Preparation of Aromatic Poly(ether ketones) from an Aromatic Dihalide and Sodium Carbonate

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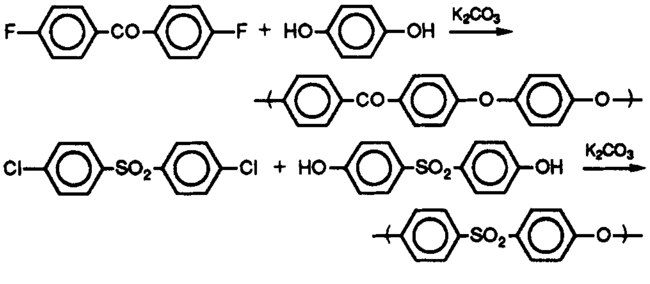
ABSTRACT: A novel synthetic method of semicrystalline poly(oxy-1,4-phenylenecarbonyl-1,4-phenylene), commonly known as poly(ether ketone) (PEK), by the reaction of 4,4′-dichlorobenzophenone with sodium carbonate in the presence of silica/Cu salt catalyst has been investigated. High molecular weight poly(ether ketone) (PEK) with satisfactory mechanical properties was obtained. The reaction mechanism in which the silyl ether formed by the reaction of 4,4′-dichlorobenzophenone and the silanol on the surface of silica is the intermediate of the etherification is proposed. Aromatic poly(ether sulfone) and aromatic poly(ether ketones) with a higher ketone content such as poly(oxy-1,4-phenylenecarbonyl-1,4-phenylenecarbonyl-1,4-phenylene), commonly known as poly(ether ketone ketone) (PEKK), were prepared by the same reaction by using various aromatic halides and alkali carbonates.

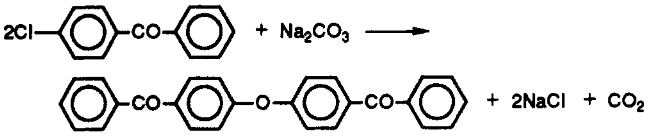
Introduction

Many studies are reported on aromatic poly(ether ketones) and poly(ether sulfones), which are useful as high-performance engineering plastics. These polymers are synthesized by a nucleophilic reaction of alkali salts of diphenols such as hydroquinone, 4,4′-dihydroxybenzophenone and 4,4′-dihydroxydiphenyl sulfone with aromatic dihalides such as 4,4′-difluorobenzophenone and 4,4′-dichlorodiphenyl sulfone[1,2] or by the electrophilic reaction of acid dichlorides such as phosgene or terephthaloyl chloride with aromatic ethers such as diphenyl ether.[3,4] There are some reports in which silyl ethers are used instead of alkali phenolates and aromatic poly(ether sulfones) and aromatic poly(ether ketones) are obtained from the trimethylsilyl ether or diphenols and difluorodiphenyl sulfone or difluorobenzophenone.[5,6] Among these polyethers, poly(oxy-1,4-phenyleneoxy-1,4-phenylcarbonyl-1,4-phenylene), commonly known as poly(ether ether ketone) (PEEK), and poly(oxy-1,4-phenylenesulfonyl-1,4-phenylene), commonly known as poly(ether sulfone) (PES), manufactured by nucleophilic reaction are commercialized.

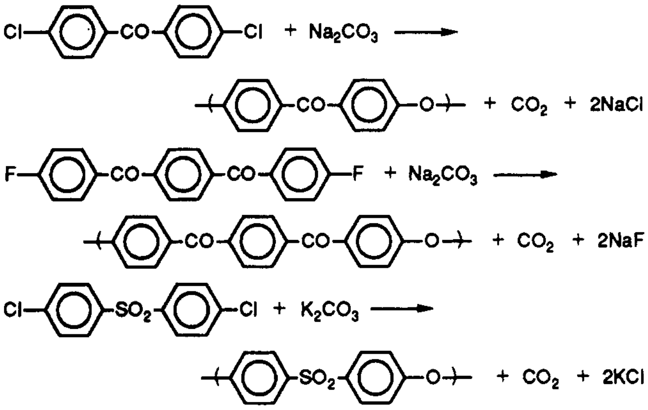


Aromatic poly(ether ketones) of a high molecular weight have not been prepared by the reaction of dichlorobenzophenone and diphenol because the reactivity of dichlorobenzophenone is considerably lower compared with difluorobenzophenone or dichlorodiphenyl sulfone. As aromatic chlorides are much more inexpensive compared with corresponding fluorides, the preparation of high molecular weight aromatic poly(ether ketone) from dichlorobenzophenone is of an industrial importance.

Recently we found a novel etherification reaction. Aromatic halides activated by electron-withdrawing groups such as nitro, cyano, sulfone, and carbonyl react with alkali carbonates or bicarbonates in the presence of silica or silica/Cu salt catalyst to form ethers in a high yield.[7] Under suitable conditions, 4,4′-dibenzoyldiphenyl ether was obtained in yields of over 95% from *p*-chlorobenzophenone and sodium carbonate.



In this report, this reaction was applied to aromatic dihalide and high molecular weight aromatic polyethers were prepared.



The polymerization behavior of dichlorobenzophenone with sodium carbonate in the presence of silica/Cu salt catalyst was investigated in detail, and the reaction mechanism is proposed. The characterization of some other aromatic poly(ether ketones) is also described.

