

## Trans-Etherification of Aromatic Polyetherketone and Trans-Etherification between Aromatic Polyetherketone and Aromatic Polyethersulfone

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**ABSTRACT:** Poly(oxy-1,4-phenylene-carbonyl-1,4-phenylene-oxy-1,4-phenylene-carbonyl-1,4-phenylene-carbonyl-1,4-phenylene) (PEKEKK) was heated in the presence of potassium carbonate at 340°C to yield another aromatic polyetherketone, which contained not only the original EKEKK repeating unit but also the EK and EKK repeating units. This indicates that trans-etherification reaction occurs between molecules of PEKEKK. Poly(oxy-1,4-phenylene-carbonyl-1,4-phenylene) (PEK) reacted with poly(oxy-1,4-phenylene-sulfonyl-1,4-phenylene) (PES) in the presence of potassium carbonate at 300°C to yield a trans-etherification product, *i.e.*, a block copolymer of P(EK)/(ES). A further reaction decreased the crystallinity of the block copolymer to yield a random copolymer.

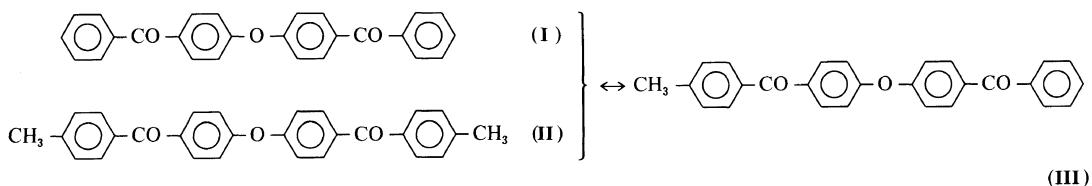
**KEY WORDS** Trans-Etherification / Aromatic Polyetherketone / Aromatic Polyethersulfone / Potassium Carbonate / NMR Spectra / Block Copolymer / Random Copolymer /

Several polyetherketones<sup>1-4</sup> have been prepared by nucleophilic polycondensation (NP)<sup>5-7</sup> or electrophilic polycondensation (EP).<sup>8-11</sup> Poly(oxy-1,4-phenylene-oxy-1,4-phenylene-carbonyl-1,4-phenylene) (PEEK) is produced by the condensation of 4,4'-difluorobenzophenone with hydroquinone in the presence of potassium carbonate by the NP method.

PEK was produced by the condensation of 4,4'-difluorobenzophenone and dipotassium salt of 4,4'-dihydroxybenzophenone by the NP

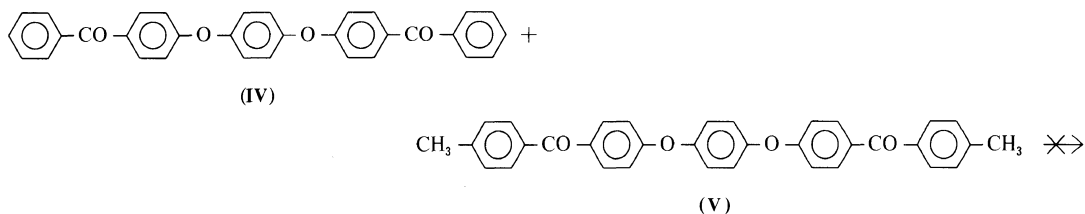
method. PEK was also produced by self-condensation of 4-phenoxybenzoyl chloride in the presence of Friedel-Crafts catalyst by the EP method.

We recently found that the heating of 4,4'-(dibenzoyl)diphenyl ether (KEK) (I) and 4,4'-bis(4-methylbenzoyl)diphenyl ether (II) at 300°C in the presence of potassium carbonate gave 4-(4-methylbenzoyl)-4'-(benzoyl)diphenyl ether (III). III is trans-etherification product of I and II as shown below.



On the other hand, heating KEEK (IV) with methyl substituted KEEK (V) in the presence

of potassium carbonate at 300°C gave no trans-etherification product.



This fact indicated that the consecutive ether linkage such as KEEK was stable against the trans-etherification reaction.

We assumed that the trans-etherification reaction occurred between molecules of aromatic polyetherketones. However, it was not easy to confirm this trans-etherification reaction on the typical polyetherketones such as PEEK and PEK. The trans-etherification reaction would not take place on PEEK, considering the behavior of KEEK as described above. The trans-etherification reaction of PEK cannot be detected by NMR even if the trans-etherification occurs, because the chemical structure of PEK is not changed by the trans-etherification reaction.

To clarify the trans-etherification reaction of aromatic polyetherketone, PEKEKK was prepared and reacted with potassium carbonate. Then the chemical structure of the reaction product was analyzed by NMR spectra.

Furthermore, utilizing the trans-etherification reaction, the block copolymers of P(EK)/(ES) were produced from PEK and PES.

## EXPERIMENTAL

### Materials

4,4'-dihydroxybenzophenone, 4,4'-difluorobenzophenone, diphenyl sulfone, benzophenone, terephthaloyl chloride, aluminum chloride, dimethylformamide, benzoyl chloride, and methylene chloride were purchased from Tokyo Kasei Co., Ltd. and purified by distillation or recrystallization before use.

Potassium carbonate powder was purchased from Takasugi Seiyaku Co., Ltd. and was dried

*in vacuo* before use. PES was purchased from ICI Co., Ltd.

### Monomer Synthesis

1) 1,4-Bis(4-fluorobenzoyl)benzene was prepared by the reaction of terephthaloyl chloride with excess fluorobenzene in the presence of aluminum chloride. 2) 4,4'-diphenoxybenzophenone was prepared by the reaction of 4,4'-difluorobenzophenone with phenol in the presence of potassium carbonate in benzophenone solvent at 260°C.

### Polycondensation

**PEKEKK (NP).** A mixture of 36.4 g (0.17 mol) of 4,4'-dihydroxybenzophenone, 56.9 g (0.18 mol) of 1,4-bis(4-fluorobenzoyl)benzene, 25.0 g (0.18 mol) of potassium carbonate, and 300 g of benzophenone was placed in a 1 liter autoclave with a stirrer. After replacing the atmosphere with nitrogen, the temperature was raised to 300°C in 35 min and kept at 300°C for 30 min. Generated water was continuously removed from the autoclave with nitrogen gas flow. Then the autoclave was closed and the temperature was raised to 340°C. The temperature was kept at 340°C for 4 hours.

