Effects of polymer structure and thermal treatment on gas permeability of poly(ether ketone)s

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A series of poly(ether ketone) copolymers were synthesized by the Friedel–Crafts reaction of diphenyl ether and a mixed acid chloride comprising isophthaloyl chloride and terephthaloyl chloride. The permeabilities of H_2, O_2, CO and N_2 through the as-cast films at 30°C were influenced by the catenation effect, that is, increase of *m*-catenation ratio relative to *p*-catenation induces denser packing of the polymer chains and reduces gas diffusion. The difference of crystallinity among the polymers was too small to exhibit a clear influence on the gas permeability. Changes of permeability through the copolymer films by thermal treatment were interpreted as being due to the decrease of the amorphous region caused by thermal crystallization. Densification of the polymer matrix in the amorphous region was not observed.

(Keywords: poly(ether ketone); gas permeability; chain packing; thermal treatment; crystallization)

INTRODUCTION

Gas permeabilities for aromatic amorphous polymers have been actively studied recently; for example, polyimides[1,2], polyarylates[3,4] and polycarbonates[5,6]. In these systems, gas permeation is discussed from several viewpoints: the relationship of chain stiffness and segment mobility, the chain packing from free-volume analysis or intersegmental spacing from X-ray diffraction.

The author and others studied hydrogen separation membranes made from aromatic amorphous polyamide containing sulphone linkages in the main chain (this polymer is called poly(sulphone–amide))[7–9]. In the case of poly(sulphone–amide), as the content of amide linkages in the polymer chain increased, the polymer became stiffer and gas permeation was restricted. Intermolecular hydrogen bonding may play some role in this effect. When the poly(sulphone–amide)s had the same amide-bond concentration, increase of *m*-catenation ratio relative to *p*-catenation induced more compact packing of the polymer chains and gas diffusivity decreased. This catenation effect was also reported recently for other polymers[10–15]. In order to design a H_2/CO separation membrane made of poly(sulphone–amide), a suitable polymer structure should be selected by considering these two effects.

In this report, concern was paid to gas permeability through poly(ether ketone) copolymers. Poly(ether ketone)s such as poly(ether ether ketone) (PEEK) are well known as high-performance semicrystalline engineering plastics with excellent heat stability and solvent resistance. PEEK, however, dissolves only in few solvents such as sulphuric acid, and it is hard to obtain a uniform film by the casting method. Therefore, reports about gas permeability through PEEK are very few. There are some reports on gas permeability through modified poly(ether ketone)s that are soluble in organic solvents with cardo-substituents[16,17] or fluorine-containing structure[18].

The poly(ether ketone)s described in this paper have simple structures consisting of ether, carbonyl and phenylene groups. These polymers were prepared by Friedel–Crafts reaction between diphenyl ether and a mixed acid chloride comprising terephthaloyl chloride and isophthaloyl chloride. Most of these copolymers dissolved in hexafluoroisopropanol and their films could be obtained by the casting method. The effects of the catenation structure and thermal treatment on gas permeability were studied by consideration of the influence of crystallinity.

EXPERIMENTAL

Materials

Isophthaloyl chloride (IPC), terephthaloyl chloride (TPC), obtained from Mitsubishi Gas Chemical Co. Inc., and aluminium chloride (Nacalai Tesque, EP) were crushed to a powder under a nitrogen atmosphere. 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP) (Nacalai Tesque, GR) was purified by distillation. Diphenyl ether and 1,2-dichloroethane (Nacalai Tesque, GR) were used without further purification.

Polymerization

The polymerization procedure for the poly(ether ketone) from diphenyl ether and isophthaloyl chloride is described below as a typical example.

In a 300 ml four-necked flask, equipped with a mechanical stirrer, a nitrogen inlet and a thermometer,

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were placed diphenyl ether (12.22 g, 0.0718 mol), IPC (14.58 g, 0.0718 mol) and 200 ml of dichloroethane. This solution was cooled below 5°C in an ice bath and then $AlCl_3$ (24.96 g, 0.187 mol) was added. After the reaction mixture was stirred for 2 h in the ice bath, the polymerization was continued for 16 h at room temperature. The dichloroethane was decanted from the reaction mixture, and methanol was mixed with the product. The polymer obtained was washed twice with 10% HCl aqueous solution and several times with pure water by use of a blender, and then dried at 150°C for 17 h under reduced pressure.