Experimental Section

Reagents. 4,4′-Dichlorobenzophenone and diphenyl sulfone were supplied by Ihara Chemical Co., Ltd., and Sanko Chemical Co., Ltd., respectively, and used without purification. 4,4″-Difluoroterephthalophenone was synthesized from terephthaloyl chloride and fluorobenzene and recrystallized from toluene. 4,4′-Difluorobenzophenone, 4,4′-dichlorodiphenyl sulfone, 4,4′-difluorodiphenyl sulfone, and benzophenone were purchased from Tokyo Kasei Co., Ltd., and recrystallized from toluene or hexane. Fine-powder-grade sodium carbonate was supplied by Takasugi Seiyaku Co., Ltd., and dried at 200 °C for 8 h in vacuo before use. Aerosil 300 and Siloyd 244 (silica) were supplied by Nippon

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Aerosil Co., Ltd., and Fuji Davison Co., Ltd., respectively, and dried at 200 °C for 8 h in vacuo before use.

Polymerization. The following is a typical procedure for the preparation of poly(ether ketone) (PEK) from 4,4'-dichlorobenzophenone and sodium carbonate.

In a 1-L reaction vessel fitted with a mechanical stirrer, nitrogen inlet, and nitrogen outlet are placed 125 g (0.498 mol) of 4,4'-dichlorobenzophenone, 59.2 g (0.548 mol) of fine-powder sodium carbonate, 10 g of silica (Aerosil 300), 0.27 g (0.002 mol) of cupric chloride, and 300 g of diphenyl sulfone. After the atmosphere was replaced with nitrogen, the mixture was heated to 200 °C. The atmosphere was replaced with nitrogen again, and the stirring was started. The polymerization was conducted for 2 h at 280 °C, 1 h at 300 °C, and an additional 2 h at 320 °C. During the polymerization, a part of the reaction mixture was taken out from the nitrogen outlet for the analysis. The start and the end of the reaction can be monitored by the evolution of carbon dioxide. In the polymerization of aromatic poly(ether ketones), the produced polymer crystallizes and precipitates in the reaction mixture with the progress of polymerization. Therefore, it is preferable that the reaction temperature is raised gradually or in a stepwise manner so as to keep the reaction mixture in a homogeneous state. The precipitation of the polymer can also be monitored by a sudden increase of the stirrer torque. The time when the polymer precipitates depends on the polymerization condition. After the polymerization was conducted at a fixed time, the product was cooled, pulverized in water, and washed several times with acetone and water. Silica was removed by washing with 4% sodium hydroxide solution at 60 °C.

Analysis. Intrinsic viscosities were measured on 0.1% solution at 25 °C by using an Ubbelohde viscometer. Concentrated sulfuric acid (98%) and *N*-methyl-2-pyrrolidone were used as solvents for aromatic poly(ether ketone) and aromatic poly(ether sulfone), respectively. ^1H and ^{13}C NMR spectra were measured on 2% solution of deuteriosulfuric acid (D_2SO_4) by a JEOL FX-400 spectrometer. Hexamethyldisiloxane (0.0 ppm) and dioxane (67.4 ppm) were used as an internal standard for ^1H and ^{13}C NMR, respectively. Acquisition parameters for ^{13}C NMR measurements are as follows: acquisition time 0.328 s, pulse delay 2.0 s, pulse width 10 μs (45°), and SGBCM mode. Mass spectra were measured by a JEOL JMS-HX 110 spectrometer. DSC was measured by a Perkin-Elmer DSC-2 instrument in a nitrogen atmosphere with a heating rate of 10 °C/min. The melting point of polymer was measured on a 5-mg sample, which was heated once to 400 °C and cooled to 50 °C at a cooling rate of 320 °C/min in DSC. A high-pressure liquid chromatogram was measured by a JASCO LC-800 system (Japan Spectroscopic Ltd.) on a 0.1% *N*-methyl-2-pyrrolidone solution: column, Finepak SIL C18-S; eluent, methanol/water 80/20 by volume, 1 mL/min; detector, UV (254 nm). WAXD spectra were measured by a Rigaku RAD-B system by using a Cu Kα beam.

Results and Discussion

NMR Spectra of Products. Figure 1-I shows the ^{13}C NMR spectrum of the poly(ether ketone) (PEK) prepared by the reaction of 4,4'-dichlorobenzophenone and Na_2CO_3 in the presence of a $SiO_2/CuCl_2$ catalyst. Five peaks are observed corresponding to the five carbons in the poly(ether ketone) (PEK), and the spectrum is essentially the same as that prepared from 4,4'-difluorobenzophenone and 4,4'-dihydroxybenzophenone in the presence of K_2CO_3 by the conventional polycondensation reaction (Figure 1-II). Thus, it is confirmed that the following reaction has occurred:

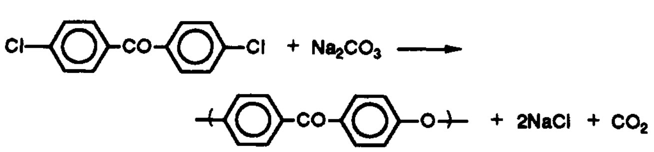


Figure 2 shows the ^1H NMR spectra of poly(ether ketones) (PEK) with various degrees of polymerization prepared by using dichlorobenzophenone and Na_2CO_3. In addition to large peaks corresponding to the main chain (7.03 and 7.73 ppm), the peaks assigned to chlorobenzoyl (7.28 and 7.50 ppm) and hydroxybenzoyl (6.77 and 7.60 ppm) chain ends are observed. As the polymerization proceeds, the peaks of the chlorobenzoyl terminal decrease, whereas the intensities of the hydroxybenzoyl peaks are constant. This will be discussed in the latter part of this paper in connection with the polymerization mechanism. Other small peaks are probably assigned to other structures formed by side reactions.