After that, 8 g (0.036 mol) of 4,4'-difluorobenzophenone was added to the reaction mixture and was made to react with the polymer for 20 min. Solidified product was crushed in water and washed with acetone and water several times.

Reduced viscosity (RV) of the obtained polymer was 0.81 dl g<sup>-1</sup>.

**PEKEKK (EP).** 10.2 g (50 mmol) of terephthaloyl chloride, 18.4 g (51 mmol) of 4,4'-diphenoxybenzophenone, 75.3 g (565 mmol) of

aluminum chloride, 0.05 g (0.4 mmol) of benzoyl chloride, 16.5 g of dimethylformamide, and 200 ml of methylene chloride were mixed at  $-30^{\circ}\text{C}$  and allowed to react at  $0^{\circ}\text{C}$  for 15 min and then at  $20^{\circ}\text{C}$  for 1.5 hours. The reaction mixture was pulverized in methanol and washed well with methanol, 7 wt% hydrochloric acid, hot water and hot acetone. RV of the obtained polymer was  $0.98\text{ dl g}^{-1}$ .

#### Trans-Etherification

**PEKEKK.** A mixture of 20 g of PEKEKK and 3 g of potassium carbonate was heated in 100 g of diphenyl sulfone solvent at  $340^{\circ}\text{C}$  for 6 hours. The obtained reaction mixture was treated as the same manner as the preparation of PEKEKK (NP) described above.

**PEK/PES.** A mixture of 5 g of PEK (RV  $0.7\text{ dl g}^{-1}$ ), 5 g of PES (RV  $0.4\text{ dl g}^{-1}$ ) and 5 g of potassium carbonate was heated at  $300^{\circ}\text{C}$  in the presence of 20 g of benzophenone solvent for 3 hours. Then the reaction product was crushed to powder in water and the powder was washed with acetone and NMP. Thus obtained polymer was a block copolymer with

RV of  $0.81\text{ dl g}^{-1}$ .

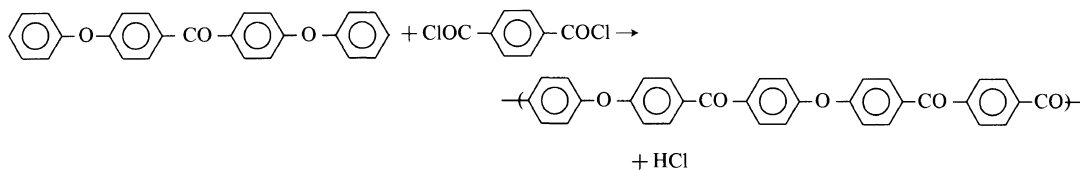
#### Analysis

RV was measured at a concentration of  $0.1\text{ g dl}^{-1}$  at  $25^{\circ}\text{C}$  by using an Ubbelohde viscometer. Concentrated sulfuric acid (98%) was used as a solvent for crystalline polymers and NMP was used for amorphous polymers.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured on 2 wt% solution of deuteriosulfuric acid ( $\text{D}_2\text{SO}_4$ ) by a JEOL FX-400 spectrometer. Hexamethyldisiloxane (0.0 ppm) and dioxane (67.4 ppm) were used the internal standards for  $^1\text{H}$  and  $^{13}\text{C}$  NMR, respectively.

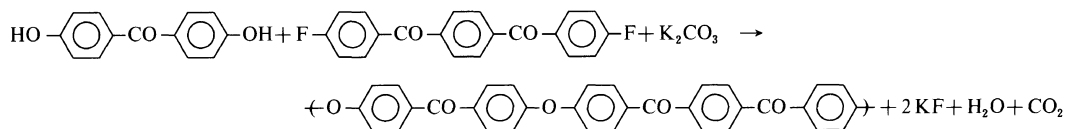
## RESULTS AND DISCUSSION

#### Trans-Etherification of PEKEKK

**Synthesis of PEKEKK.** PEKEKK (EP) was prepared by electrophilic polycondensation of 4,4'-diphenoxybenzophenone with terephthaloyl chloride in the presence of aluminum chloride catalyst. The  $^{13}\text{C}$  NMR spectrum of PEKEKK (EP) was shown in Figure 1.



PEKEKK (NP) was produced by the nucleophilic polycondensation of 4,4'-dihydroxybenzophenone with 1,4-bis(4-fluorobenzoyl) benzene in the presence of potassium



**Trans-Etherification of PEKEKK.** PEKEKK (NP or EP) was heated in the presence of potassium carbonate at  $340^{\circ}\text{C}$  for 6 hours.  $^{13}\text{C}$  NMR spectrum of the reaction product was

shown in Figures 3—5. The spectrum was more complex than that of the original PEKEKK (NP or EP). Extra peaks appeared in the spectrum of the product and were coincident

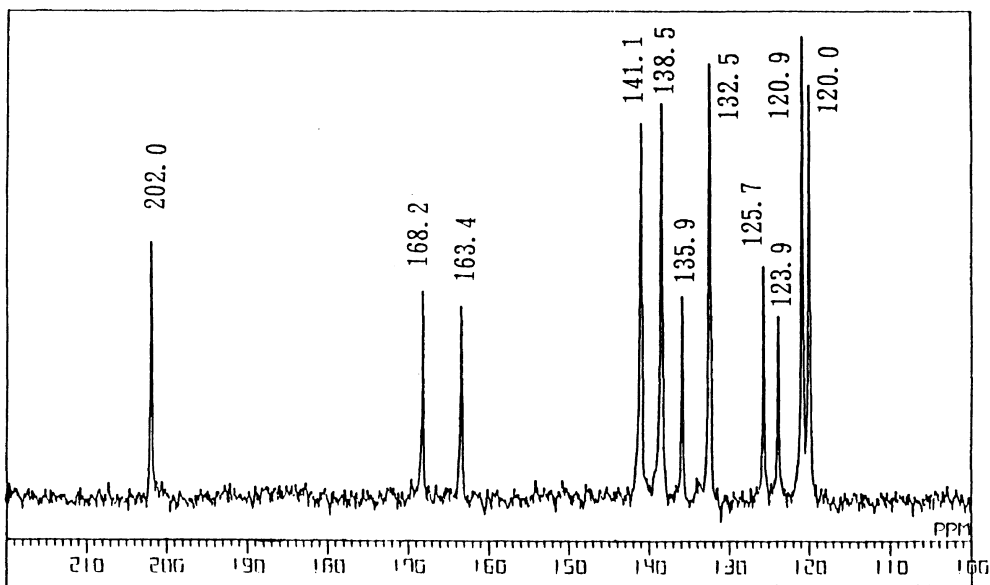


Figure 1.  $^{13}\text{C}$  NMR spectra of PEKEKK. Electrophilic polycondensation.