The other polymers were prepared using the same method, except that the mixed monomers were used with several ratios of IPC and TPC.

Film preparation

The polymer (500 mg) was dissolved in 5 ml of HFIP and filtered. The solution was cast onto a glass plate, and the solvent was evaporated by irradiation with an infra-red lamp. The film obtained was immersed in acetone for more than one day to extract the casting solvent, and dried at 120°C for 17 h in a vacuum oven.

Thermal treatment of the poly(ether ketone) films was carried out at 195°C in the vacuum oven.

Permeability measurement

The permeabilities of H_2, O_2, CO and N_2 were measured with a permeation apparatus made by Rika Seiki Kogyo, and an MKS Baratron pressure transducer was used for detection of the pressure increase in the downstream gas reservoir. Gas samples of purity exceeding 99.9% were used. All measurements were carried out at 30°C.

The permeability coefficient was determined from the steady-state permeation rate at a constant pressure of upstream gas (1 atm), and the apparent diffusion coefficient was determined using the time-lag method[19]. The apparent diffusion coefficient (D_{app}) was calculated from the following equation:

$$D_{app} = l^2/6L$$

where L is the time lag and l is the thickness of the membrane.

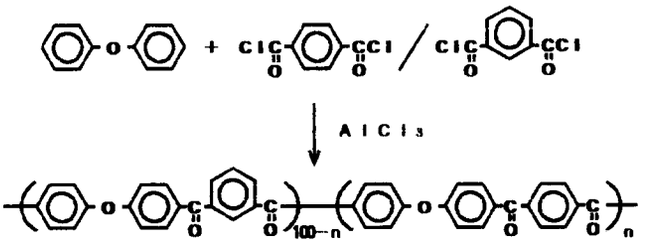
Characterization

Inherent viscosities of the polymers were measured at a concentration of 0.5 g dl^{-1} in 95% sulphuric acid at 30°C. D.s.c. measurement was carried out on a Perkin–Elmer DSC-1B with a 10 mg sample at a heating rate of 20°C min^{-1} under argon flow. Thermogravimetric analysis (t.g.a.) was performed on a Shimadzu TG-30 with a 3–6 mg sample at a heating rate of 10°C min^{-1} in air. The densities of the membranes were measured by use of a density gradient column, which consisted of n-heptane and carbon tetrachloride at 30°C. Wide-angle X-ray scattering was conducted on a Rigaku X-ray diffractometer with nickel-filtered Cu Kα radiation (40 kV, 100 mA).

RESULTS AND DISCUSSION

Preparation of poly(ether ketone)s

Synthesis of poly(ether ketone)s by Friedel–Crafts reaction was reported by Marvel *et al.*[20–22]. Compared with the preparation by aromatic nucleophilic displacement reaction[23], many kinds of polymer structure can be easily obtained by this method. In this report, the poly(ether ketone)s from diphenyl ether and the mixed acid chloride comprising IPC and TPC were prepared as shown below:



The results of preparation and characterization are shown in *Table 1*. Each polymerization gave an almost quantitative yield and an inherent viscosity more than 0.8. The glass transition temperature increased monotonically from 156°C to 174°C with increase of the content of TPC unit. EI and ET showed a clear melting point at 274°C and 378°C, respectively. Copolymerization decreased the melting point and broadened the melting peak. All the polymers except ET easily dissolved in HFIP.

Gas permeability of the as-cast films

The films of EI, EIT25, EIT50 and EIT75 were prepared by the casting method. The films prepared were immersed in acetone for more than one day to extract the HFIP completely. The permeability coefficients P for H_2, O_2, CO and N_2 at 30°C are illustrated in

Table 1 Preparation and characterization of poly(ether ketone)s

Polymer	Monomer ratio IPC	Monomer ratio TPC	Yield (%)	η_{inh}[a] (dl g^{-1})	T_g[b] (°C)	T_m[b] (°C)	T.g.a.[c] (°C)	Solubility[d]
EI	100	0	97	0.87	156	274	505	Soluble
EIT25	75	25	94	0.94	160	227	492	Soluble
EIT50	50	50	94	0.80	161	232	502	Soluble
EIT75	25	75	95	0.96	168	333	482	Soluble
ET	0	100	94	0.92	174	378	492	Insoluble