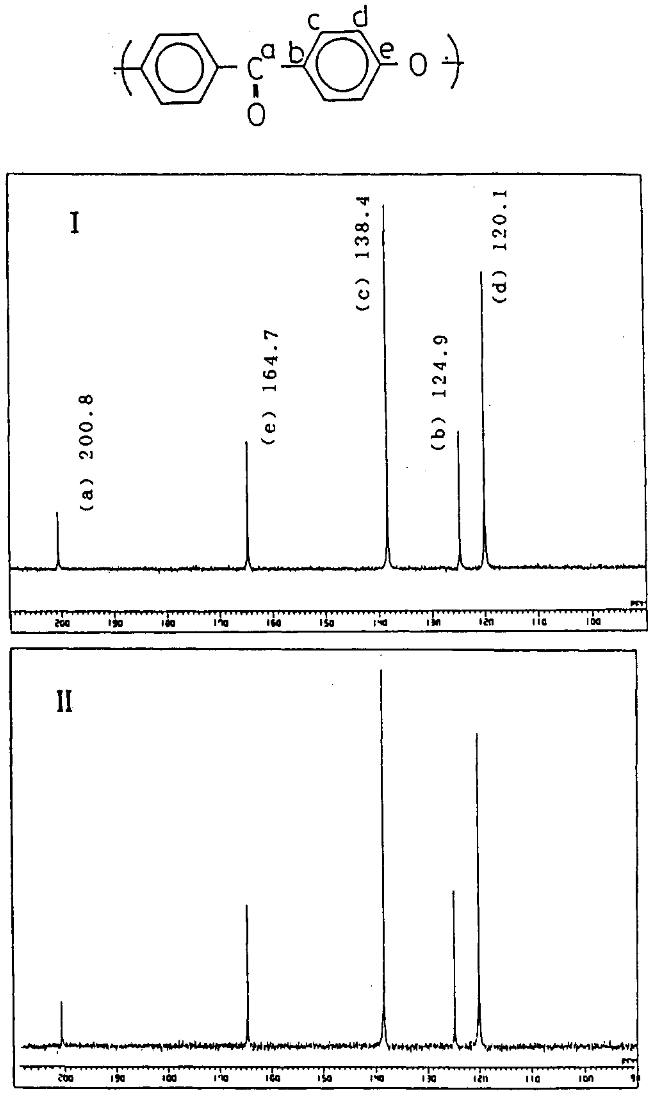


Figure 1. ^{13}C NMR spectra of poly(ether ketones) (PEK): (I) prepared from 4,4'-dichlorobenzophenone and sodium carbonate; (II) prepared from 4,4'-difluorobenzophenone and 4,4'-dihydroxybenzophenone.

Polymerization Behavior. Table I and Figure 3 summarize the inherent viscosities, the amount of the unreacted monomer (*R*), and the intensities of the NMR peaks of the chain end of the samples taken out in the course of the polymerization. The conversion of the chlorobenzoyl group (*p*) and the number-average degree of polymerization (P_n) can be calculated from the amount of the unreacted monomer (*R*) by eqs 1 and 2.

