and found that **1** showed remarkably high solubility and thermostability simultaneously.<sup>1</sup> The excellent nature of **1** can be accounted for by the fact that the 1,5-naphthylene unit induces the crankshaft structure in the main chain and that the steric repulsion of the methyl groups makes the benzoyl group perpendicular to the naphthalene plane which reduces the planarity of the polymer chain.

On the other hand, aromatic PEKs have been synthesized generally from corresponding difluoroketones and biphenols as monomers. Since aromatic difluoroketones are expensive and are sometimes difficult to prepare, PEKs are expensive polymers. Although corresponding dichloroketones is cheap and easy to prepare, high polymer could not be obtained from dichloroketone because of their low electrophilicity. However, dichloroketone can be a good monomer if nucleophilicity of the counterpart is sufficiently higher than that of phenol. In fact, high polymers of poly(thioether-ketone) (PTEK) have been successfully prepared from dichloroketone when highly nucleophilic thiophenol derivatives were used as monomers. However, PTEKs have been paid much less attention than PEKs because only PTEKs showing less thermostability and poor solubility have been prepared. Use of the 2,6-dimethyl-1,5-naphthylene unit may smash the present constraint out. In this paper, we wish to report the successful synthesis of novel aromatic PTEKs combining high solubility and thermostability from aromatic dihaloketones and aromatic dithiols.<sup>2,3</sup>

The polycondensations of aromatic dihaloketones **2** and **3** bearing the 2,6-dimethyl-1,5-naphthylene skeleton and aromatic dithiols **4** and **5** were investigated in the presence of

$K_2CO_3$  in polar solvents. The polycondensation using corresponding phenols **6** and **7** was also investigated. The resulting polymers **8-11** were characterized by  $^1H$  NMR,  $^{13}C$  NMR, IR, and elemental analysis. Table 1 shows the results of the polycondensation.

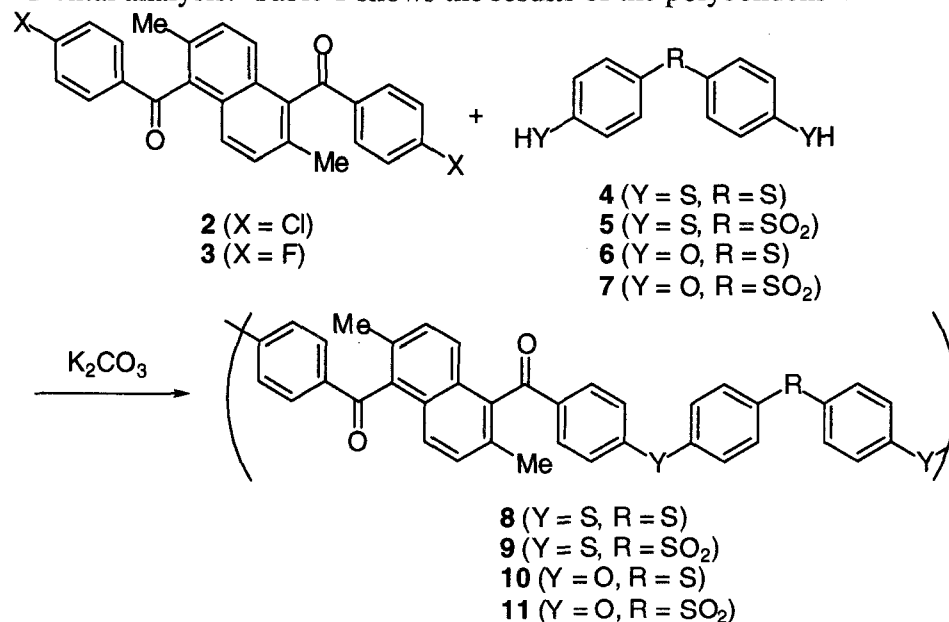


Table 1. The polycondensation of aromatic dihaloketones and dithiols or diphenols.