[a] Inherent viscosity measured at a concentration of 0.5 g dl^{-1} in H_2SO_4 at 30°C
[b] Glass transition and melting temperatures determined by d.s.c. in argon at a heating rate of 20°C min^{-1}
[c] The 5% weight-loss temperature measured by thermogravimetric analysis in air at a heating rate of 10°C min^{-1}
[d] Solubility in hexafluoroisopropanol at room temperature

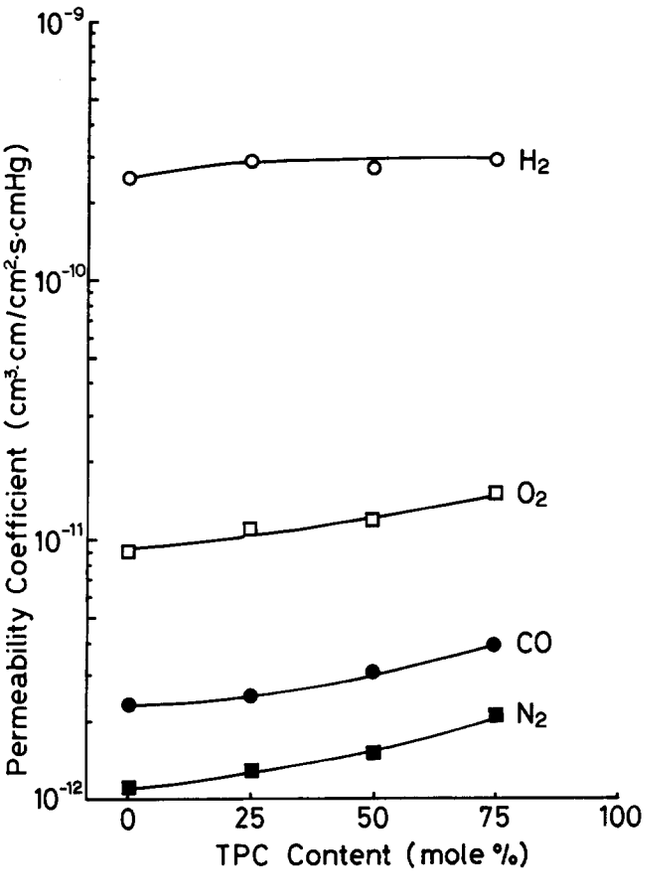


Figure 1 Correlation between the chemical composition of as-cast films of poly(ether ketone) copolymers and the gas permeability coefficients for H_2, O_2, CO and N_2 at 30°C

Figure 1. P_{H_2} was between 2.5×10^{-10} and 2.9×10^{-10} cm^3 cm cm^{-2} s^{-1} cmHg^{-1}, and no remarkable tendency was observed for the polymer composition. On the other hand, in the case of larger molecules, O_2, CO and N_2, the permeability coefficients increased with increase of the TPC content; for example, P_{N_2} increased twofold from 0 to 75 mol% TPC.

The apparent diffusion coefficients D_{app} for O_2 are plotted against TPC content in *Figure 2a*. D_{app} increased with increase of the TPC content. In *Figure 2b* are shown the apparent solubility coefficients S_{app} for O_2, which were calculated by using the formula $S = P/D$. Though measurements are limited to only one upstream pressure, the solubility coefficient seems to be independent of the TPC content. Therefore, it is considered that the increase of the permeability with increase of the TPC content was caused by the diffusivity change. This tendency is consistent with the results of poly(sulphone–amide)s[7–9]; the increase of the ratio of *p*-catenation content relative to *m*-catenation makes the chain packing less compact and the gas diffusivity higher.

