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Synthesis and Properties of Novel Aromatic Poly(thioether−ketone)s as Sulfur-Containing High-Performance Polymers

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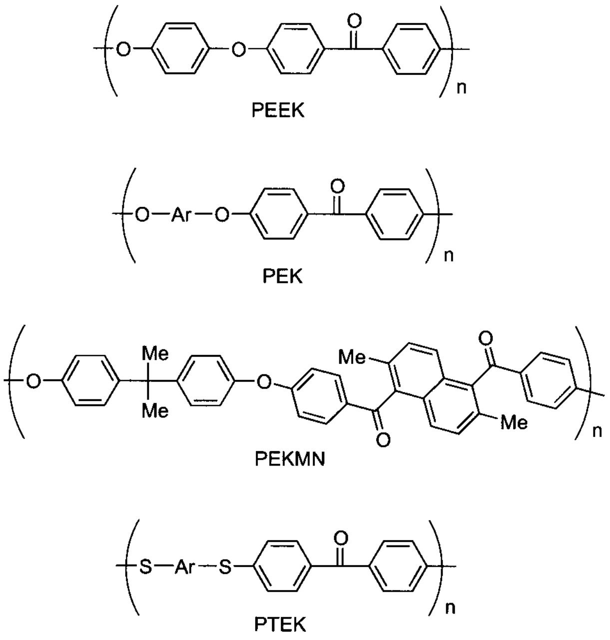
ABSTRACT: Novel aromatic poly(thioether−ketone)s (**PTEKs**) bearing the 2,6-dimethyl-1,5-naphthylene units were synthesized by the polycondensation of aromatic dihaloketones and aromatic dithiols in the presence of K_2CO_3. **PTEKs** with molecular weight ($M_n \sim 65\,000$, $M_w \sim 350\,000$) were obtained in quantitative yields. The molecular weights and yields of **PTEKs** obtained from aromatic dichloroketone and aromatic dithiols were much higher than those of the corresponding poly(ether−ketone)s (**PEKMNs**) obtained from aromatic dichloroketone and biphenols and were nearly the same as those of **PTEKs** obtained from aromatic difluoroketone and aromatic dithiols. The effect of reaction conditions on yield and molecular weight of **PTEKs** was investigated. The **PTEKs** had high solubility in ordinary organic solvents. Flexible, transparent, and strong films were cast from $CHCl_3$ solution. **PTEK-1** and **PTEK-2** had high glass transition temperatures (T_g; **PTEK-1** 245 °C, **PTEK-2** 215 °C) and 5% weight loss temperatures (T_{d5}; **PTEK-1** 435 °C, **PTEK-2** 436 °C).

Introduction

Poly(ether−ether−ketone) (PEEK), the most well-known example of poly(ether−ketone)s (PEKs), is a high-performance engineering plastic displaying high thermostability, chemical resistance, and mechanical properties (Scheme 1). PEEK is used widely in the fields of aerospace, transportation, electrical industries, and so on. However, PEEK cannot be processed by the casting method because of its low solubility and requires a high molding temperature because of its high melting point (T_m) around 340 °C. In addition, it has a fairly low glass transition temperature (T_g 143 °C), and the dimensional stability is relatively low because it is semicrystalline.[1] Many studies have been carried out to improve the low solubility and high T_m, that is, low processability and low T_g.[2−9] Replacement of the 1,4-phenylene group in PEEK with a 4,4′-biphenylene[2,3] or 1,5-naphthylene[4] group raised the T_g, although such polymers showed higher T_m's. Introduction of long alkoxy side chains enhanced the solubility of PEK, although such polymers showed low thermostability.[6] We have previously demonstrated that the introduction of the 2,6-dimethyl-1,5-naphthylene unit into the PEK's main chain remarkably raised its solubility and thermostability simultaneously, due to the zigzag and crankshaft structure of the 2,6-dimethyl-1,5-naphthylene unit.[7,8] Such polymers (PEKMNs) are one of the best alternates of PEEK.