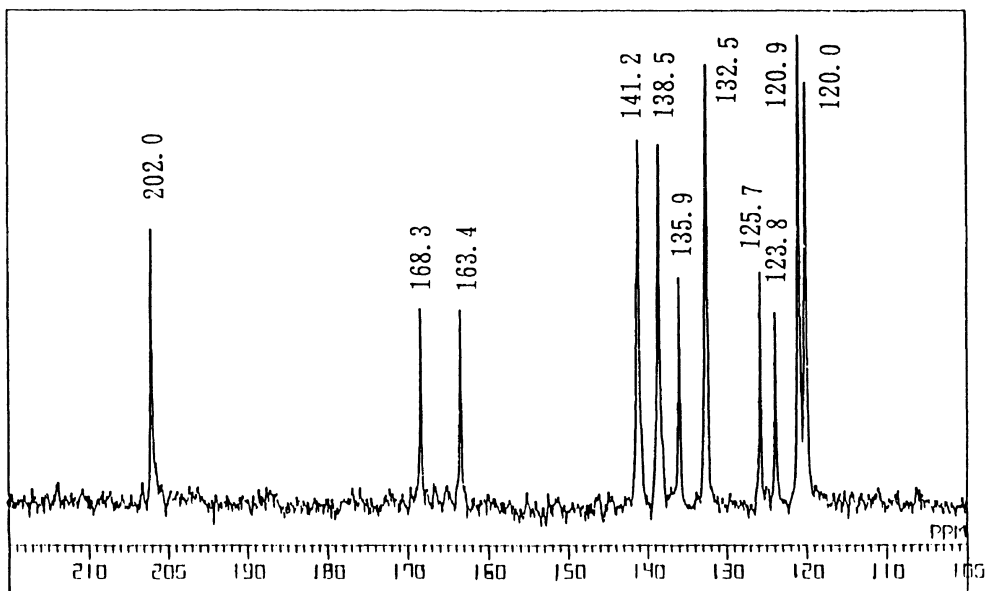


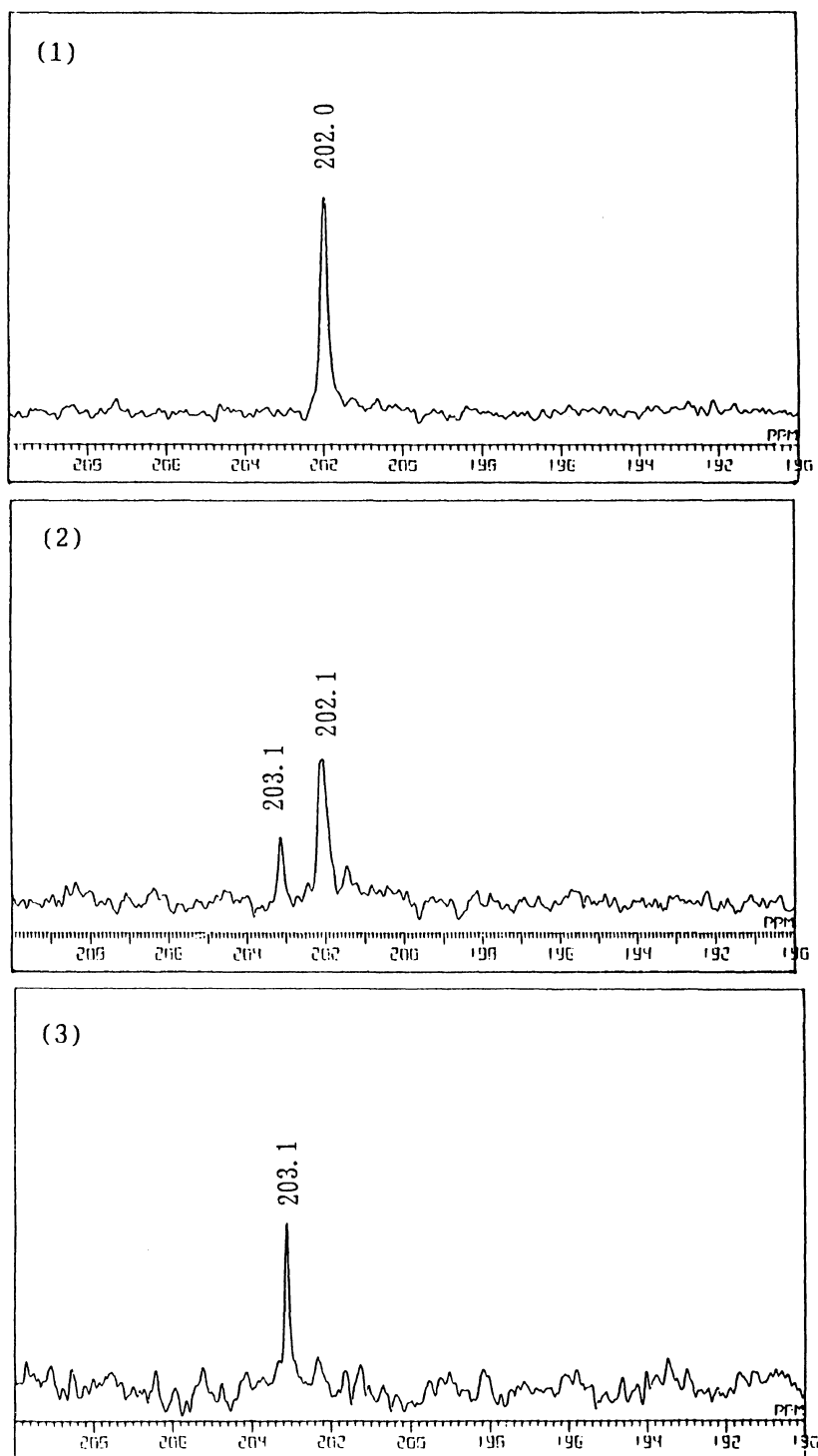
Figure 2.  $^{13}\text{C}$  NMR spectra of PEKEKK. Nucleophilic polycondensation.

with the peaks of PEKK or PEK.

$^{13}\text{C}$  NMR spectra of PEK, PEKEKK and PEKK were assigned and are summarized in Table I. The peaks of tertiary carbons and

quaternary carbons were distinguished by a comparison of proton coupled spectra and decoupled spectra.