$$p = 1 - R^{1/2} \quad (1)$$

$$P_n = 1/(1 - p) = 1/R^{1/2} \quad (2)$$

The degree of polymerization can be also calculated from

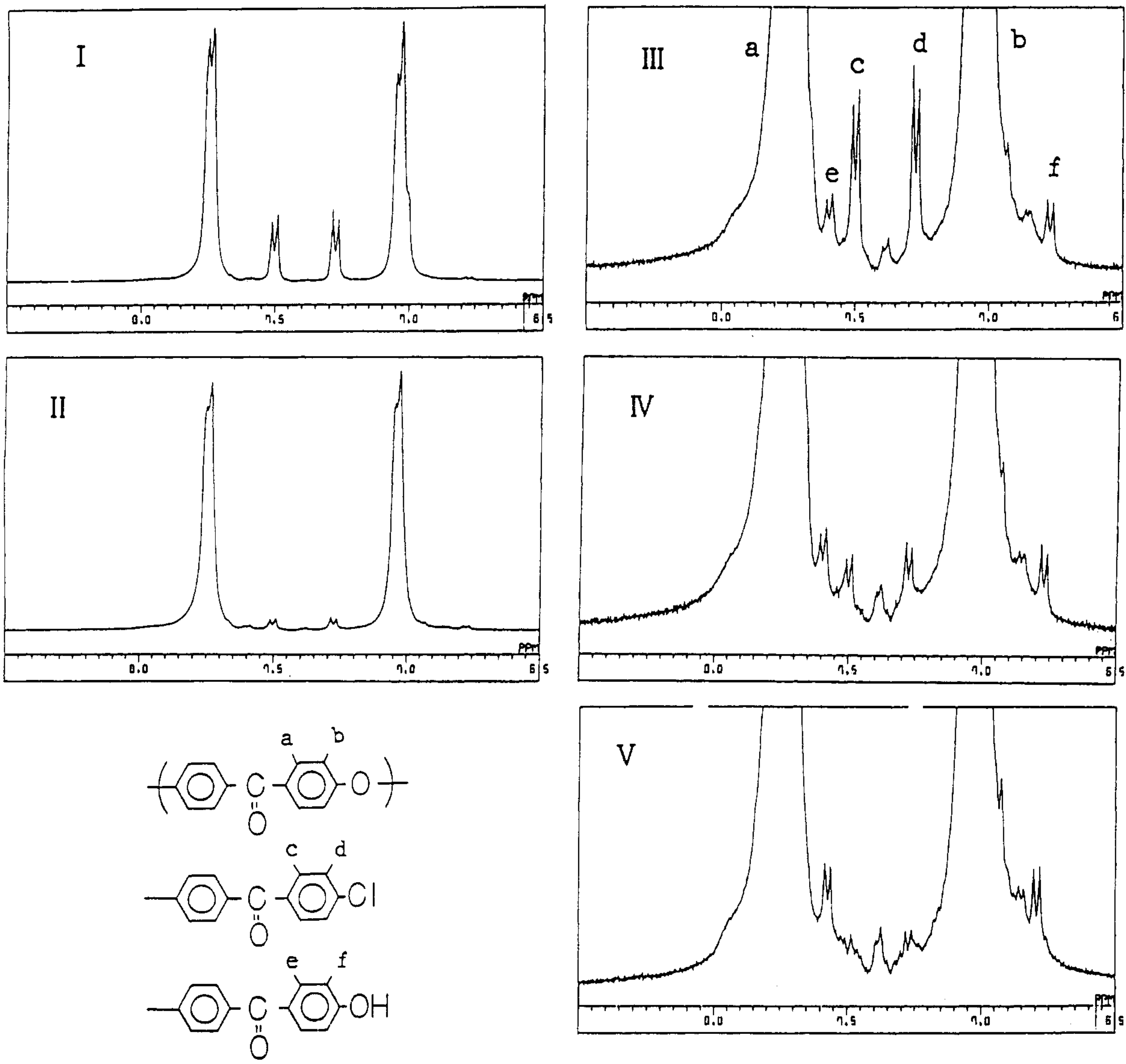


Figure 2. ^{1}H NMR spectra of poly(ether ketones) (PEK) prepared from 4,4′-dichlorobenzophenone and sodium carbonate: (I) sample no. 4 in Table I, (II and III) no. 9, (IV) no. 10, (V) no. 11. Spectra III–V are enlarged 20 times.

Table I
Polymerization of 4,4′-Dichlorobenzophenone with Na_2CO_3[a]

no.	polymn time,[b] h	η_{sp}/C, dL/g	R,[c] %	convn[d] p	P_n[e]	A(Cl)[f]	A(OH)[g]	P_n(NMR)[h]
1	1.0		54.9	0.259	1.4			
2	1.5		37.1	0.391	1.6			
3	2.0	0.06	24.0	0.510	2.0	40.5	1.05	3.4
4	2.25	0.08	15.6	0.605	2.5	29.1	1.16	4.3
5	2.5	0.09	7.83	0.720	3.6	23.8	1.11	4.9
6	2.75	0.10	5.81	0.759	4.2	21.2	1.16	5.2
7	3.0	0.12	2.96	0.828	5.8	16.9	1.14	6.5
8	3.25	0.18	1.23	0.889	9.0	9.5	1.17	11
9	3.5	0.40	0.37	0.939	16.4	4.37	1.19	19
10	3.75	0.65	0.09	0.970	33.3	1.32	1.21	36
11	4.0	0.76	0.03	0.983	58.8	0.39	1.32	60
12	5.0	0.92				0.26	1.48	59

[a] Dichlorobenzophenone, 125 g (0.498 mol). Na_2CO_3, 59.2 g (0.548 mol). Aerosil 300, 12 g. Cu_2O, 0.3 g. Diphenyl sulfone (as solvent), 250 g. [b] Polymerization temperature: 0–2 h, 280 °C; 2–3 h, 300 °C; 3–5 h, 320 °C. [c] Unreacted monomer measured by HPLC. [d] Calculated by eq 1. [e] Calculated by eq 2. [f] ^{1}H NMR chlorobenzoyl peak area (main peak area = 100). [g] ^{1}H NMR hydroxybenzoyl peak area (main peak area = 100). [h] Calculated by eq 3 (A(main) = 100).

the peak intensities of the NMR spectra

$$P_n(\mathrm{NMR}) = A(\mathrm{main})/(A(\mathrm{Cl}) + A(\mathrm{OH})) + 1 \qquad (3)$$

where A(main), A(Cl), and A(OH) are the peak areas of the main chain, the chlorobenzoyl group, and the hydroxybenzoyl group, respectively. The degrees of polymerization calculated by both methods agree within experimental error. As shown in Figure 4, the plot of $-\ln(1 - p)$ vs polymerization time shows the linear relationship at each temperature, suggesting that the reaction obeys the first-order concerning the terminal chloride.