Aromatic PEKs, including PEEK and PEKMN, have been generally synthesized from the corresponding difluoroketones and biphenols as monomers. Aromatic difluoroketones such as 4,4′-difluorobenzophenone are expensive and are sometimes difficult to prepare, so that the polymers produced from them cost very much.[10] Although the corresponding dichloroketones are readily available, they have not been used as monomers due to their relatively low electrophilicity. The dichloroketones can be good monomers if the nucleophilicity of the coreactant is higher than that of the phenol. It has been reported that high molecular weight poly(thioether−ketone)s (PTEKs)[10,11] or poly(thioether−sulfone)s[12,13] have been obtained when highly nucleophilic thiophenol derivatives were used as monomers with a dichloroketone or dichlorosulfone, respectively. However, PTEKs have been paid much less attention. The thermostability of PTEKs reported are not sufficiently high, and PTEKs reported have poor solubility in ordinary organic solvent as well as the corresponding PEKs. If aromatic dichloroketone bearing the 2,6-dimethyl-1,5-naphthylene skeleton is employed as a monomer, PTEKs thus formed should have not only high thermostability but also high solubility. Thus, the preparation of novel PTEKs corresponding to PEKMN has been investigated from dithiols, instead of biphenols, and the dichloroketone. The introduction of thioether linkage instead of ether linkage can vary the properties of polymer. For example,

Scheme 1



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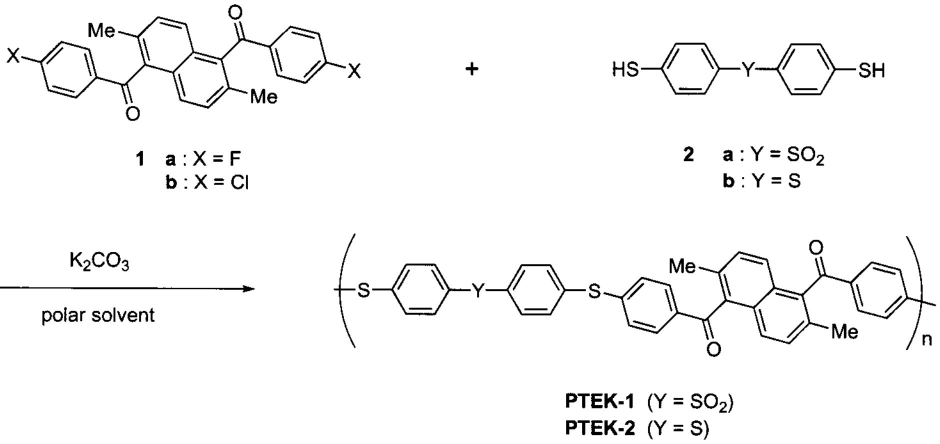
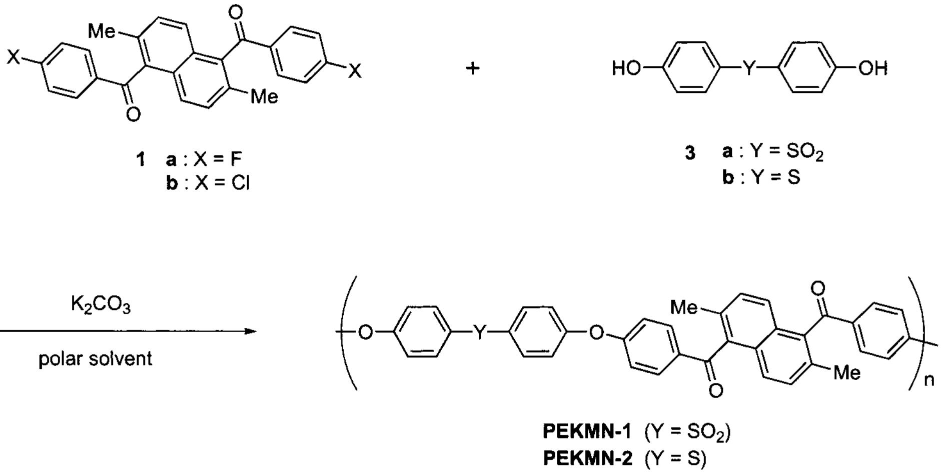
Scheme 2. Synthesis of PTEKs



Scheme 3. Synthesis of PEKMNs



PTEK will have less water absorption nature than the corresponding PEK because sulfide is generally more hydrophobic than the corresponding ether.[14,15] Recently, much attention has been attracted to the development of plastic optical materials with high refractive index,[16] and PTEKs can exhibit the higher refractive index than the corresponding PEKs, because the atomic refraction of the sulfur in thioether group is much bigger than that of the oxygen in ether group.

In this paper we report the successful synthesis of novel aromatic poly(thioether−ketone)s (**PTEKs**) having high solubility and thermostability from aromatic dihaloketones and aromatic dithiols.