To elucidate the crystallinity effect on the gas permeability, wide-angle X-ray scattering (WAXS) measurements were carried out. The X-ray diffractograms of the copolymers are shown in *Figure 3*. The diffraction peaks from crystalline structure were observed for the EIT75 film (D). For the other polymer films, however, no apparent crystalline peak was observed, and the films are considered to be almost amorphous. Though EIT75 has a certain extent of crystalline area into which a gas molecule can hardly permeate[24,25], no influence of

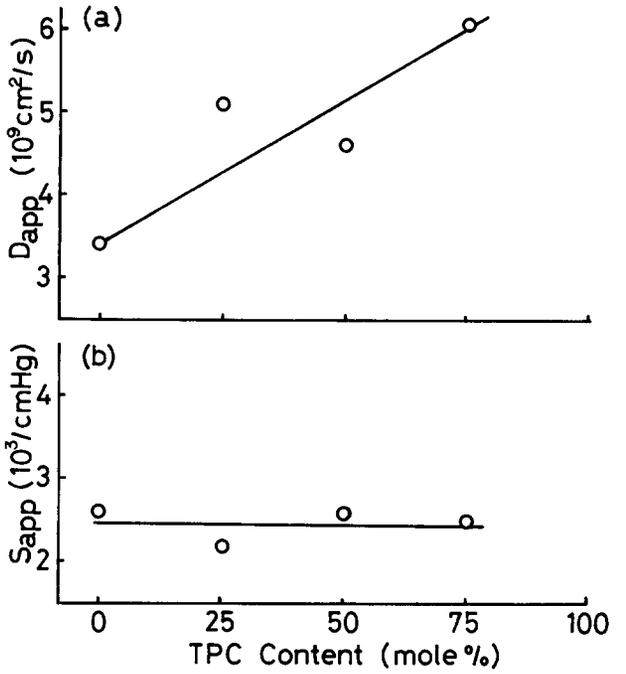


Figure 2 Effect of chemical composition on (a) the apparent diffusion coefficient and (b) the apparent solubility coefficient of as-cast poly(ether ketone) films for O_2

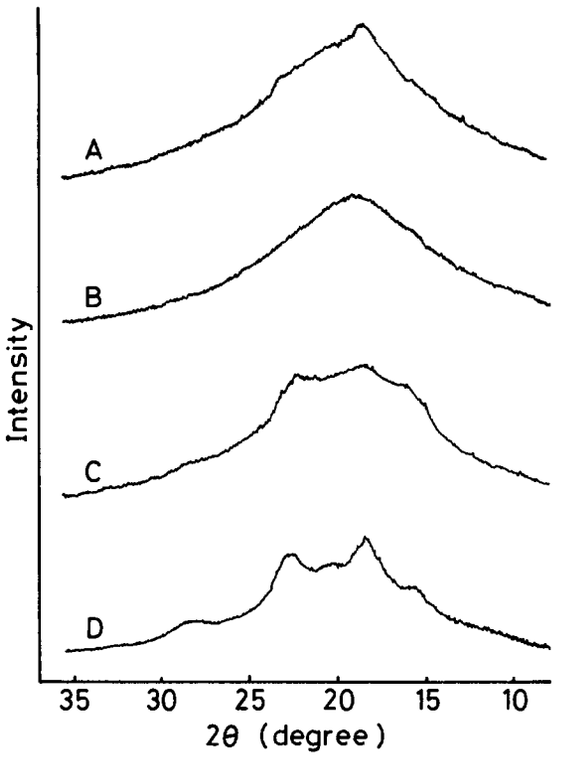


Figure 3 X-ray diffractograms of the poly(ether ketone) films without thermal treatment: (A) EI; (B) EIT25; (C) EIT50; (D) EIT75

crystallinity was observed in the results of permeability measurements. In the amorphous region of EIT75, the polymer chains would have less compact packing to offset the crystallinity effect. Also, there may exist some fine defects, which favour high gas diffusivity, in the amorphous region of EIT75.

Gas permeability of the thermally treated films

The poly(ether ketone) films were treated at 195°C under reduced pressure, above their glass transition temperatures. The permeability coefficients of the films after 1 h treatment for the four gases are illustrated in *Figure 4*. In all the polymers except EIT25, the permeability coefficients for every gas decreased by 10–60% with the thermal treatment. For EIT25 films, P_{H_2} showed no change, and the permeabilities of the other gases increased about 10–45% with the thermal treatment.

