

The Absorption Behavior and Crystallization of Poly(Aryl Ether Ketone) Films

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ABSTRACT: The absorption and subsequent desorption behaviors of amorphous polymer films of PEEK poly(ether ether ketone), PEEKK poly(ether ether ketone ketone), and PEKK poly(ether ketone ketone) in solvent of 1,2-dichloroethane ($C_2H_4Cl_2$) are investigated and compared. The equilibrium absorption weight (M_∞) of these polymers is related to their molecular ketone content or molecular chain rigidity and also to the experimental conditions. Especially, at a certain temperature, the molecular chains in the solvent can be polarized, which leads to producing greater M_∞ for polymer films; for example, at 60°C, $M_\infty = 46\%$ for PEEK and $M_\infty = 65\%$ for PEKK. The pseudodiffusion coefficients for PEEK, PEEKK, and PEKK all surpass the $6.0 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$. The polymer's molecular polarization has been proved in concentrated sulfur acid. Results also show that amorphous resin's films become white and crepted in dichloroethane, which is more serious when metaphenyl links are introduced into PEEKK or PEKK molecular main chains. The residual solvent of 1% or so often exists in the films, even though a long desorption time (over 100 h) has been proceeded. Absorption has induced crystallization of amorphous polymer films, but this crystallization process is slightly different from that of the films crystallized from both the glassy state and the melting state in the solvent, which makes the amorphous interlayers grow progressively and more condensely; thus, the crystallized films will have higher T_g 's than these crystallized under annealing condition. The morphology results have shown that the solvent-crystallized films are less toughened than the amorphous ones because of the intermediate layer between the induced crystallized area and the amorphous area in the core.
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Key words: absorption; desorption; poly(aryl ether ketone) films; molecular polarization; chain rigidity

INTRODUCTION

Poly(aryl ether ketone)s is a family of high-performance engineering thermoplastics. Since the 1980s, they have attracted more and more attention from researchers in many countries. These kinds of plastics usually have excellent thermal

and mechanical performance, especially resistance to acidity, alkali, and oxidation due to aging. Thus, they have been processed into different machine parts and applied to wider fields, such as these in automobile and airplane industries. More recently, many composites based on resins of polymers of poly(aryl ether ketone)s, especially PEEK, with a molecular repeat unit of (—ArOAr—OArCO—) have been reported. Meanwhile, new kinds of poly(aryl ether ketone)s, for example, PEEKK, with repeat unit of (—ArOArOAr—

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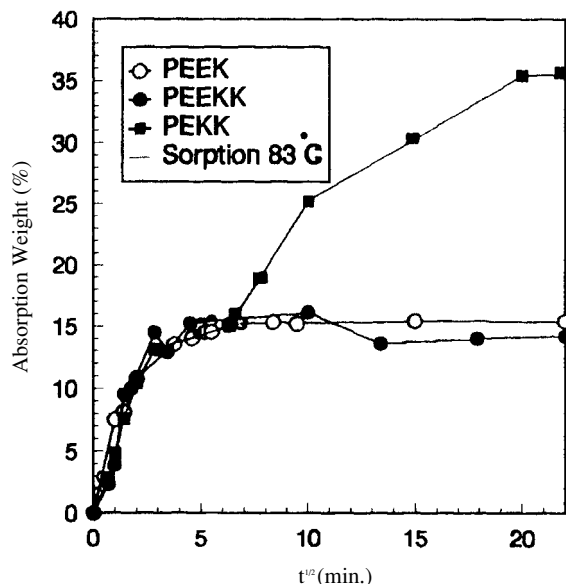


Figure 1 Vapor weight absorption of PEEK, PEEKK, and PEKK in a solvent of $C_2H_4Cl_2$ at $83^\circ C$.