The extra peaks were 203.1 ppm (PEKK



**Figure 3.** Comparison of  $^{13}\text{C}$  NMR spectra (190—210 ppm): (1) PEKEKK; (2) PEKEKK after the heating with  $\text{K}_2\text{CO}_3$  at  $340^\circ\text{C}$ ; (3) PEKK.

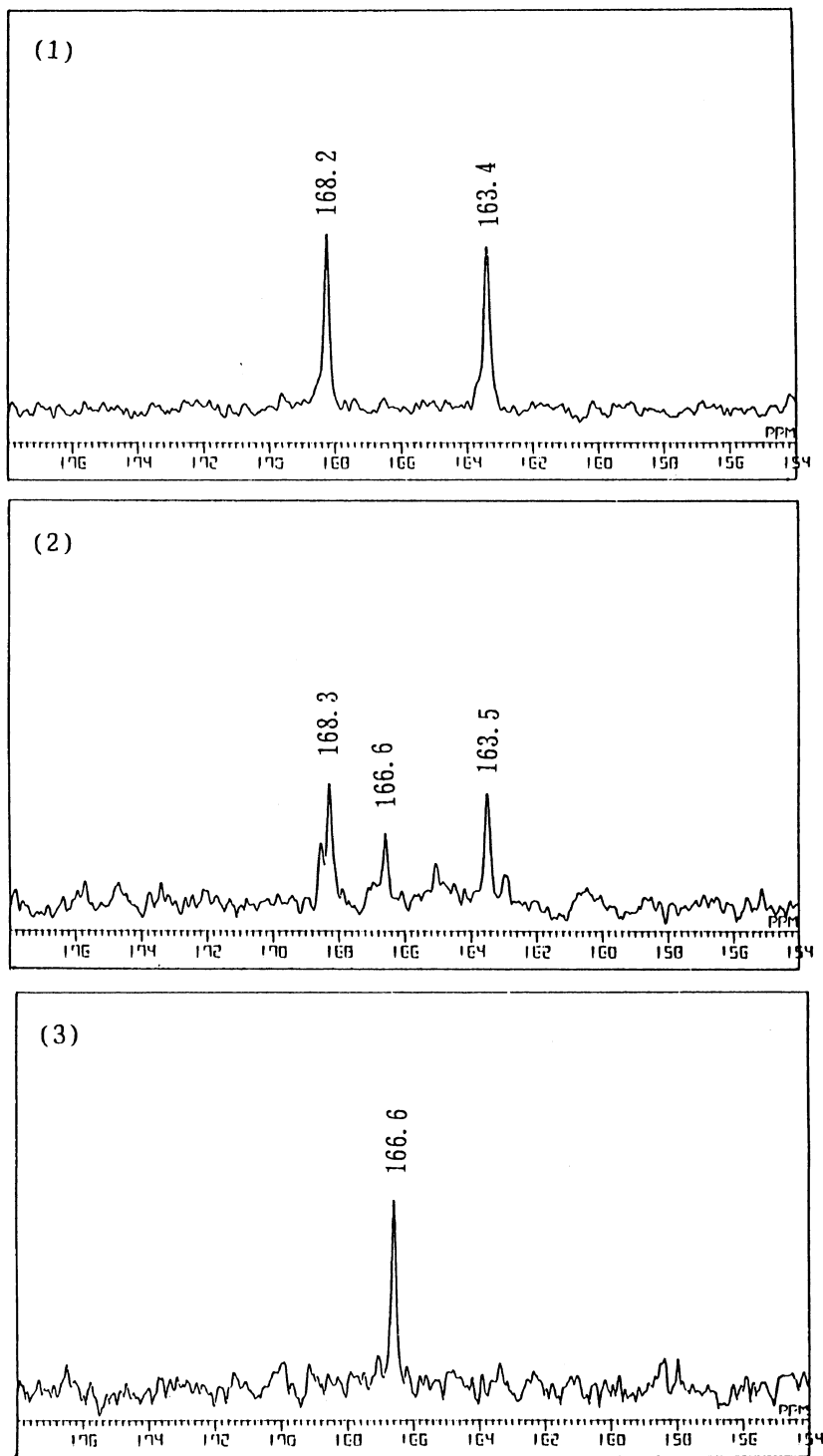
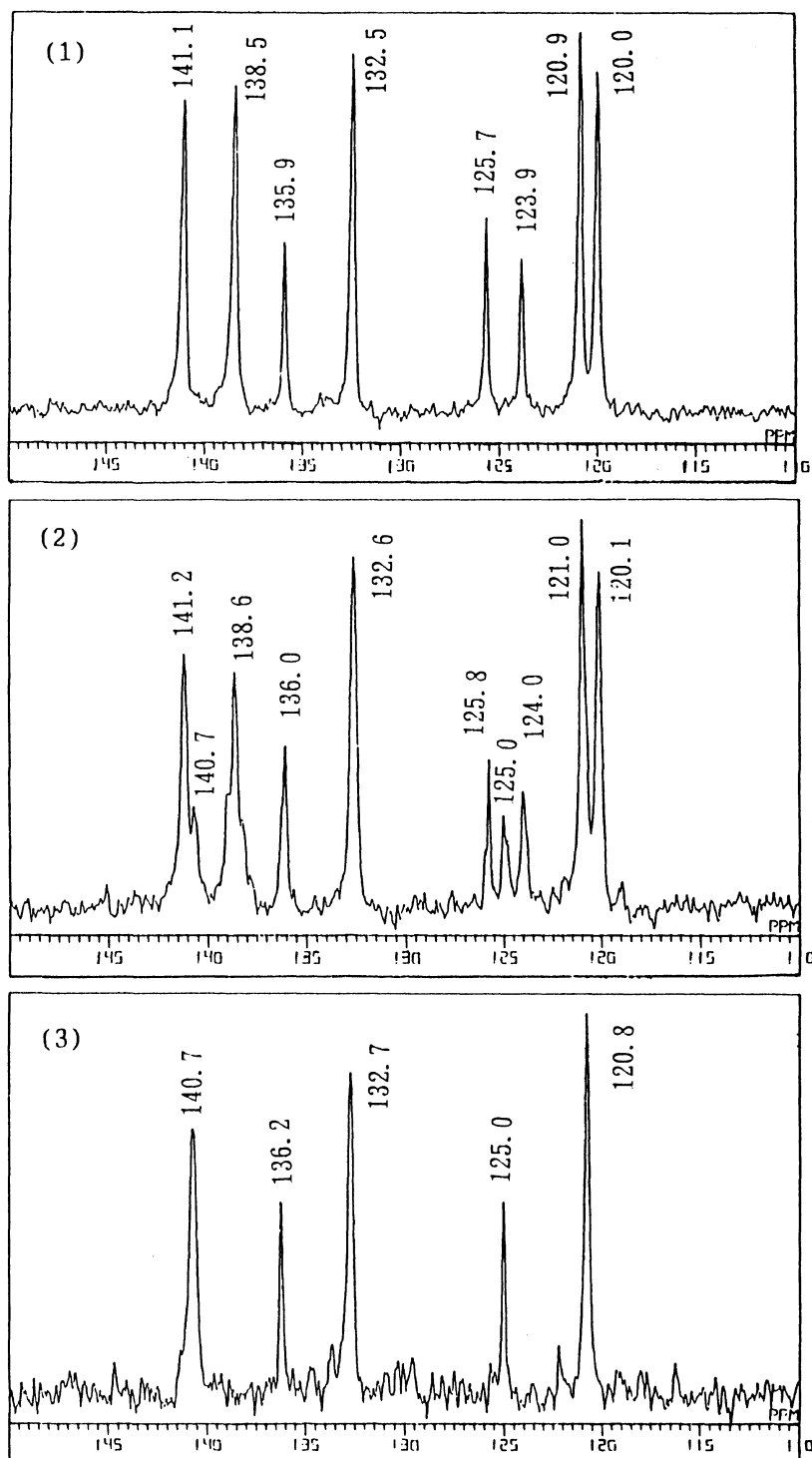