Mechanistic Discussion. Figure 5 shows the FD-MS spectra of sample 4 in Table I. The oligomers of various degrees of polymerization with chlorobenzoyl groups at

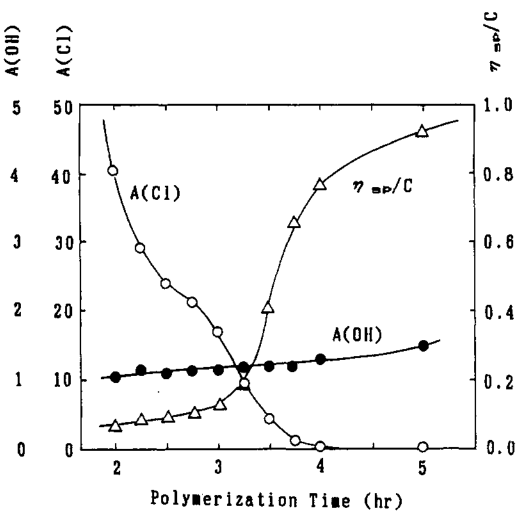


Figure 3. Change of the concentration of the chlorobenzoyl and hydroxybenzoyl chain ends and the inherent viscosity with polymerization time (see Table I).

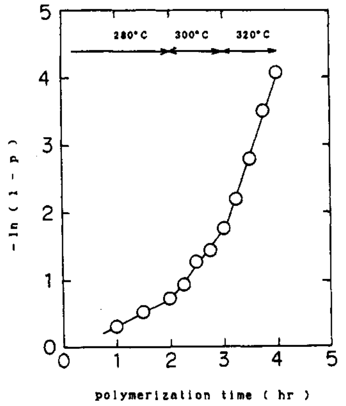
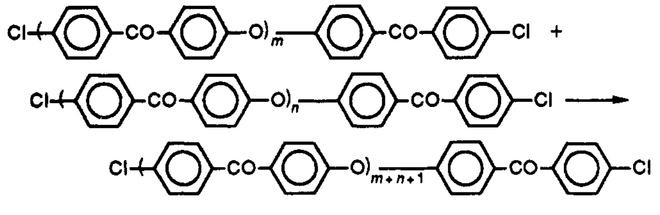


Figure 4. Plot of $-\ln(1 - p)$ vs polymerization time.

both chain ends are the main product at the early stage of the polymerization. It is supposed that the polymerization proceeds through the statistical reaction of oligomers with various degrees of polymerization.



In the preceding paper,[7] we reported that a small amount of *p*-hydroxybenzophenone (PHBP) was observed in the reaction of *p*-chlorobenzophenone (PCBP) with sodium carbonate in the presence of a silica/Cu salt catalyst to 4,4′-dibenzoyldiphenyl ether and that the amount of PHBP does not change with the reaction time and is proportional to the amount of silica catalyst. We proposed that the silyl ether formed by the reaction of the silanol group on the surface of silica and PCBP is the intermediate of the etherification.

The hydroxybenzoyl terminal in the polymerization of dichlorobenzophenone corresponds with PHBP in the reaction of PCBP. As described earlier, the intensity of the hydroxybenzoyl chain end does not change with the polymerization time and with the degree of polymerization of the product except in the final stage of polymerization. Figure 6 shows the relationship between the ^{1}H NMR peak area of the hydroxybenzoyl group of the polymers with an inherent viscosity of 0.2–0.6 dL/g and the amount of silica added. The intensity of the hydroxy chain end increases proportionally with the amount of silica. Therefore, it is supposed that the etherification mechanism proposed for the model reaction can also be applied to the polymerization (Scheme I).

Here, the intermediate silyl ether on the surface of silica is hydrolyzed to the hydroxy chain end. According to this mechanism, the fact that the intensity of the hydroxy chain end does not change with polymerization time and is proportional to the amount of silica is well explained.

Dihalides and Alkali Carbonates. Table II summarizes the reaction of *p*-halobenzophenones with alkali carbonates to 4,4′-dibenzoyldiphenyl ether. This model reaction is useful for obtaining information on the reactivity and the selectivity of the present polymerization reaction. The fluoride shows a much higher reaction rate and selectivity compared with chloride, suggesting that high molecular weight polymers are obtained more easily when difluoride is used. The reaction rate of *p*-fluorobenzophenone is especially high when potassium carbonate is used. This is also true for the polymerization reaction. A high molecular weight poly(ether ketone) (PEK) is produced from 4,4′-difluorobenzophenone and potassium carbonate with silica in a very short polymerization time. However, potassium carbonate may cause the scission of the ether linkage, and the molecular weight of the products sometimes decreases in the final stage of the polymerization. Moreover, the free phenols produced by the ether scission can cause side reactions, and gels are often observed in the polymer when the polymerization was conducted for a long time. Therefore, the use of sodium carbonate or a mixture of sodium carbonate and potassium carbonate is preferred in the polymerization of aromatic difluorides.

Sodium carbonate is preferable to potassium carbonate also for the polymerization of dichlorobenzophenone. Gels are sometimes observed in the polymer prepared with potassium carbonate. As the reaction rate of chloride and sodium carbonate is not high enough to obtain a high molecular weight polymer even in the presence of silica catalyst, cuprous or cupric compound should be added as the cocatalyst to enhance the polymerization rate.

In the usual polycondensation reaction, high molecular weight polymers are obtained only when the molar ratio of two monomers is the same. Although alkali carbonate works as the oxygen source and is a monomer in the present reaction, excess alkali carbonate can be used. The polymerization rate increases with the amount of alkali carbonate especially in the final stage of polymerization. However, too much excess carbonate may cause side reactions, and the preferable molar ratio of carbonate to dihalide is 1.0 to 2.0. High molecular weight polymers are not obtained when alkali carbonate is deficient.