COArCO—) and a PEKK unit of (—ArOArCOArCO—), have been developed by different researchers.¹⁻³ These para-substituted polymers can be modified by introduction of meta-phenyl links into their molecular main chains, for example, PEK_mK with a repeat unit of (—ArOArCOAr*CO—) (Ar = 1,4-phenylene; Ar* = 1,3-phenylene hereinafter). All these polymers can usually be made into different thickness of films when there is enough large molecular weight. Based on the films, these polymers' different properties in mechanics and solvent resistance can be revealed. In recent years, the absorption behavior of PEEK has been investigated in many reports in which different solvents are adopted, and its maximum absorption levels (equilibrium weight gain^{4,5}) are shown as 23.5, 20, 51, and 21.2% for solvents of benzene, toluene, chloroform, and carbon disulfide,^{4,6} respectively.

The diffusion of a penetrant (solvent) into a PEEK polymer resin matrix can be described by Fick's law as $F = D \times \partial c / \partial x$,⁵ where D is the diffusion coefficient, F is flux rate through a surface, and $\partial c / \partial x$ is concentration gradient. Absorption is related to the thickness of films. For a thin film, the weight gain is linear with time ($n = 1$) but it is linear with time^{1/2} ($n = 1/2$) for the thick film described by formulae of $M_t / M_\infty = kt^n$, where M_t is weight gain at time of t and M_∞ weight gain at ultimated time. This kind of description is often

called the Fickian model. In fact, the penetrants into amorphous PEEK films are not exactly Fickian since the absorption and desorption processes are not equal. Thus, researchers took a pseudo-Fickian model by using a pseudo-Fickian diffusion coefficient in thick films to estimate the film's absorption behavior. In practice, this diffusion coefficient is estimated by the initial slope (straight line) in curves of weight gain—time^{1/2}. The diffusion behavior of rigid chain polymers can be corrected as the follows.⁵ $D = \pi l^2 / 16 [S / M_\infty]^2$ (where S is the slope of the initial linear part of the weight absorption—time^{1/2} curves).

In this article, different poly(aryl ether ketone)s, such as PEEK, PEEKK, and PEKK have been adopted to investigate their absorption and desorption behaviors. Their crystallization under different conditions are compared. These properties are related to the molecular structure.

EXPERIMENTS

Materials and Samples

Different poly(aryl ether ketone)s (PAKEs) are synthesized by both nucleophilic and electrophilic substitution routes.^{1,2,7,8,16} In this article, PAEKs by nucleophilic substitution route are carefully chosen except PEK_mK. Their molecular weight is expressed by apparent viscosity. The viscosity of

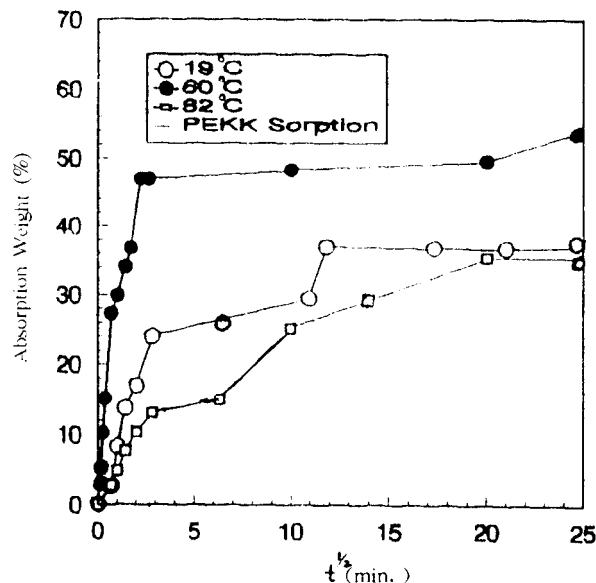


Figure 2 Sorption behavior for PEKK in a solvent of $C_2H_4Cl_2$ at different temperatures.