Figure 4. Comparison of  $^{13}\text{C}$  NMR spectra (155—176 ppm): (1) PEKEKK; (2) PEKEKK after the heating with  $\text{K}_2\text{CO}_3$  at  $340^\circ\text{C}$ ; (3) PEKK.



**Figure 5.** Comparison of  $^{13}\text{C}$  NMR spectra (110–145 ppm): (1) PEKEKK; (2) PEKEKK after the heating with  $\text{K}_2\text{CO}_3$  at  $340^\circ\text{C}$ ; (3) PEKK.

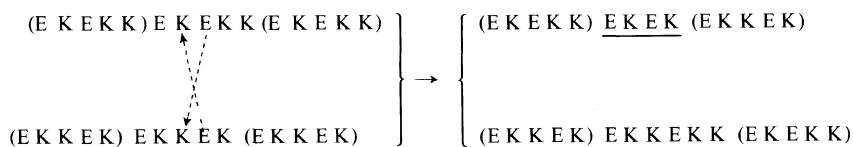
**Table I.** Assignment of  $^{13}\text{C}$  NMR spectra of PEK, PEKK, and PEKEKK<sup>a</sup>

Structure		Tertiary carbon			Quaternary carbon		
Adjacent	Next-adjacent	PEK	PEKK	PEKEKK	PEK	PEKK	PEKEKK
			132.7 ( 7)	132.5 (12)		136.2 ( 6)	135.9 (11)
			140.7 ( 3)	141.1 ( 8)		125.0 ( 4)	125.7 ( 9)
		138.4 ( 3)		138.5 ( 3)	124.9 ( 4)		123.9 ( 4)
			120.8 ( 2)	120.9 ( 7)		166.6 ( 1)	168.2 ( 6)
		120.1 ( 2)		120.0 ( 2)	164.7 ( 1)		163.4 ( 1)
					200.8 ( 5)		202.0 ( 5)
						203.1 ( 5)	202.0 (10)
<sup>a</sup> PEK		PEKEKK					
PEKK							

<sup>b</sup> The sign of \* represents para-phenylene unit.

203.1 ppm), 201.5 (PEK, 200.8), 166.6 (PEKK, 166.6), 165.0 (PEK, 164.7), 140.7 (PEKK, 140.7), and 125.0 (PEKK, 125.0). These results indicate that both repeating units of EKK and

EK were formed by the trans-etherification reaction between the molecules of PEKEKK as shown below.



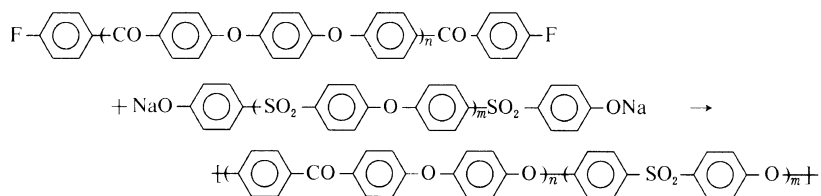
*Trans-Etherification during Polycondensation.* When the nucleophilic polycondensation reaction of 4,4'-dihydroxybenzophenone with 1,4-bis(4-fluorobenzoyl)benzene was carried out at higher temperature in the presence of higher amount of potassium carbonate, these extra peaks were also observed in the NMR spectrum of the obtained PEKEKK. This

shows that the trans-etherification also occurs during polycondensation.

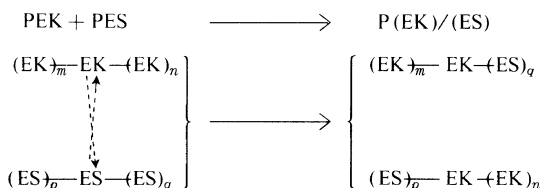
#### *Trans-Etherification between PEK and PES*

*Block copolymer of PEK and PES.* It was reported that the stepwise polycondensation of PEEK and PES gave a P(EEK)/(ES) block copolymer.<sup>12</sup>



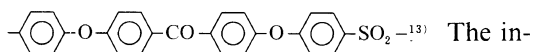


We tried to prepare the P(EK)/(ES) block copolymer using the trans-etherification reaction between PEK and PES.



PEK was reacted with PES in the presence of potassium carbonate in benzophenone solvent or in diphenyl sulfone solvent. The reaction product was wholly insoluble in NMP solvent. This shows that the unreacted PES did not remain in the reaction product because PES is soluble in NMP, though PEK is insoluble in NMP. The formation of the block copolymer was confirmed by the  $^1\text{H-NMR}$  spectra of the products.

*Reaction of PEK with PES in benzophenone solvent.* For example, 5 g of PEK (RV  $0.7 \text{ dl g}^{-1}$ ) and 5 g of PES (RV  $0.4 \text{ dl g}^{-1}$ ) was heated at  $300^\circ\text{C}$  for 3 hours in the presence of 5 g of potassium carbonate in benzophenone solvent to yield 9.9 g of the product, which was insoluble in NMP. The product showed new peaks at 6.83, 6.91, 7.54, and 7.66 ppm in addition to the peaks of PEK (7.03, 7.78 ppm) and PES (6.73, 7.43 ppm) as shown in Figure 6. The new peaks coincided with those of the alternate copolymer (PEKES) and were assigned to the structure of



The intensity ratio of new peaks, PEK block peaks and PES block peaks in the NMR spectrum, indicated that the average number of repeating

unit of PEK or PES block was about 20.