monomers	polymer	solvent	temp	time / °C	yield <sup>a</sup> / h	$M_n^b$ / %	$M_w/M_n^b$
<b>2</b> <b>4</b>	<b>8</b>	NMP	150	8	98	19000	2.88
<b>3</b> <b>4</b>	<b>8</b>	NMP	150	8	91	12000	1.99
<b>2</b> <b>6</b>	<b>10</b>	NMP	150	8	90	3900	1.59
<b>2</b> <b>5</b>	<b>9</b>	sulfolane	180	4	95	24000	2.95
<b>3</b> <b>5</b>	<b>9</b>	sulfolane	180	4	94	31000	3.42
<b>2</b> <b>7</b>	<b>11</b>	sulfolane	180	4	67	2900	1.47
<b>2</b> <b>4</b>	<b>8</b>	sulfolane	180	0.16	100	37000	3.14
<b>2</b> <b>4</b>	<b>8</b>	NMP	180	0.5	95	13000	1.93
<b>2</b> <b>4</b>	<b>8</b>	diphenyl sulfone	180	0.5	95	21000	1.79
<b>2</b> <b>4</b>	<b>8</b>	NMP	150	16	99	420	23.8
<b>2</b> <b>4</b>	<b>8</b>	sulfolane	150	16	78	17000	3.64
<b>2</b> <b>4</b>	<b>8</b>	NMP	r.t.	24	38	710	5.67

<sup>a</sup> methanol-insoluble part. <sup>b</sup> estimated by GPC (THF, PSt standards) after elimination of cyclic oligomers.

High molecular weight of PTEK **8** was quantitatively obtained from dichloroketone **2** while low molecular weight of PEK **10** was obtained from **2**. Similar result was obtained in the synthesis of PTEK **9** although slightly harder condition was necessary to obtain **9** in high yield because the nucleophilicity of thiol group of **5** decreased due to the electron-withdrawing sulfonyl group. The molecular weight and yield were essentially independent of the electrophilicity of the haloketone monomers, **2** and **3**. Aromatic dichloroketone can be used as a monomer, as well as difluoroketone, when dithiol is used instead of biphenol to prepare PTEK possessing high molecular weight. Because of high nucleophilicity of thiol moiety, difference of electrophilicity between chloroketone and fluoroketone was apparently hidden in polymerization. When the polycondensation of **2** and **4** was carried out at 180 °C in

sulfolane, the polymerization completed within 10 min. Further reaction resulted in gelation. While sulfolane was the best solvent, various polar solvents were also available for the polycondensation. When the polycondensation was carried out in NMP, molecular weight of **8** drastically decreased as the reaction time was prolonged. Nitrogen atom contamination in the polymer was confirmed by elemental analysis of **8** thus obtained. When a solution of **8** was heated at 150 °C in NMP, no molecular weight change was observed, but molecular weight considerably decreased in the presence of K<sub>2</sub>CO<sub>3</sub>. These results suggest that enolate anion derived from NMP decomposed the main chain of PTEK. This type of degradation was not observed in sulfolane. The polycondensation at room temperature was very slow, and a large amount of unreacted monomer remained even after 24 h. It is summarized that higher molecular weight PTEK can be obtained by the polycondensation at higher temperature in sulfolane.

Although wholly aromatic polymers are generally insoluble in ordinary organic solvents, PTEKs **8** and **9** were completely soluble in solvents such as NMP, nitrobenzene and CHCl<sub>3</sub>. 2,6-Dimethyl-1,5-naphthylene unit in PTEKs would ensure their high solubility. Because of the good solubility, flexible, transparent, and strong cast films were easily obtained from CHCl<sub>3</sub> or THF solution.

Table 2 showed the thermal properties of PTEKs and PEKs. Each PTEK had 5 % weight loss temperatures ( $T_{d5}$ ) around 435 °C, and the  $T_g$  of PTEK is much higher than that of PEEK. The  $T_g$  of **9** was higher than that of **8** probably due to the polar and bulky sulfonyl group. In this case, the  $T_{d5}$  and  $T_g$  values of PTEKs were essentially same to those of PEK, indicating the replacement of ether linkage with thioether linkage did not affect  $T_{d5}$  and  $T_g$ . Therefore, **8** and **9** are one of the most thermally stable PTEKs.