Results and Discussion

Synthesis of PTEKs. (a) Effect of Aromatic Dithiol. PTEKs and the corresponding PEKs (**PEKMNs**) were synthesized by the polycondensation of aromatic dihaloketones **1** bearing the 2,6-dimethyl-1,5-naphthylene skeleton with aromatic dithiols **2** or biphenols **3**, respectively, in the presence of K_2CO_3 in polar solvents such as sulfolane and 1-methyl-2-pyrrolidinone (NMP) (Schemes 2 and 3). The resulting polymers were characterized by ^{1}H NMR, ^{13}C NMR, IR, and elemental analysis.

Figure 1 shows the typical gel permeation chromatography (GPC) profile of **PTEK-2**. When high molecular weight polymers were obtained, some small peaks (ca. 5% in area) were observed in the low molecular weight region as Figure 1 shows. These peaks were identified as cyclic oligomers produced at early stage of the polymerization, because their retention time and area did not change after prolonged reaction periods. Therefore, number-averaged molecular weight (M_n), weight-averaged molecular weight (M_w), and molecular weight distribution (MWD) were expressed in two ways

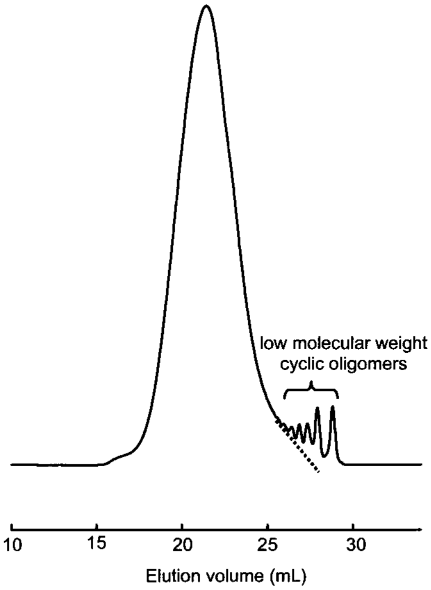


Figure 1. Typical GPC profile of **PTEK-2**. A line for the chromatogram to exclude cyclic oligomers is shown as a dotted line.

Table 1. Synthesis of PTEKs and PEKMNs

monomer													
1	**2** or **3**	polymer	solvent	temp (°C)	time (h)	yield[a] (%)	M_{nw}[b]	M_{ww}[b]	MWD$_w$[b]	M_{nm}[b]	M_{wm}[b]	MWD$_m$[b]	η_{inh}[c] (dL/g)
1b	**3a**	**PEKMN-1**	sulfolane	180	4	67	2900	4300	1.47	*e*	*e*	*e*	0.14
1b	**2a**	**PTEK-1**	sulfolane	180	4	95	17 000	70 000	4.14	24 000	72 000	2.95	0.57
1a	**2a**	**PTEK-1**	sulfolane	180	4	94[d]	18 000[d]	100 000[d]	5.78[d]	31 000[d]	110 000[d]	3.42[d]	0.69[d]
1b	**3b**	**PEKMN-2**	NMP	150	8	90	3900	6300	1.59	*e*	*e*	*e*	0.29
1b	**2b**	**PTEK-2**	NMP	150	8	98	9100	51 000	5.60	19 000	55 000	2.88	0.86
1a	**2b**	**PTEK-2**	NMP	150	8	91	8500	23 000	2.76	12 000	24 000	1.99	0.31

[a] MeOH-insoluble part. [b] THF-soluble part. Estimated by GPC in THF on the basis of polystyrene standards. M_{nw}, M_{ww}, and MWD$_w$: calculated from the whole chromatogram of the product including cyclic oligomers. M_{nm}, M_{wm}, and MWD$_m$: calculated for polymer from the chromatogram with exclusion of cyclic oligomers, when the peaks of cyclic oligomers were observed. [c] Measured at a concentration of 0.1 g/dL in NMP at 30 °C. [d] After $CHCl_3$ extraction. [e] No cyclic oligomer was observed.