The  $T_m$  of the product was  $342$  and  $384^\circ\text{C}$  and its  $T_g$  was  $222^\circ\text{C}$ . Its RV was  $0.8 \text{ dl g}^{-1}$  and its X-ray diffraction pattern (Figure 7) was similar to that of PEK.

*Reaction of PEK with PES in Diphenyl Sulfone Solvent.* The reaction of PEK with PES in the presence of potassium carbonate was carried out in diphenyl sulfone solvent instead of benzophenone solvent (Table II).

A mixture of PES and PEK with several weight ratios (PES/PEK = 1/9–9/1) reacted with potassium carbonate at  $260^\circ\text{C}$  for 3 hours or  $300^\circ\text{C}$  for 1, 3 or 5 hours in order to clarify the effect of the reaction conditions on the properties of the product. The product was characterized by DSC ( $T_c$ ,  $T_m$ , and  $T_g$ ) and X-ray diffraction. A higher melting point and larger heat of fusion ( $\Delta H$ ) indicated the presence of a more perfect PEK block or higher molecular weight PEK block in the product. Higher  $T_g$  indicated the presence of a more perfect PES block or the higher molecular weight PES block in the product. As the  $T_g$  of PES was higher than that of PEK, the  $T_g$  of any copolymer of PES/PEK were lower than that of PES.

Higher reaction temperature gave a block copolymer with lower melting point and lower crystallinity (No. 01 vs. No. 08, No. 02 vs. No. 09, and No. 03 vs. No. 10 in Table II). The longer reaction time at  $300^\circ\text{C}$  decreased the melting point and crystallinity of the block copolymer (No. 04, 08, and 12 of PES/PEK = 3/7 in Table II, and No. 05, 09, and 13 of PES/PEK = 5/5 in Table II). The  $T_g$  of block copolymer decreased with increase of reaction time.

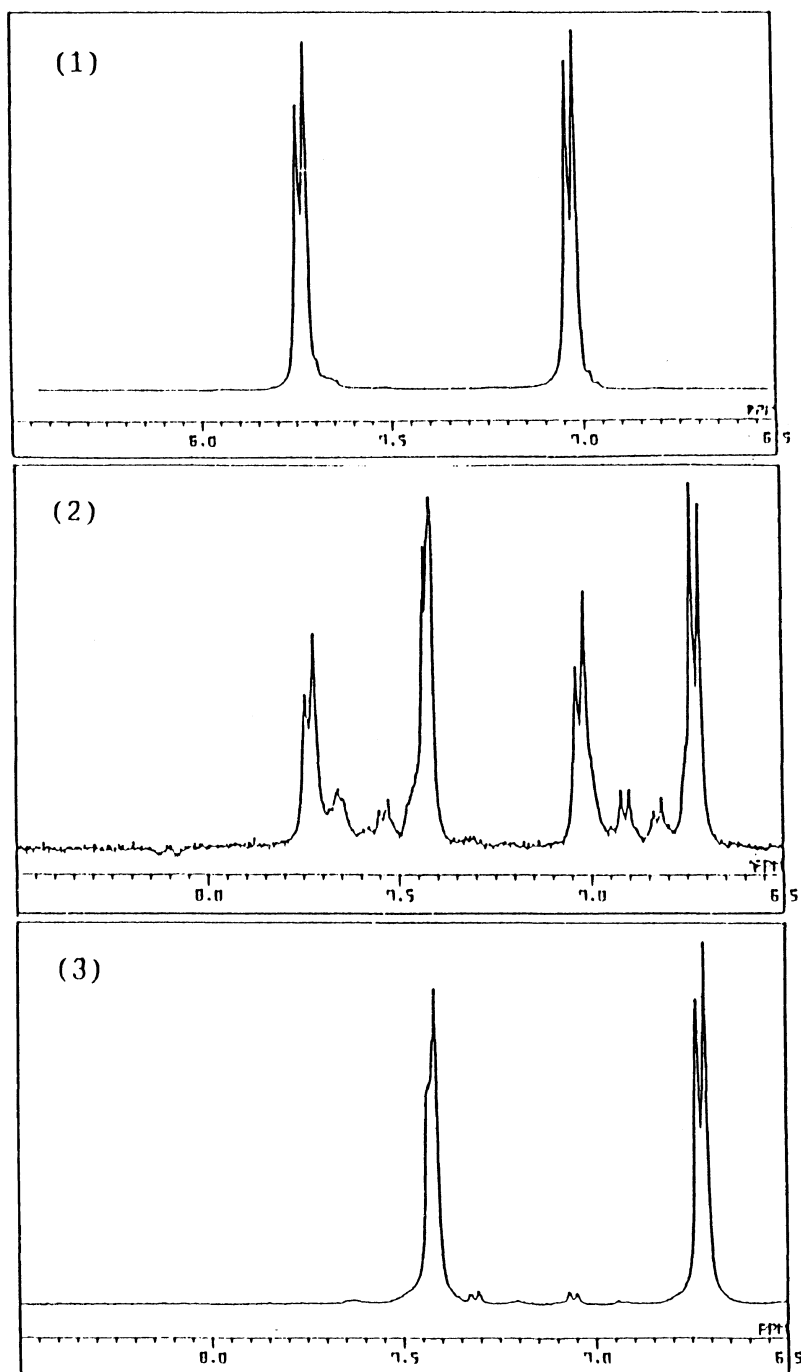


Figure 6. Comparison of  $^1\text{H}$  NMR spectra: (1)  $^1\text{H}$  NMR spectrum of PES; (2)  $^1\text{H}$  NMR spectrum of P (EK)/(ES) block copolymer; (3)  $^1\text{H}$  NMR spectrum of PEK.