The X-ray diffraction patterns of the films after 1 h treatment are shown in *Figure 5*. The crystalline peaks were observed clearly in EI (A) and EIT75 (D), and to some extent in EIT50 (C). On the other hand, EIT25 (B) still showed a broad amorphous pattern. After further thermal treatment for 5 h, no more change was detected in EI, EIT25 and EIT75, and the crystalline peaks became higher in EIT50. These results indicate the fast crystallization in EI and EIT75, the slow crystallization in EIT50, and no crystallization in EIT25. The crystallization behaviour was also confirmed with the density measurement as shown in *Table 2*. The densities of the films except EIT25 increased with the thermal treatment. From these evaluations, it is considered that the permeability change by the thermal treatment was clearly related to the crystallization.

The apparent diffusivity change of O_2 by the thermal treatment is shown in *Figure 6a*. The diffusion coefficients for EI, EIT25 and EIT50 increased slightly at the early stage of the thermal treatment. Although the amorphous

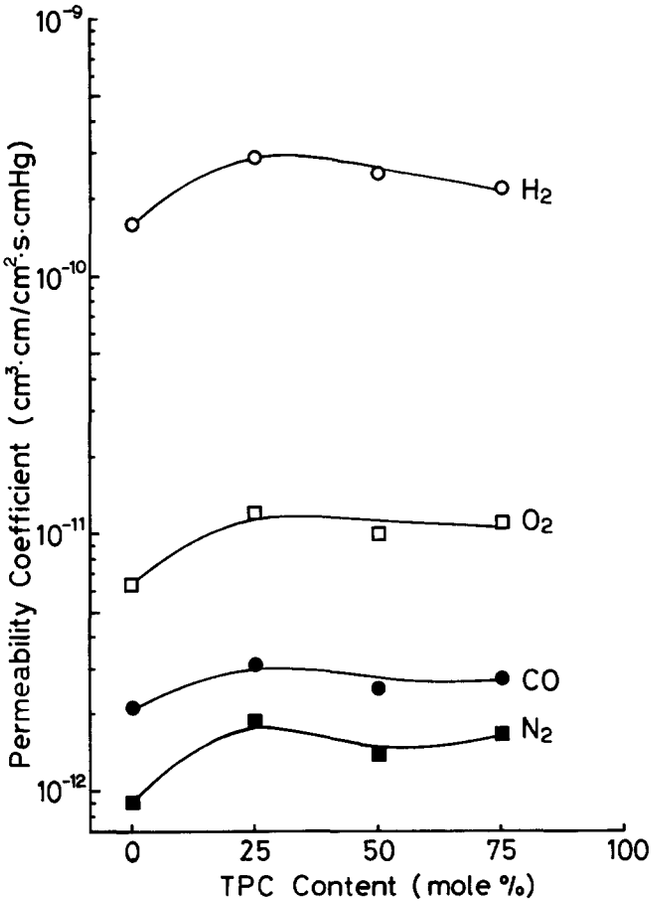


Figure 4 Correlation between the chemical composition of poly(ether ketone) copolymers thermally treated for 1 h and the gas permeability coefficients for H_2, O_2, CO and N_2 at 30°C

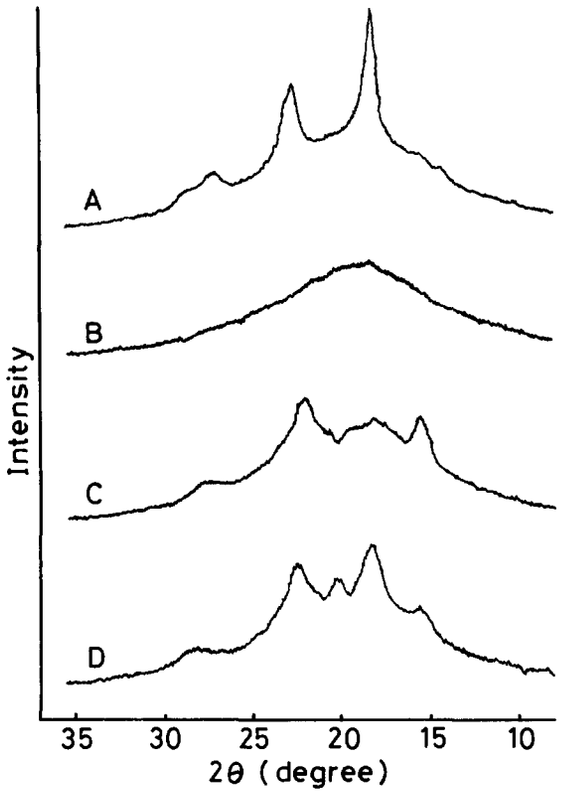


Figure 5 X-ray diffractograms of the poly(ether ketone) films after 1 h thermal treatment at 195°C: (A) EI; (B) EIT25; (C) EIT50; (D) EIT75