Table I The Equilibrium Absorption Weight (M_∞) for PAEKs in Solvent of Dichloroethane

Sample	$K/K + E^a$ (%)	Rigidity ^a (%)	Crystallinity at 60°C	M_∞ (%)		
				19°C	60°C	83°C
PEEK	33.3	55.3	30.5	43	46	16
PEEKK	50.0	57.9	38.8	46	50	17
PEKK	66.7	60.4	44.3	39.5	55	37.7

^a K or E stands for the ketone or ether group molar content in the polymer main chain.

^b Chain rigidity (R) is calculated from molecular chain length, $R = L_{\text{rigid}}/L_{\text{total}}$ (L_{rigid} or L_{total} is the rigid chain length and the length of total repeat unit in a polymer main chain).

PEKK, PEEKK, PEK_mK, and PEEK_mK in a solvent of H₂SO₄ is corrected based on the relative standard of PEEK.⁶ They have η_{iv} of 0.70 or so (corrected value). Many amorphous PAEKs films are obtained by melt-quenching process. But, the thickness of samples ranging from 0.35 to 0.45 mm is chosen, especially the thick films of 0.45 mm for PAEKs without metaphenyl links, which are chosen for comparison. All samples are carefully cut into 10 × 20 mm films.

The absorption experiment was done in a flask with a wide mouth and a round bottom by immersing the samples into solvents there. The temperature of flask is controlled by a heating bath at a given time interval. The samples were withdrawn from the solvents, quickly blotted dry, and then weighted on an optical analytical balance (accuracy of +0.0001 g). These samples should be immediately put into the experimental device in each subsequent absorption and desorption weighting. Desorption experiments of samples in saturation absorption were processed at fixed temperatures in a special oven, vacant of air, and weighted at given interval time.

The crystallization experiments and thermal analysis of samples were done on differential scanning calorimetry (DSC) equipment (Dupont-910 DSC under 2000 system). The sample weights

Table II Pseudo-Fickian Diffusion Coefficients for Different PAEKs Polymers in Dichloroethane

Sample (°C)	Pseudodiffusion Coefficient ($1 \times \text{m}^2 \text{s}^{-1}$) 10^{-12}		
	PEEK	PEEKK	PEKK
19	0.43	0.56	0.71
60	3.10	6.57	9.41

ranged from 6.80 to 8.0 mg, the scanning rate from 10 to 20°C/min, and the scanning scope from 50 to 80°C over each sample's melting point. Some samples were analyzed on PE DSC-7 under the same conditions as above. Their crystallinity degree (X_c) is calculated by $X_c = \Delta H_c / \Delta H_f^\circ \times 100\%$, where ΔH_c and ΔH_f° are the heat of fusion for the crystallized samples and the 100% crystallinity samples; ΔH_f° is 130.1 J g⁻¹ for PEEK,¹⁷ 124.0 J g⁻¹ for PEEKK,³ and 140.0 J g⁻¹ for PEKK.^{7,16}

X-ray analysis of samples is made on 12kv Regaku D/Max RA with rotated anode scanning from 5 to 50° at rate of 2°/min. The determined crystallinity degree in this method is obtained by analytical calculus of X-ray curves.

Ultraviolet-visible experiments were made on Shimadzu-3100 equipment with a double optical tunnel with a sample concentration from 1×10^{-7} to 1×10^{-3} g L⁻¹.

Scanning electron microscopy (SEM) of PAEKs samples on Japan Hitachi S-530 SEM equip-

Table III The Apparent Physical Property of Poly(arylether ketone) Films Exposed to the Solvent of Dichloroethane Under Vapor Conditions

T_c/t (°C/min)	I ^a	II	III	IV	V
50/10	W/C	U/U	U/U	W/S	U/U
80/20	W/C	sW/C	U/U	W/C	U/U
87/240	vW/C	sW/U	sW/U	W/C	U/U
89/1020	vW/C	W/sC	sW/sC	vW/C	sW/sC
85/1320	vW/C	W/sC	sW/sC	vW/C	sW/sC
84/2400	vW/C	W/sC	sW/C	vW/C	sW/sC

^a I represents PEEK_mK; II, PEEK; III, PEEKK; IV, PEEK_mK; V, PEKK; W, white color; C, creped; U, unchanged; S, soft; vW, very white; and sW or sC, slightly white or slightly creped.