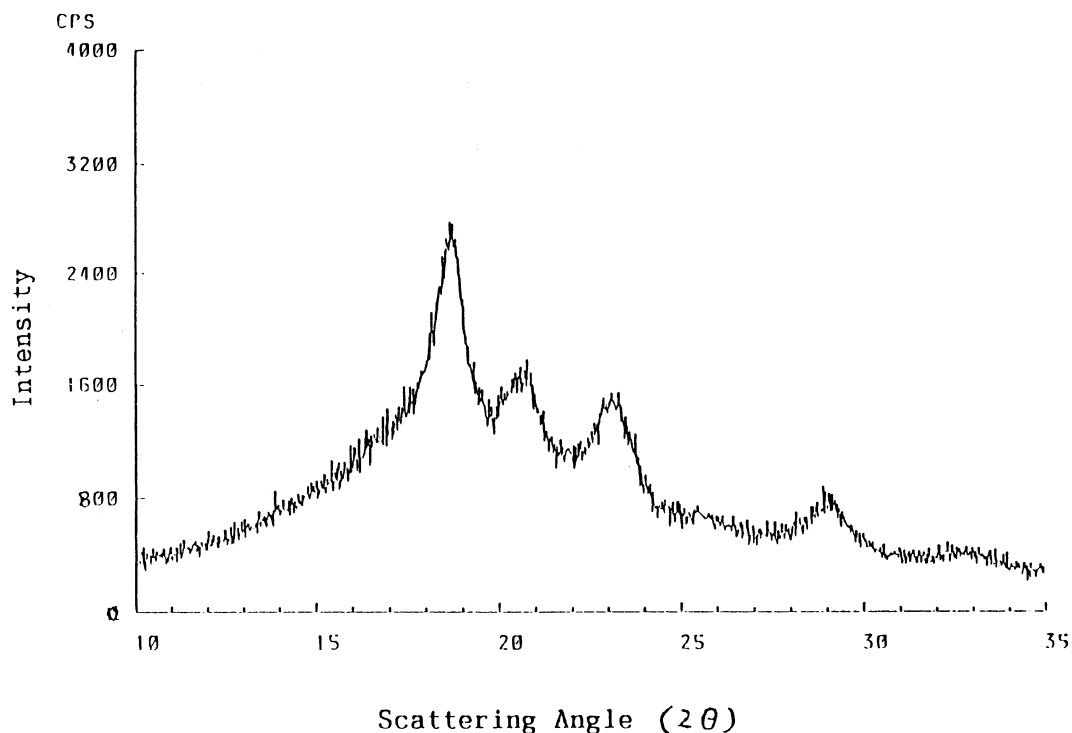


Figure 7. X-Ray diffraction patterns of P (EK)/(ES) block copolymer.

Table II. PES/PEK block copolymer by trans-etherification

No.	Reaction condition <sup>a</sup>			Yield %	R.V. dl g <sup>-1</sup>	DSC			(ΔH)		Crystalline index <sup>b</sup>
	PES/PEK (weight ratio)	Temp. °C	Time h			T <sub>c</sub> °C	T <sub>g</sub> °C	T <sub>m</sub> °C	T <sub>c</sub> J g <sup>-1</sup>	T <sub>m</sub> J g <sup>-1</sup>	
01	3/7	260	3	93	1.15	—	225	370	—	30.7	58
02	5/5	260	3	92	0.95	—	222	369	—	18.2	45
03	7/3	260	3	91	0.95	—	217	360	—	12.4	39
04	3/7	300	1	95	1.11	242	227	363	3.0	26.7	47
05	5/5	300	1	93	1.09	—	207	361	—	15.6	37
06	7/3	300	1	92	0.93	—	212	361	—	7.4	33
07	1/9	300	3	95	1.65	—	160	359	—	35.2	47
08	3/7	300	3	93	1.84	241	170	334	9.7	20.8	35
09	5/5	300	3	90	0.84	—	182	—	—	0	26
10	7/3	300	3	79	0.45	—	192	—	—	0	0
11	9/1	300	3	81	0.37	—	—	—	—	0	0
12	3/7	300	5	94	0.76	237	167	304, 309	19.2	19.8	30
13	5/5	300	5	76	0.40	—	168	—	—	0	14
14	7/3	300	5	45	0.28	—	176	—	—	0	0
15	Original	PEK			0.87	—	155	374	—	44.5	48
16	Original	PES			0.45	—	220	—	—	0	0

<sup>a</sup> Total amounts of PES and PEK, 10 g; K<sub>2</sub>CO<sub>3</sub>, 7 g; diphenyl sulfone, 20 g.

<sup>b</sup> Relative crystalline index was determined by X-Ray diffraction patterns.

The block copolymer with higher PEK content (PES/PEK = 1/9 or 3/7) showed higher  $T_m$  and higher crystallinity (No. 01, 04, 07, 08, and 12 in Table II and Figure 8). The melting points and crystallinity were observed in the products obtained by reaction of a mixture of PES/PEK = 5/5 and 7/3 at 300°C for 1 hour.

However, no melting points or crystallinity were observed in the product obtained by the reaction of a mixture of PES/PEK = 5/5, 7/3, 9/1 at 300°C for 3 hours. Thus, obtained amorphous polymers showed lower  $T_g$  than that

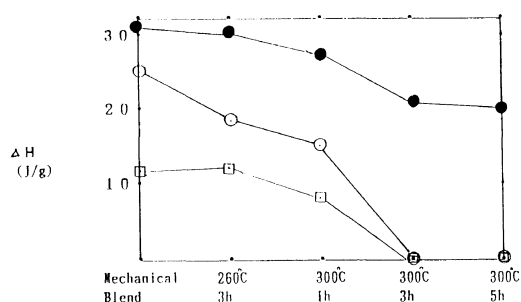
of PES.

We assumed that the trans-etherification reaction formed the block copolymer but the further trans-etherification reaction caused randomization of the block copolymer to finally a random copolymer.

*Comparison with blend polymers and copolymers.* Mechanical (melt) blend polymers, random copolymers, and an alternate polymer were prepared to compare with the copolymer prepared by trans-etherification reaction. Their properties are shown in Table III.

Mechanical blend polymers were prepared by melt blending of PES and PEK at 300°C for 3 hours. The blend polymers showed the melting point and crystallinity of original PEK because no trans-etherification reaction occurred even in a melt condition without potassium carbonate. Each blend polymer showed a higher melting point and larger heat of fusion than those of the corresponding trans-etherification products with the same PES content.

The random copolymers were prepared by polycondensation of 4,4'-difluorobenzophenone, 4,4'-difluorodiphenyl sulfone, 4,4'-di-



**Figure 8.** Heat of crystal fusion of a mechanical blend of PES & PEK and trans-etherification reaction products of PES & PEK: ●, PES/PEK (3/7); ○, PES/PEK (5/5); □, PES/PEK (7/3).