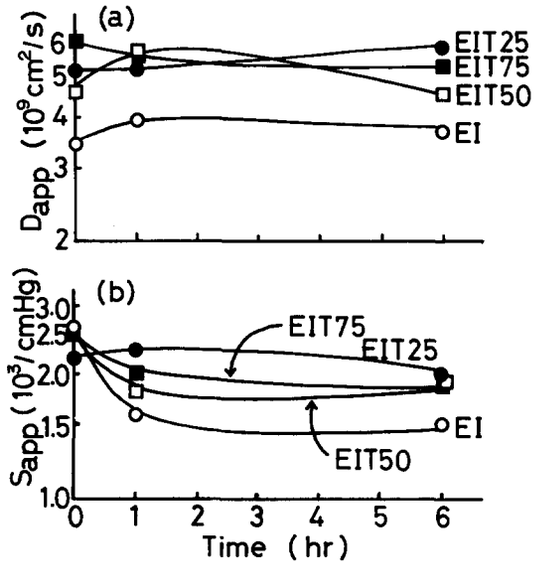


Figure 6 Change of (a) the apparent diffusion coefficient and (b) the apparent solubility coefficient for O_2 by thermal treatment at 195°C

Table 2 Density of the poly(ether ketone) films[a]

Polymer	Thermal treatment[b]		
	None	1 h	6 h
EI	1.27	1.30	1.30
EIT25	1.28	1.28	1.28
EIT50	1.27	1.29	1.30
EIT75	1.29	1.31	1.31

[a] Density measurement was performed at 30°C
[b] Thermal treatment was carried out at 195°C under vacuum

region in EI and EIT50, which allows gas diffusion, became smaller with the growth of the crystalline region by the thermal treatment, the apparent gas diffusivity did not decrease. This would be considered as due to the creation of some fine defects in the amorphous region by the thermal treatment. In the case of EIT75, the existence of defects before the thermal treatment is supposed, and further defect formation may be small. A similar effect was also observed in the thermal treatment of amorphous poly(sulphone–amide) films[26]. It seems difficult to bring about homogeneous densification in the amorphous region, which is effective in reducing gas diffusion, by thermal treatment without solvent.

The decrease of apparent solubility coefficients for O_2 was found in EI, EIT50 and EIT75 as shown in *Figure 6b*. This is consistent with the fact that a gas hardly dissolves in a crystalline region. No crystallization occurred in EIT25, and no remarkable solubility change was detected. The permeability change in the poly(ether ketone) films by the thermal treatment seems to be dominated by the solubility change rather than the diffusivity change.

From the discussion mentioned above, the decrease of gas permeability by the thermal treatment may be concluded to be caused by increase of degree of crystallinity of the semicrystalline poly(ether ketone)s induced by the thermal treatment. In the case of amorphous poly(ether ketone), the homogeneous densification due to rearrangement of polymer chains does not seem to be easy without the presence of solvent molecules, and the gas permeability did not decrease.

CONCLUSIONS

Gas permeability of the as-cast films of poly(ether ketone) copolymers made from diphenyl ether and the mixed acid chloride comprising IPC and TPC was influenced by the chain-packing character with the catenation effect. Increase of *m*-catenation ratio relative to *p*-catenation made chain packing more compact and reduced the gas diffusivity. The difference of crystallinity among the polymers was too small to exhibit a clear effect on the gas permeability.

The permeability change of the poly(ether ketone) films by thermal treatment was interpreted as due to the decrease of the content of the amorphous region, in which gases can permeate, by the thermal crystallization. Densification in the amorphous region was not observed, and the diffusivity change was explained in terms of the formation of small defects.

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