Catalysts and Cocatalysts. The catalytic activity of silica increases with the surface area and is independent of its manufacturing process. Wet-process silica (Siloyd 244) and dry-process silica manufactured by the reaction of $SiCl_4$, H_2, and O_2 (Aerosil 300) give almost the same results. Aerosil 300 is the nonporous silica with a very small particle size (7 μm) and has a surface area of 300 m^2/g. Siloyd 244 is the colloidal silica with about the same surface area as that of Aerosil 300. It is larger in particle size (1.8 μm) and is highly porous, and the average pore size is reported to be 210 Å. Therefore, most of its surface area comes from the internal surface of the pore. Considering that the catalytic activities of Siloyd 244 and of Aerosil 300 are almost the same, the polymerization

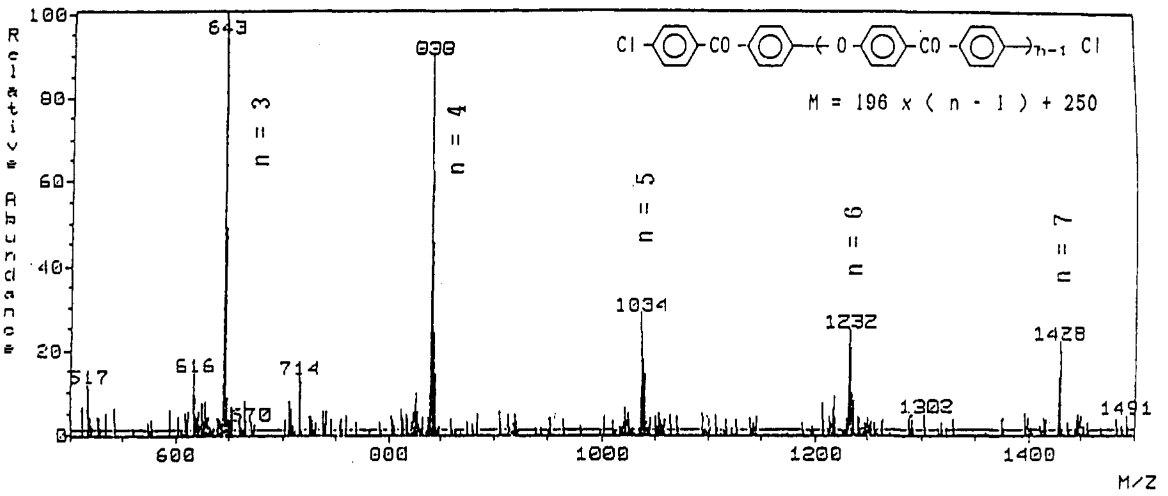


Figure 5. FD-MS spectra of a poly(ether ketone) (PEK) oligomer.

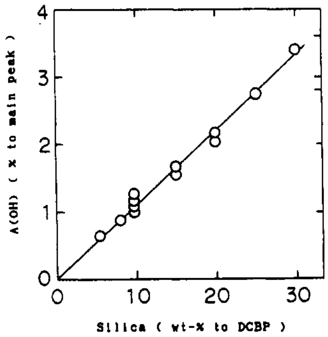


Figure 6. Effect of the amount of silica on the intensity of the hydroxybenzoyl chain end.

Scheme I

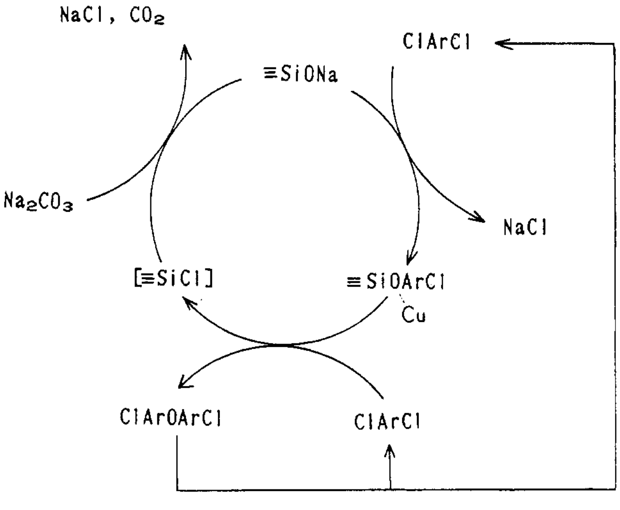


Table II
Reaction of *p*-Halobenzophenones with Alkali Carbonates[a]

halogen	alkali	catalyst	conv, %	selectivity, %
F	K	none	20	97
F	K	SiO_2	95	99
F	Na	SiO_2	60	99
Cl	K	none	5	40
Cl	K	SiO_2	51	82
Cl	K	SiO_2/Cu_2O	90	81
Cl	Na	SiO_2	8	97
Cl	Na	SiO_2/Cu_2O	72	97

[a] $[M_2CO_3]/[\text{halobenzophenone}] = 0.6$. SiO_2 (Aerosil 300) 10 wt % to halobenzophenone. Cu_2O 5 wt % to SiO_2. Solvent: diphenyl sulfone; same weight as halobenzophenone. 300 °C 1 h.

proceeds on the internal surface as fast as on the external surface. It is interesting that the polymerization proceeds in the pore of a size of 210 Å.