Table 2. Thermal properties of PTEK and PTK.

polymer	$T_g^a$ /°C	$T_{d5}^b$ /°C	$T_m^a$ /°C
<b>8</b>	215	436	ND <sup>c</sup>
<b>9</b>	245	435	ND <sup>c</sup>
<b>10</b>	228	430	ND <sup>c</sup>
<b>11</b>	232	436	ND <sup>c</sup>

<sup>a</sup> measured by DSC (10 °C/min, N<sub>2</sub> atmosphere, second scan).

<sup>b</sup> measured by TG (10 °C/min, N<sub>2</sub> atmosphere). <sup>c</sup> not detected.

Since neither **8** nor **9** exhibited  $T_m$  presumably due to their amorphous nature, they have potential advantages of higher dimensional stability and lower anisotropy to be handled readily in processing. Thus, the average linear thermal expansion coefficients of **8** and **9** were measured at room temperature. These values ( $5.1 \times 10^{-5} \text{ K}^{-1}$  for **8** and  $5.4 \times 10^{-5} \text{ K}^{-1}$  for **9**) are similar to those of typical high-performance polymers.<sup>4</sup>

Further, the dielectric breakdown strength and volume resistivity of the polymers were

measured. PTEK and PEK showed the volume resistivity ( $>1 \times 10^{16} \Omega \cdot \text{cm}$ ) similar to that of polyethylene, which is a representative of electric insulation materials. PTEK showed higher dielectric breakdown strengths than PEK. The dielectric breakdown strengths ( $220 \text{ kV mm}^{-1}$  for **8**,  $170 \text{ kV mm}^{-1}$  for **9**, and  $90.5 \text{ kV mm}^{-1}$  for **10**) were much higher than those of other typical high performance polymers ( $<25 \text{ kV mm}^{-1}$ ).

PTEK **8** absorbed less water (0.13 %) than PEK **10** (0.16 %) probably because sulfide is more hydrophobic than the corresponding ether, indicating has high water resistance ability of PTEK. Thus, change in volume resistivity of the polymers by the treatment with water was examined. While no decrease in volume resistivity was observed for **8**, that of **10** decreased to  $7.5 \times 10^{14}$  after water absorption. PTEK can be regarded as a novel insulation material even under extremely moist atmosphere.

Because of large atomic refraction of sulfur atom, the refractive index of PTEK is of interest. Both PTEK **8** and **9** showed the high refractive index (1.66), which is higher than that of typical sulfur-containing polymers and close to that of poly(vinylcarbazole) (1.67), a representative of optical materials with high refractive index. Not only sulfur atom incorporation but also wholly aromatic structure resulted in the high refractive indices.

The Young's modulus and tensile strength of PTEKs were measured. The results are summarized in Table 3. It is found that PTEKs show excellent tensile strength and modulus, which are comparable to those of commercially available engineering plastics such as polyimide, although the modulus drastically decreased above  $T_g$ .

Table 3. Mechanical Properties of PTEKs.

PTEK	tensile strength <sup>a</sup> / $\text{N} \cdot \text{mm}^{-2}$	elongation at break <sup>a</sup> / %	Young's modulus <sup>b</sup> / MPa			tear resistance <sup>c</sup> / $\text{N} \cdot \text{mm}^{-2}$	static friction coefficient <sup>d</sup>	kinetic friction coefficient <sup>d</sup>
			r.t.	190 °C	235 °C			
<b>8</b>	91.2	10	1770	1500	28.7	-	-	-
<b>9</b>	106	11	2330	2200	1720	223	0.43	0.36

<sup>a</sup> cross head speed: 5 mm/min. <sup>b</sup> measured by DMA (fiber-film-tension geometry, 2 °C/min, 10 Hz, dynamic strain 0.1 %). <sup>c</sup> cross head speed: 200 mm/min. <sup>d</sup> cross head speed: 150 mm/min using aluminum sheet.

Wholly aromatic polymers generally show good flame resistance. The limiting oxygen index values of PTEKs were calculated to be 0.32.<sup>5</sup> Thus, PTEKs are expected to have good flame resistance, in spite of the presence of methyl group, which is known to decrease the flame resistance. The flame resistant property of **9** measured by UL 94 VTM method was sufficiently high to attain VTM-0 without any flame retardant, as expected.

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