**Table III.** Blend of PES/PEK and several copolymers of PES/PEK

No.	Type of polymer	Content of PES/PEK (weight/ratio)	R.V. dl g <sup>-1</sup>	DSC			ΔH		Crystal-line index <sup>d</sup>
				$T_c$ °C	$T_g$ °C	$T_m$ °C	$T_c$ J g <sup>-1</sup>	$T_m$ J g <sup>-1</sup>	
01	Mechanical blend <sup>a</sup>	3/7	0.81	—	221	371	—	31.2	55
02	Mechanical blend <sup>a</sup>	5/5	0.74	—	221	374	—	25.5	54
03	Mechanical blend <sup>a</sup>	7/3	0.66	—	222	374	—	11.1	35
04	Random copolymer <sup>b</sup>	3/7	0.39	—	—	—	—	—	31
05	Random copolymer <sup>b</sup>	5/5	0.29	—	171	—	—	—	0
06	Random copolymer <sup>b</sup>	7/3	0.26	—	180	—	—	—	0
07	Alternate copolymer <sup>c</sup>	5/5	0.71	—	190	—	—	—	0
08	Original PEK	0/10	0.87	—	155	374	—	44.5	48
09	Original PES	10/0	0.45	—	220	—	—	0	0

<sup>a</sup> No. 01—03: Mechanical blend polymer prepared by mixing PES and PEK at 300°C for 3 h.

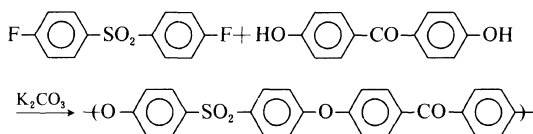
<sup>b</sup> No. 04—06: Random Copolymer prepared by polycondensation of F\*SO<sub>2</sub>\*F, HO\*SO<sub>2</sub>\*OH, F\*CO\*F and HO\*CO\*OH. (The sign of \* represents *para*-phenylene unit).

<sup>c</sup> No. 07: Alternate copolymer prepared by the reaction of F\*SO<sub>2</sub>\*F and HO\*CO\*OH.

<sup>d</sup> Relative crystalline index was determined by X-ray diffraction patterns.

hydroxybenzophenone and 4,4'-dihydroxydiphenyl sulfone. If the reactivity of these monomers are equivalent, the polycondensation might give an ideal random copolymer. The random polymer with EK/ES = 1/1 was amorphous and its  $T_g$  was 171°C.

The alternate copolymer (PEKES) was prepared by polycondensation of 4,4'-difluorodiphenyl sulfone with 4,4'-dihydroxybenzophenone. Its  $T_g$  was 190°C, which was slightly higher than that of the above random copolymer.

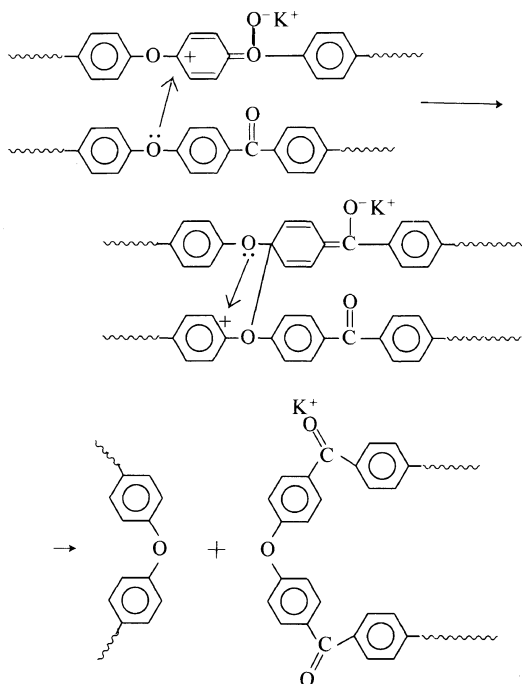


#### Mechanism of the trans-Etherification Reaction

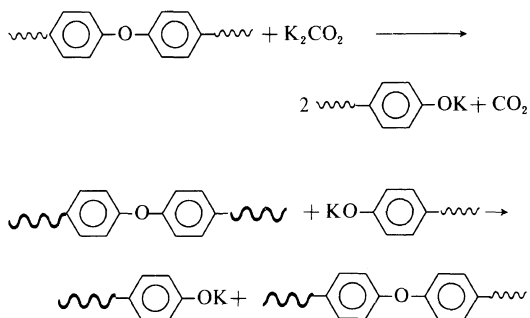
The effects of the end groups of PEKEKK on the trans-etherification reaction can be neglected because the similar reaction products were obtained by the trans-etherification of PEKEKK (EP) and PEKEKK (NP). Most of the end groups of PEKEKK (EP) were benzoyl groups because benzoyl chloride was used as a capping agent in the polycondensation reaction. The chain ends of PEKEKK (NP) were 4-fluorobenzoyl groups and no 4-hydroxybenzoyl end groups were observed by NMR, as 4,4'-difluorobenzophenone was used as a terminator in the polycondensation reaction.

Methyl groups were detected as the end groups of PES by its NMR spectrum. It is also assumed that the end groups of PES and PEK did not play an important role in the trans-etherification reaction.

Therefore, the reaction was initiated in the main chain of polyether and we assumed the following two mechanisms. One is a mechanism of simultaneous trans-etherification of activated ether as shown below.



The other is a two step mechanism. Potassium carbonate breaks the ether linkage and then the formed phenolate reacts with another ether linkage to yield a new phenolate and a new ether linkage. A very small, or catalytic, amount of phenolate may be enough to bring about the trans-etherification if the reaction of phenolate with ether linkage is very fast.



Further studies are necessary to determine which mechanism is more feasible.

## CONCLUSIONS

Trans-etherification reaction of polyetherketones was confirmed by the reaction of PEKEKK with potassium carbonate, using the  $^{13}\text{C}$  NMR spectra of the product. The trans-etherification reaction was also observed at the polycondensation reaction of 4,4'-dihydroxybenzophenone with 1,4-bis(4-fluorobenzoyl)benzene under severer reaction conditions. The  $^{23}\text{C}$  NMR spectra of PEKEKK were assigned by comparing with those of PEK and PEKK.

Trans-etherification between PES and PEK in the presence of potassium carbonate gave a block copolymer of PEK and PES. Further trans-etherification reaction changed the block copolymer into random copolymer. The block copolymers were compared with the melt blend of PEK and PES, the alternate copolymer (PEKES), and random copolymers.

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