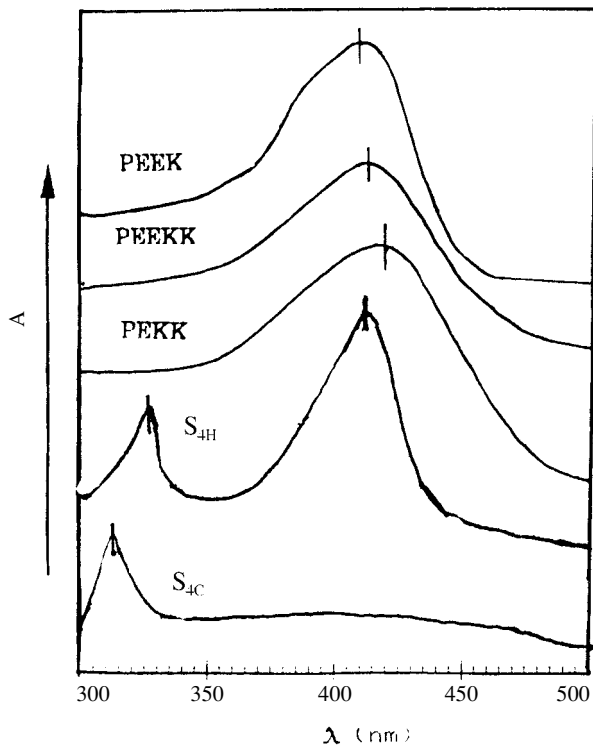


Figure 3 UV spectra of PEEK, PEEKK, PEKK, and a model compound of S_4 in solvent of concentration of H_2SO_4 (S_{4H}), together with S_4 in a solvent of $C_2H_4Cl_2$ (S_{4C}).

ment. The samples are obtained in a melt-quenching process, then fractured under liquid nitrogen and/or by impact.

RESULTS AND DISCUSSIONS

Vapor Absorption of PAEKs

Vapor absorption behavior for PEEK, PEEKK, and PEKK has been shown in Figure 1. During the vapor absorption process, desorption occurs after initial absorption stage (overshoot). High-temperature vapor can easily make absorption in each equilibrium level. In fact, the equilibrium absorption weight occurs at 25 min or so ($t^{1/2} = 5$) for PEEK and 100 min for PEEKK after absorption began. This absorption time is defined as the equilibrium absorption time. It is thought that the equilibrium absorption time is related to the ketone content in a molecular repeat unit of polymers. That is, the higher the ketone content, the longer the equilibrium absorption time.

The interesting is that, in Figure 1, PEKK (ketone content of 66.7%) has an equilibrium absorption time greater than 400 min ($t^{1/2} = 20$). Thus, it is noted that PEKK has quite different vapor absorption behavior from that of PEEK. Figure 2 has listed the absorption behavior of PEKK in different temperature. It is clearly seen that there are several absorption plateaus in the absorption curve at different temperature, while their absorption behavior is quite similar. Especially, at 60°C, the greatest equilibrium absorption weight of 55% is obtained. It seems that temperature at 60°C is the best condition for penetration of dichloroethane into PAEKs amorphous films, which has been strongly proven in Table I.

From Table I, it is shown that equilibrium absorption weight for each sample is greatest at 60°C. As such a vapor absorption temperature increases, the equilibrium absorption weight (M_∞) linearly increases with ketone content or chain rigidity. The most probable reasons for this will be explained later. At 60°C, sample's crystallization tends to be perfect, their crystallinity is greater than that of the counterpart annealing samples⁶ (see Table I). For PAEKs, their pseudo-Fickian diffusion coefficients at different temperature are shown in Table II. These coefficients approximately reflect their absorption rate at the initial stage. Temperature has increased this initial absorption rate.