Table 2. Effect of Reaction Conditions on the PTEK Synthesis from 1b and 2a or 2b

run	dithiol **2**	PTEK	solvent	temp (°C)	time (h)	yield[a] (%)	M_{nw}[b]	M_{ww}[b]	MWD$_w$[b]	M_{nm}[b]	M_{wm}[b]	MWD$_m$[b]	η_{inh}[c] (dL/g)
1	**2b**	**PTEK-2**	sulfolane	180	10 min	100	14 000	110 000	7.74	37 000	120 000	3.14	0.36
2	**2b**	**PTEK-2**	sulfolane	180	0.5	100	17 000	73 000	4.44	26 000	75 000	2.84	0.47
3	**2b**	**PTEK-2**	sulfolane	180	1	69[d]	14 000[d]	320 000[d]	22.7[d]	65 000[d]	350 000[d]	5.45[d]	*e*
4	**2b**	**PTEK-2**	diphenyl sulfone	180	0.5	95	14 000	36 000	2.64	21 000	37 000	1.79	0.40
5	**2b**	**PTEK-2**	NMP	180	0.5	95	8 900	24 000	2.72	13 000	25 000	1.93	0.29
6	**2b**	**PTEK-2**	NMP	150	8	98	9 100	51 000	5.60	19 000	55 000	2.88	0.86
7	**2b**	**PTEK-2**	NMP	150	16	99	420	9 900	23.8	*f*	*f*	*f*	0.32
8	**2b**	**PTEK-2**	sulfolane	150	8	95	12 000	43 000	3.48	20 000	44 000	2.24	0.37
9	**2b**	**PTEK-2**	sulfolane	150	16	78[d]	12 000[d]	58 000[d]	4.75[d]	17 000[d]	61 000[d]	3.64[d]	*e*
10	**2b**	**PTEK-2**	NMP	RT	8	51	490	1 600	3.23	*f*	*f*	*f*	0.13
11	**2b**	**PTEK-2**	NMP	RT	24	38[d]	710[d]	4 000[d]	5.67[d]	*f*	*f*	*f*	*e*
12	**2a**	**PTEK-1**	sulfolane	180	4	95	17 000	70 000	4.14	24 000	72 000	2.95	0.57

[a] MeOH-insoluble part. [b] THF-soluble part. Estimated by GPC in THF on the basis of polystyrene standards. M_{nw}, M_{ww}, and MWD$_w$: calculated from the whole chromatogram of the product including cyclic oligomers. M_{nm}, M_{wm}, and MWD$_m$: calculated for polymer from the chromatogram with exclusion of cyclic oligomers, when the peaks of cyclic oligomers were observed. [c] Measured at a concentration of 0.1 g/dL in NMP at 30 °C. [d] After $CHCl_3$ extraction. [e] Not determined. [f] No cyclic oligomer was observed.

in this paper: M_{nw}, M_{ww}, and MWD$_w$ were calculated from the whole chromatogram of the product including cyclic oligomers, and M_{nm}, M_{wm}, and MWD$_m$ were also calculated for the main polymer after tailing treatment of chromatogram to exclude the effect of cyclic oligomers as shown in Figure 1. Table 1 shows the reaction conditions, yields, M_{nw}, M_{ww}, MWD$_w$, M_{nm}, M_{wm}, MWD$_m$, and inherent viscosities (η_{inh}'s) of **PTEKs**. Synthesis of the corresponding PEKs (**PEKMNs**) was also carried out under the same conditions to compare the reactivity of dithiol with biphenol.

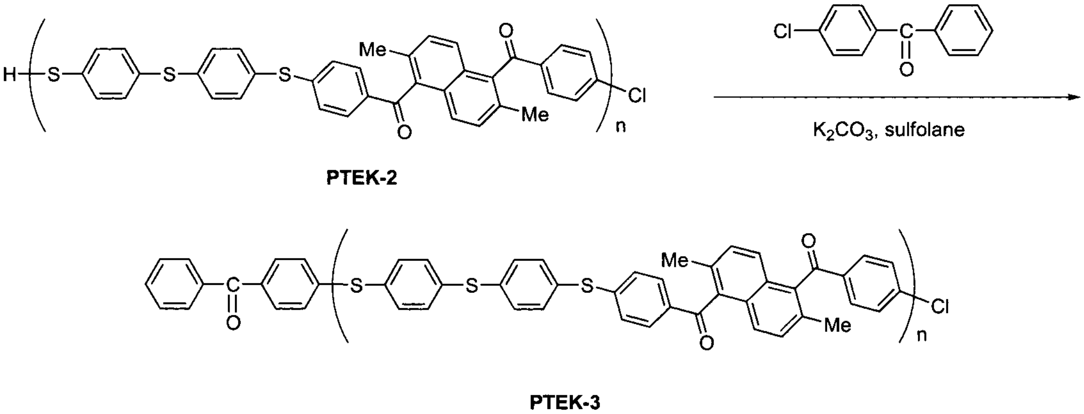
While high molecular weight **PEKMN-1** was obtained when difluoroketone **1a** was used as a monomer, low molecular weight (M_{nw} 2900) **PEKMN-1** was obtained in low yield (67%) when dichloroketone **1b** was used as a monomer with biphenol **3a** at 180 °C for 4 h in sulfolane. A similar result was obtained in the synthesis of **PEKMN-2**. Contrary, high molecular weight **PTEK-1** (M_{nw} 17 000) was obtained in quantitative yield using dithiol **2a** under the same conditions, but the molecular weight and yield were independent of the electrophilicity of haloketone monomers **1b** and **1a**. Similar results were obtained in the synthesis of **PTEK-2**. We therefore concluded that when aromatic dithiol is used instead of biphenol for the preparation of PTEK, an aromatic dichloroketone can be used as a monomer as well as difluoroketone. Because of the high nucleophilicity of thiol moiety, the difference of electrophilicity between chloroketone and fluoroketone was apparently hidden in polymerization.