As mentioned earlier, the concentration of the hydroxyl chain end does not change with the polymerization time. This means that the concentration of the silanol group is constant. Therefore, the cleavage of the Si–O–Si linkage of silica by alkali carbonate does not occur in the present reaction conditions.

As predicted from Scheme I, silica works not only as the catalyst but the molecular weight controlling agent. When too much silica is used, a low molecular weight polymer with a hydroxyl terminal at both ends is produced. The maximum molecular weight obtained is inversely proportional to the amount of silica. The appropriate amount of silica to obtain high molecular weight polymer is 5–20 wt % of dihalide when Siloyd 244 or Aerosil 300 is used.

Cuprous and cupric salts work as the cocatalyst of silica and promote the reaction. They have no catalytic actiity in the absence of silica. The activity of Cu salt is practically independent of anionic species, and almost the same results are obtained when $CuCl_2$, CuCl, or Cu_2O is used. The appropriate amount of Cu salt is 0.5–3 wt % as Cu atom to silica. The polymerization rate increases proportionally with the amount of Cu salt within this range. In the presence of too much Cu salt, polymers tend to contain some gel.

Polymerization Solvents. The polar solvents that are stable at polymerization temperature such as diphenyl sulfone and benzophenone are preferably used. Practically no reaction occurs in nonpolar solvents such as aromatic or aliphatic hydrocarbons. Diphenyl sulfone is mainly used in this study because the reaction rate is higher in diphenyl sulfone than in benzophenone, and the polymerization can be conducted at atmospheric pressure (boiling point: diphenyl sulfone, 379 °C; benzophenone, 304 °C). The polymerization rate is maximized when 1–2 times the weight of diphenyl sulfone to dihalide is used.

Mechanical Properties of PEK. The poly(ether ketone) (PEK) thus prepared from 4,4′-dichlorobenzophenone and Na_2CO_3 has a melting point of 365–373 °C and can be formed into a very tough film by compressing at 400 °C. It has the 5% weight loss temperature of 560 °C in nitrogen. A polymer with an inherent viscosity of 0.95 was injection molded at 400 °C, and the mechanical properties were measured: tensile strength, 13 kg/mm^2; flexial strength, 21 kg/mm^2; flexial modulus, 500 kg/mm^2. These values are satisfactory for practical use.

Preparations and Characterizations of Other Polyethers. An aromatic poly(ether ketone) with a higher

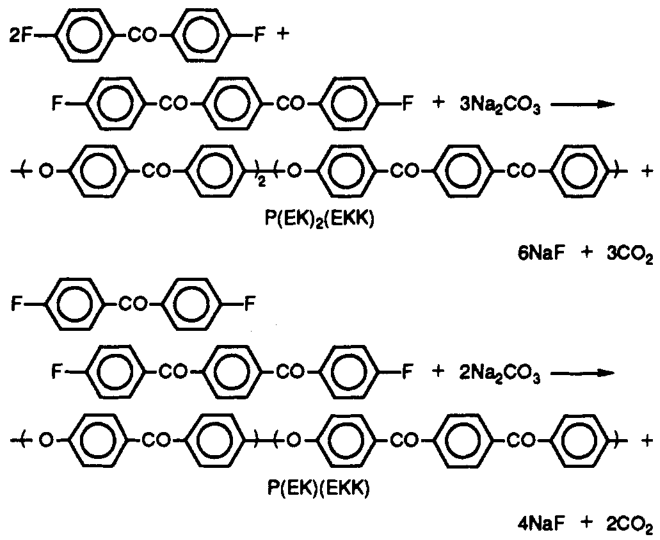
Table III
Poly(ether ketones) Prepared from DFBP and/or DFTP[a]

polymer	[DFBP]/[DFTP]	polymn temp, °C	η_{sp}/C, dL/g	T_m, °C	δH_m, J/g
PEK	100/0	320	1.15	373	46
$P(EK)_2(EKK)$	67/33	320	0.93	380	49
P(EK)(EKK)	50/50	325	0.85	387	53
PEKK	0/100	335	0.95	398	61

[a] $[Na_2CO_3]/[dihalide] = 1.5$. Silica (Siloyd 244) 15 wt % to dihalide. Solvent: diphenyl sulfone; 3 times the weight of dihalide. Polymerization time 3-5 h.

ketone content can be prepared in the same manner by using 4,4″-dihaloterephthalophenone as a monomer or a comonomer. As the melting point and the dissolving temperature of aromatic poly(ether ketones) increase with the increase of ketone content, it is necessary to conduct polymerization at a higher temperature. Table III shows some properties of aromatic poly(ether ketones) prepared from 4,4′-difluorobenzophenone (DFBP) and/or 4,4″-difluoroterephthalophenone (DFTP) with Na_2CO_3 in the presence of silica.

One of the advantages of the present polymerization reaction is that the random copolymers of the ether ketone unit (EK) and ether ketone ketone unit (EKK) are prepared from two kinds of halides, as shown in the following equations.



At least three monomers are necessary to prepare the copolymers in the conventional method in which dihalides and diphenols are used.