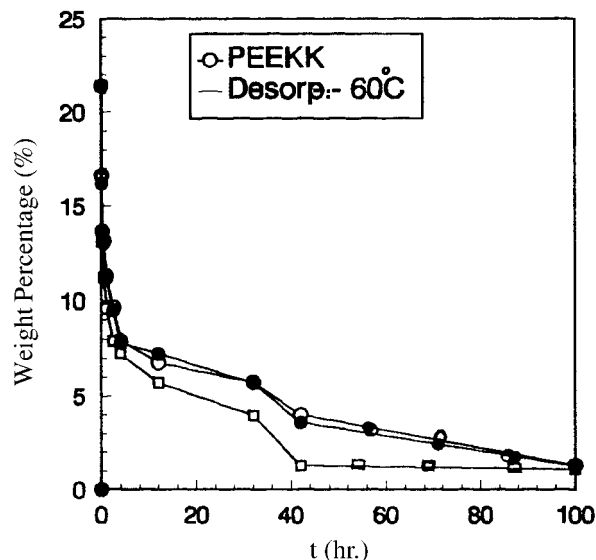


Figure 4 Desorption behavior of PEEKK at 60°C in solvent of $C_2H_4Cl_2$ (three repeated results are shown).

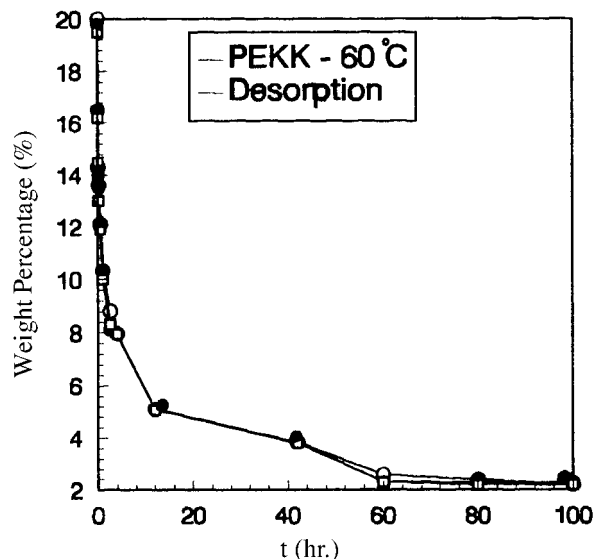


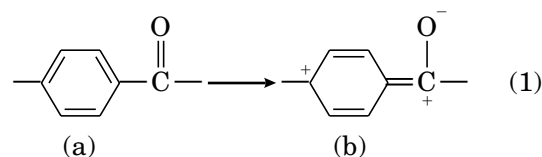
Figure 5 Desorption behavior of PEKK at 60°C in a solvent of $C_2H_4Cl_2$ (two repeated results are shown).

Effect of Penetrants on Polymer Performances

The vapor of solvents has great effects on the polymer's film physical and chemical properties. It is known that PAEKs have good performance in resistance to solvents, for example, acidity and alkali; however, this greatly changes with the polymer molecular structure and the involved experimental conditions. Table III lists the effects of solvent vapor on PAEKs, where PEEKmK poly(ether ether ketone metaphenyl link ketone)⁹ has molecular unit chain structure of $(-ArOArOArCOAr^*CO-)$, PEBEKmK of $(-ArOArOArCOAr^*CO-)$ poly(ether biphenyl links ether ketone metaphenyl links ketone)⁸ ($Ar = 1,4$ -phenylene; $Ar^* = 1,3$ -phenylene). It is clearly shown that at the time of 10 min, PEEKmK film becomes white and creped, while PEBEKmK has become white too. At the time of 30 min, both PEEKmK and PEBEKmK become white and creped. For all parasubstituted PAEKs, metaphenyl links have introduced asymmetrical factors^{9,17} into their molecular chains. This metaphenyl links also introduced unstable conformations so that PAEKs containing metaphenyl links can easily change their chain conformations when exposed to polar solvent, such as dichloroethane. This has been shown in Table III.