(b) Effect of Reaction Conditions on PTEK Synthesis. Table 2 shows the effect of reaction conditions on the **PTEK** synthesis. The polycondensation of **1b** and **2b** at 180 °C in sulfolane gave **PTEK-2** having M_{nm} (37 000) and M_{wm} (120 000) in 100% yield after the polymerization time of only 10 min (run 1). The polycondensation for 1 h yielded polymer containing a $CHCl_3$-insoluble part (run 3). The wide MWD$_m$ (5.45) of the $CHCl_3$-soluble part indicates that a slight amount of cross-linking occurred during the polycondensation. Although the nature of the cross-linking reaction is not clear at the present time, the nucleophilic attack of the thiol on the carbonyl group is one of the most plausible reactions.

Various solvents such as sulfolane, diphenyl sulfone, and NMP were available for the polycondensation to afford **PTEK-2** in quantitative yields. Sulfolane was the best solvent to give the highest molecular weight of **PTEK-2** (runs 2, 4, and 5).

PTEK-2 obtained in NMP at 150 °C for 8 h exhibited M_{nw} 9100, but M_{nw} of **PTEK-2** drastically decreased as the reaction time was prolonged (runs 6 and 7). The polymer main chain was apparently cleaved by the reaction with a NMP derivative, since nitrogen atom contamination in the polymer was confirmed by elemental analysis of **PTEK-2** obtained in NMP, and considerable tailing was observed in their GPC chromatograms. No spectral change was observed in the polymer after the main chain cleavage. No chain cleavage occurred in sulfolane (runs 8 and 9). To elucidate this side reaction, **PTEK-2** was treated at 150 °C for 16 h in NMP in the presence and absence of K_2CO_3. To evaluate the effect of the terminal thiol group, **PTEK-3** was prepared by end-capping of the terminal thiol group in **PTEK-2** by the reaction with 4-chlorobenzophenone (Scheme 4) and was treated as above in NMP. While M_{nw} of **PTEK-2** was not changed by heating in NMP, **PTEK-2** and **PTEK-3** degraded by treatment with K_2CO_3 in NMP (for **PTEK-2**, M_{nw} 9100 → 240; for **PTEK-3**, M_{nw} 15 000 → 280). These results suggest that (1) an

Scheme 4. Synthesis of PTEK-3



Scheme 5. A Possible Decomposition of PTEK-2 during the Polycondensation in NMP

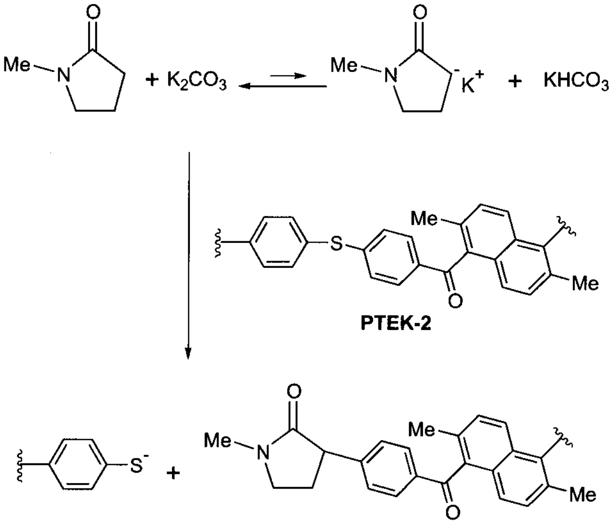


Table 3. Solubility of PTEKs[a]

solvent	δ (MPa$^{1/2}$)	PTEK PTEK-1	 PTEK-2
DMSO	26.5	+	+
EtOH	26.0	−	−
AN	24.3	−	−
DMF	24.1	+	+
NMP		++	++
DMA		+	+
nitrobenzene	22.6	++	++
dioxane	20.5	+	+
acetone	20.2	−	−
dichloromethane	20.0	+	+
chlorobenzene	19.4	+	+
chloroform	19.0	++	++
benzene	18.8	+	+
THF	18.6	+	+
toluene	18.2	+	+
Et_2O	15.1	−	−
hexane	14.9	− (±)	− (±)