The melting point increases with the increase of ketone content and reaches 398 °C in poly(ether ketone ketone) (PEKK). This polymer is formed into a very tough film by compression at 420 °C. As far as we know, this is the first example of the synthesis of a high molecular weight PEKK with an all-para structure. An attempt to synthesize high molecular weight PEKK from 4,4″-difluoroterephthalophenone and 4,4″-dihydroxyterephthalophenone was unsuccessful because the reactivity of 4,4″-dihydroxyterephthalophenone was rather low and side reactions occurred. It is reported that the PEKK prepared by Friedel-Crafts reaction of terephthaloyl chloride and diphenyl ether has a melting point of 385 °C.[3] This low value indicates the presence of a considerable amount of branches and ortho linkages.

Figure 7 shows WAXD patterns of these aromatic poly(ether ketones) together with that of PEEK manufactured by the Imperial Chemical Industry. Although aromatic poly(ether ketones) have the same crystalline structure within an ether/ketone ratio of 1/2 to 2/1, the heat of fusion (δH_m in Table III) increases and the peaks become sharper with the increase of the ketone content in the polymer.

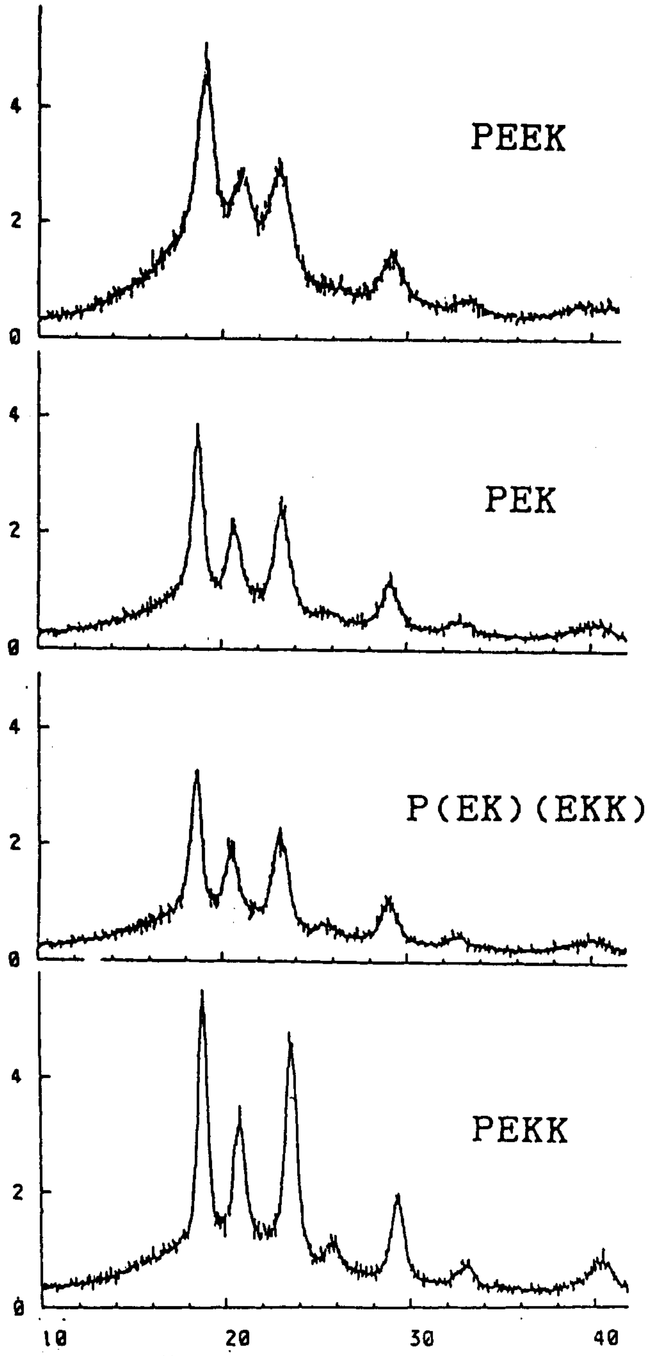


Figure 7. WAXD spectra of aromatic poly(ether ketones).

Poly(ether sulfones) (PES) are prepared in the same manner by using 4,4′-dichlorodiphenyl sulfone or 4,4′-difluorodiphenyl sulfone as a monomer. As poly(ether sulfone) (PES) is amorphous, it is not necessary to raise the polymerization temperature with the progress of polymerization. The reactivity of 4,4′-difluorodiphenyl sulfone is extremely high, and a high molecular weight polymer is obtained within 30 min at 300 °C.

Conclusion

High molecular weight aromatic poly(ether ketone) was synthesized from 4,4′-dichlorobenzophenone and sodium carbonate in the presence of a silica/Cu salt catalyst. This reaction can be applied to various kinds of aromatic dihalides to produce polyethers.

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Registry No. PEK (copolymer), 126539-67-1; PEK (SRU), 27380-27-4; PCBP, 134-85-0; P(EK)$_2$(EKK) (copolymer), 131878-86-9; PEKK (copolymer), 30604-15-0; PEKK (SRU), 74970-25-5; Na_2CO_3, 497-19-8; K_2CO_3, 584-08-7; SiO_2, 7631-86-9; $CuCl_2$, 7447-39-4; CuCl, 7758-89-6; Cu_2O, 1317-39-1; 4,4′-dichlorobenzophenone, 90-98-2; 4,4′-dibenzoyldiphenyl ether, 6966-89-8; *p*-fluorobenzophenone, 345-83-5.