Compared to the above experimental results, all parasubstituted PAEKs, such as PEEK, PEEKK, and PEKK have also been effected by such solvents as dichloroethane, which is also

shown in Table III. It is seen from Table III that, at the time of 240 min, nearly all parasubstituted PAEKs become white but not creped. When the experimental time is much longer (for example, 2400 min in Table III), only PEEK and PEKK have seen slight creeping. The reason for this phenomenon is still in argument, but molecular chain polarization is an important factor to be considered. Molecular polarization under certain conditions has been studied in detail in our previous works.¹¹⁻¹³ When the polymer of PAEKs is placed in strongly polarized solvents, its molecular chain turns to be polarized, which is shown as follows:



When the polymer of PAEKs is placed in polarized solvent (for example, dichloroethane), its molecular chains have the electrons reassign and transmit from state (a) to (b) in formulae (1). That is to say, the molecular chain polarized. The polarization of PAEKs in strongly polarized solvent of H_2SO_4 is often observed. The solution of PAEKs in H_2SO_4 usually becomes red or deep red, which proves that the electrons move and that the chain polarized. The mechanism for PAEKs polarized in H_2SO_4 has been proved to be a dipole-dipole action,¹¹ hydrogen bond action,¹² and/or protonation action.¹³ Based on these results, the model compound of S_4 with molecular structure of $ArOArCOArOAr$ for PEEK has been investigated by the UV-visible spectra method. Figure 3 has shown the results of S_4 in solvent of both $C_2H_4Cl_2$ and H_2SO_4 . When in $C_2H_4Cl_2$, S_4 has absorption peaks at 310 and 260 nm (not shown in Fig. 3), which shows slight polarization of the solvent. But when S_4 is in H_2SO_4 , the extremely strong peak at 410 nm appears due to the strong polarization of H_2SO_4 . Similarly, it has been clearly shown that the strong peaks above 400 nm for PEEK, PEEKK, and PEKK are resulted from polarization of their molecular chains by H_2SO_4 . It should be pointed out that these UV experiment proceeds very quickly (for example, less than 1 min). In such a short time, the sulphonation action of H_2SO_4 is not considered,¹¹⁻¹³ but that the solution of PAEKs in H_2SO_4 becomes red immediately. It is reasonably thought of as the physical