[a] ++, soluble; +, partially soluble; ±, swelling; −, insoluble (on heating, in parentheses.)

enolate anion derived from NMP can degrade **PTEK-2** and (2) the thiol does not play essential role in the degradation. Thus, ipso attack of the enolate anion of NMP at the polymer main chain followed by replacement of the sulfide linkage by the NMP residue is assumed (Scheme 5). Considerable tailing was observed in GPC chromatogram for **PTEK** after treatment with K_2CO_3 in NMP as well as **PTEK** obtained in NMP (Table 2), indicating the degradation of polymer by NMP residue. Although the polycondensation in NMP involves some degradation, such side reactions are slow, and high molecular weight **PTEK-2** is actually obtained in a short polymerization period. It is supposed that high electron accepting ability and polarizability of sulfur atom accelerated the above-mentioned side reactions.

When the polycondensation of **1b** and **2b** was carried out at 150 °C for 8 h in sulfolane, a part of the formed **PTEK-2** deposited during the polymerization, and M_n did not increase with successive heating. The polycondensation at room temperature was very slow, and a large amount of unreacted monomer **1b** remained even after 24 h (runs 10 and 11). It is, therefore, difficult to obtain sufficiently high molecular weight **PTEK-2** at lower temperature. It is summarized that higher molecular weight **PTEK-2** can be obtained by the polycondensation at higher temperature in sulfolane.

A longer reaction time was necessary for the polycondensation of **1b** and **2a** than that for the polycondensation of **1b** and **2b** (runs 12 and 2). This result can be accounted for by the decrease of the nucleophilicity of thiol group in **2a** by the highly electron-withdrawing sulfonyl group.

Solubility of PTEK. Table 3 summarizes the solubility behavior of **PTEK** in ordinary organic solvents, together with the solubility parameter of solvents (δ). Although wholly aromatic polymers are generally insoluble in ordinary organic solvents, both **PTEK-1** and **PTEK-2** were highly soluble in organic solvents of a wide range of δ values. They are completely soluble in NMP, nitrobenzene, and $CHCl_3$. The only extremely high molecular weight part is insoluble in THF, chlorobenzene, dioxane, and so on. The 2,6-dimethyl-1,5-naphthylene unit in **PTEKs** would increase their solubility, similarly to for the corresponding PEKs (**PEKMNs**).[7,8] Because of the good solubility, flexible, transparent, and strong cast films were easily obtained from $CHCl_3$ or THF solution.

Thermal Properties of PTEK. Table 4 shows the thermal properties of **PTEKs** and **PEKMNs**.[8] Each **PTEK** has 5% weight loss temperatures (T_{d5}) around 435 °C. The T_g's of **PTEKs** were much higher than that of the commercially available PEEK (**PTEK-1**: T_g 245 °C; **PTEK-2**: 215 °C; PEEK: 143 °C).[1] The T_g of **PTEK-1** was higher than that of **PTEK-2**, probably because the sulfonyl group is more polar and bulky than the thioether group. These results on T_g and T_{d5} indicate that both **PTEK-1** and **PTEK-2** have extremely high

Table 4. Thermal Properties of PTEKs and PEKMNs

polymer	T_{d5}[a] (°C)	T_g[b] (°C)
PTEK-1	435	245
PTEK-2	436	215
PEKMN-1	436[c]	232[c]
PEKMN-2	430[c]	228[c]

[a] Measured by TG at a heating rate of 10 °C /min in N_2 for **PTEK** and 20 °C/min in air for **PEKMN**. [b] From the second heating trace of the DSC measurement conducted at a heating rate of 10 °C/min for **PTEK** and 20 °C/min for **PEKMN** in N_2. [c] Reported previously (ref 8).

thermostability and place them among the most thermostable PTEKs. Neither **PTEK-1** nor **PTEK-2** exhibited T_m, similarly to **PEKMN-1** and **PEKMN-2**, because of their amorphous nature. **PTEKs** have potential advantages of higher dimensional stability and lower anisotropy and therefore can be readily processed.