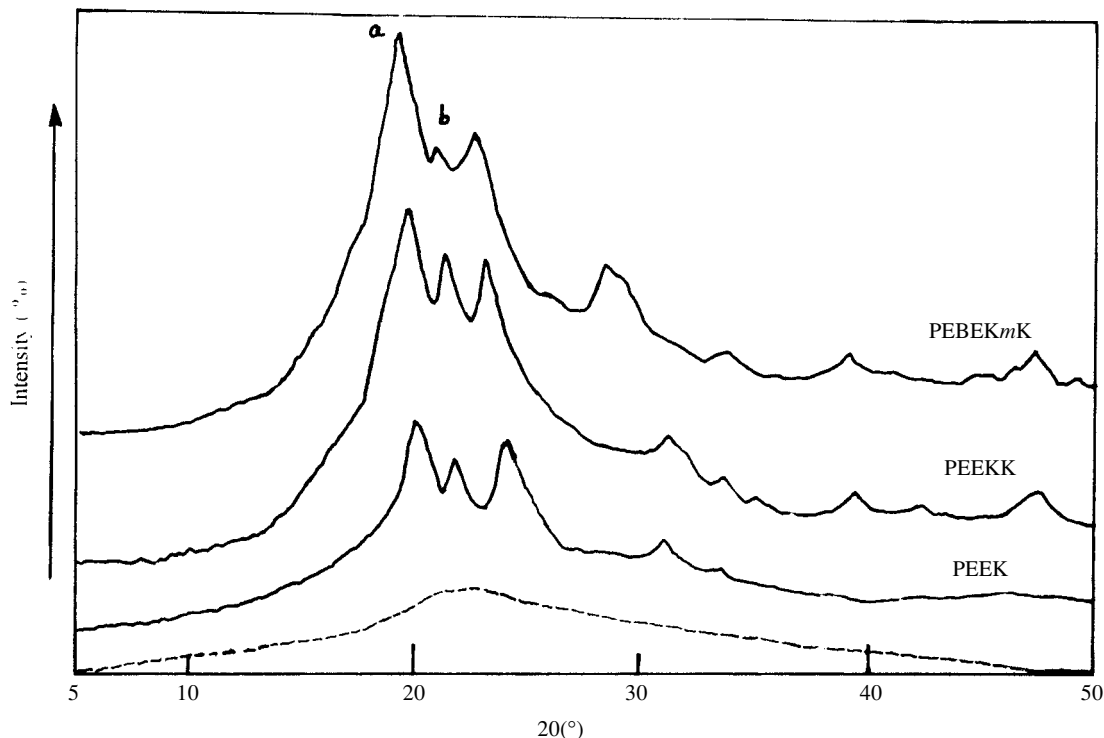


Figure 6 WAXD patterns of solvent-induced crystallization for PAEKs polymers film at 60°C.

absorption occurrence at first for all PAEKs acted on by all kinds of solvents. And then, the polarization occurs, which resulted in the color change of PAEKs. That is, PAEKs become white in $C_2H_4Cl_2$ (or similar solvent as it) while red in H_2SO_4 (or similar solvent as it) due to the polarization of polymer chain. It is thought that hydrogen bond plays a great role in the action of $C_2H_4Cl_2$ on PAEKs, while both protonation and hydrogen bond plays a great part in the action of H_2SO_4 on PAEKs. Thus, it is expected that the PAEKs molecular polarization occurs in the polar solvents, the polarization intensity of which depends on the polar intensity of solvents adopted; for example, PAEKs solution is red in H_2SO_4 while white in $C_2H_4Cl_2$.

Desorption Experiments

In the solvent absorption process, the desorption action occurs accompanying the initial absorption. The two processes will reach equilibrium at certain point after initial absorption, but it is ob-

served that desorption proceeds much slower. That is, this process will last several hundreds or even thousands of hours. While, this desorption process depends on the kind of solvent, for example, when PEEK in solvent of carbon disulfide⁵ (CS_2), desorption proceeds completely in about 100 h. But when solvents contain hydrogen or proton, this desorption will take longer time to complete. Figures 4 and 5 have shown the desorption behavior of PEEKK and PEKK at 60°C in a solvent of $C_2H_4Cl_2$.

The experiments have been repeated three times for PEEKK (Fig. 4) and two times for PEKK. When the desorption time greater than 100 h, there is also 1.3% solvent residue for PEKK. From the desorption curves of both PEEKK and PEKK (see Figs. 4 and 5), it is seen that in less than 1 h, the 50% absorption weight has been lost for both PEEK and PEKK at the initial desorption stage. Even so, the second desorption takes place at about 40 h for PEEKK while at 60 h for PEKK. It can be seen that completion of desorption will take longer time for PEKK than that for PEEKK.

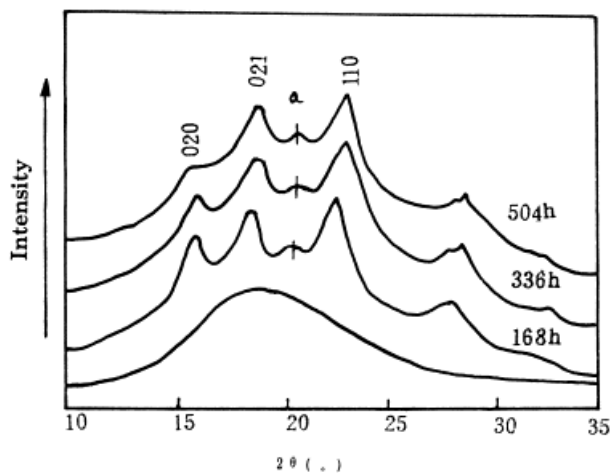


Figure 7 WAXD patterns of PEKK crystallization induced by a solvent of $C_2H_4Cl_2$ at $60^\circ C$.