It has been reported that T_g's were slightly decreased by replacing the ether linkage with a thioether linkage as the main chain functionality.[9] Although the measurement conditions were a little different, the T_{d5}'s and T_g's of **PTEKs** were essentially the same as those of **PEKMNs**.[8] In this case, the replacement of ether linkage with thioether linkage did not influence T_{d5} and T_g.

Summary

Poly(thioether−ketone)s (**PTEKs**) were synthesized quantitatively by the polycondensation of aromatic dihaloketones **1** and aromatic dithiols **2** in the presence of K_2CO_3. Although highly electrophilic difluoroketone has been usually used as a monomer for polymer synthesis via aromatic nucleophilic substitution, less electrophilic dichloroketone could be actually used as a monomer for the preparation of high molecular weight PTEKs, owing to high nucleophilicity of dithiol. The optimum condition to obtain high molecular weight **PTEK-2** was the polycondensation of dichloride **1b** and dithiol **2b** at 180 °C for 0.5 h in sulfolane. Because of the presence of the 2,6-dimethyl-1,5-naphthylene unit, **PTEKs** exhibited high thermostability (**PTEK-1**: T_{d5} 435 °C, T_g 245 °C; **PTEK-2**: T_{d5} 436 °C, T_g 215 °C) and excellent solubility. The replacement of ether group of PEKMNs with thioether group did not impair the high thermostability. **PTEKs** afforded the flexible, transparent, and strong cast films from $CHCl_3$ or THF solutions. Finally, the combination of an aromatic dithiol with a dichloroketone having a 2,6-dimethyl-1,5-naphthylene unit is economically attractive and effective for the synthesis of new sulfur-containing high-performance polymers.

Experimental Section

Materials and Instrumentation. 4,4′-Thiobis(benzenethiol), **2b**, was kindly supplied by Sumitomoseika Chemicals Co., Ltd. 4,4′-Sulfonyldiphenol and K_2CO_3 were purchased from Wako Pure Chemical Industries, Ltd. 4,4′-Thiodiphenol was purchased from Tokyo Kasei Kogyo Co., Ltd. Commercial grade NMP was dried overnight over calcium hydride and distilled prior to use. Other commercially available materials and solvents were used without further purification. 1,5-Bis(4-fluorobenzoyl)-2,6-dimethylnaphthalene (**1a**),[7] 1,5-bis(4-chlorobenzoyl)-2,6-dimethylnaphthalene (**1b**),[8] and 4,4′-sulfonylbis(benzenethiol) (**2a**)[17] were prepared according to the literature.

^1H (270 MHz) and ^{13}C (67.5 MHz) NMR spectra, reported in ppm, were recorded on a JEOL JNM-GX270 spectrometer using $CDCl_3$ as the solvent with tetramethylsilane as the internal standard. Molecular weight and its distribution were measured by gel permeation chromatography (GPC) on a JASCO HSS-1500 system equipped with three consecutive polystyrene gel columns (TOSOH TSKgel G5000HXL, G4000HXL, and G2500HXL) eluted with THF at a flow rate of 1.0 mL/min calibrated by standard polystyrenes. IR spectra were recorded on a JASCO FT/IR-230 spectrometer. The inherent viscosities were measured with an Ostwald viscometer at 30 °C in NMP at a concentration of 0.1 g/dL. Solubilities were determined using 3 mg of polymer and 3 mL of solvent. Thermogravimetry (TG) was performed on a Shimadzu TGA-50 instrument at a heating rate of 10 °C/min under N_2 atmosphere (flow rate of 40 mL/min), and T_{d5} was reported as temperature at which 5% weight loss was observed. Differential scanning calorimetry (DSC) was performed on a Shimadzu DSC-60 instrument at a heating rate of 10 °C/min under N_2 atmosphere (flow rate of 40 mL/min), and T_g was reported as temperature at the middle of the thermal transition from the second heating scan.

Polymer Synthesis. A typical polycondensation procedure follows: 1,5-Bis(4-chlorobenzoyl)-2,6-dimethylnaphthalene (**1b)** (0.13 g, 0.30 mmol), 4,4′-thiobis(benzenethiol) (**2b**) (0.075 g, 0.30 mmol, 1.0 equiv), K_2CO_3 (0.10 g, 0.72 mmol, 2.4 equiv), and sulfolane (1 mL) were charged into a 30 mL two-necked round-bottom flask equipped with a magnetic stirrer under argon atmosphere. The mixture was heated and stirred at 180 °C for 0.5 h. The resulting mixture was cooled, quenched by addition of acetic acid, and then poured into methanol to precipitate white powdery polymer. The precipitated polymer was collected by filtration and washed with boiling methanol. Crude polymer was purified by reprecipitation from chloroform solution into methanol, and the polymer collected by filtration was dried in vacuo at 40 °C for 12 h.

PTEK-1: ^1H NMR (270 MHz, $CDCl_3$): δ 7.86−7.26 (m, 20H, Ar−H), 2.27 (s, 6H, CH_3). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 198.6, 141.8, 141.1, 139.8, 136.2, 135.5, 131.9, 130.9, 130.8, 130.5, 129.4, 128.6, 128.4, 125.8, 19.6. IR (NaCl): 1666 (Ar−C═O) cm^{-1}. Anal. Calcd for $(C_{38}H_{26}O_4S_3)_n$: C, 71.00; H, 4.08; S, 14.96. Found: C, 70.03; H, 4.29; S, 14.33. **PTEK-2**: ^1H NMR (270 MHz, $CDCl_3$): δ 7.66 (d, 4H, J = 8.1 Hz, Ar−H), 7.46−7.15 (m, 16H, Ar−H), 2.24 (s, 6H, CH_3). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 198.6, 145.6, 136.3, 135.8, 134.6, 134.5, 131.8, 131.6, 130.7, 130.2, 129.2, 128.6, 127.3, 125.7, 19.6. IR (NaCl): 1664 (Ar−C═O) cm^{-1}. Anal. Calcd for $(C_{38}H_{26}O_2S_3)_n$: C, 74.72; H, 4.29; S, 15.75. Found: C, 74.27; H, 4.30; S, 15.50 for polymer prepared in diphenyl sulfone. Anal. Calcd for $(C_{38}H_{26}O_2S_3)_n$: C, 74.72; H, 4.29; N, 0.00; S, 15.75. Found: C, 74.04; H, 4.53; N, 0.25; S, 15.39 for polymer prepared in NMP. **PEKMN-1**: ^1H NMR (270 MHz, $CDCl_3$): δ 7.95−7.02 (m, 20H, Ar−H), 2.28 (s, 6H, CH_3). IR (NaCl): 1664 (Ar−C═O), 1242 (C−O−C) cm^{-1}. **PEKMN-2**: ^1H NMR (270 MHz, $CDCl_3$): δ 7.80−6.95 (m, 20H, Ar−H), 2.27 (s, 6H, CH_3). IR (NaCl): 1662 (Ar−C═O), 1242 (C−O−C) cm^{-1}.

Preparation of end-capped **PTEK-3**. A mixture of **1b**, **2b**, and K_2CO_3 was reacted under the same conditions as described above. After 0.5 h, the reaction mixture was cooled, and a large excess of 4-chlorobenzophenone was added to the mixture. The mixture was heated and stirred again at 180 °C for 20 min. The resulting mixture was cooled and was purified in the same manner as described above.

PTEK-3: ^1H NMR (270 MHz, $CDCl_3$): δ 7.66 (d, 4H, J = 8.1 Hz, Ar−H), 7.46−7.15 (m, 16H, Ar−H), 2.24 (s, 6H, CH_3). IR (NaCl): 1664 (Ar−C═O) cm^{-1}.

Control Experiments of PTEK-2 and PTEK-3 in NMP. A procedure for treatment in the absence of K_2CO_3. A mixture of **PTEK-2** (18 mg, 0.03 mmol) and NMP (1 mL) in a 30 mL two-necked round-bottom flask under argon atmosphere was heated and stirred at 150 °C for 16 h. The mixture was cooled and poured into methanol to precipitate the polymer. The precipitated polymer was collected by filtration and washed with boiling methanol. The polymer was purified by reprecipitation from chloroform solution into methanol, and the polymer collected by filtration was dried in vacuo at 40 °C for 12 h.

A procedure for treatment in the presence of K_2CO_3. **PTEK-2** (18 mg, 0.03 mmol), K_2CO_3 (17 mg, 0.12 mmol), and NMP (1 mL) were charged into a 30 mL two-necked round-bottom flask equipped with a magnetic stirrer under argon atmosphere. The mixture was heated and stirred at 150 °C for 16 h. The resulting mixture was cooled, quenched by addition of acetic acid, and then purified in the same manner as described above.

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