CRYSTALLIZATION

Crystallization Induced by Solvent

There exists interaction between solvent and molecular chains of polymer films in the solvent, as shown in the former part. In addition to this inter-

action, the solvent has also changed the film micromorphology of PAEKs in them, which has been shown by some experiment results reported recently. Cheng et al.^{5,14} and us⁶ have shown that the solvent-crystallized PEKK has no micrometer-sized crystallites (that is, very small crystal particles). The same morphology is true for PEEKmK. Solvent-crystallized PEEK has smaller and more tightly organized crystals as compared to thermally annealed specimens.^{4,15} Figure 6 has shown the wide-angle X-ray diffraction (WAXD) patterns of PAEKs crystallized in solvent of $C_2H_4Cl_2$. And it is believed that the polymer with metaphe-nyl links can also grow its crystals in solvent, but the solvent doesn't affect the crystal forms in PEEK and PEEKK, both of which have orthorhombic crystal system.^{3,5,6} However, solvent has changed the WAXD patterns of PEBEKmK in Figure 6, where peak (a) has shifted to the greater diffraction angles while peak (b) forms better than it crystallized from annealing samples. This has shown that crystals of PEBEKmK containing metaphe-nyl links grow better than those crystallized by annealing. See the details of the morphology in the latter part.

Solvent has also greatly changed the crystal

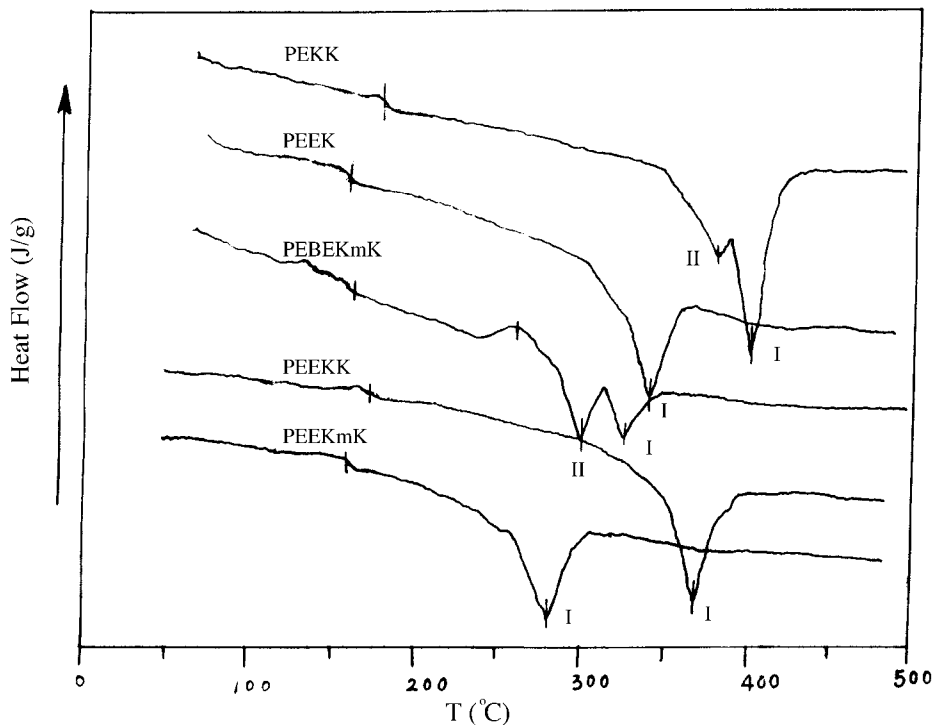


Figure 8 DSC scanning of PAEKs crystallized from the induction of a solvent of $C_2H_4Cl_2$.

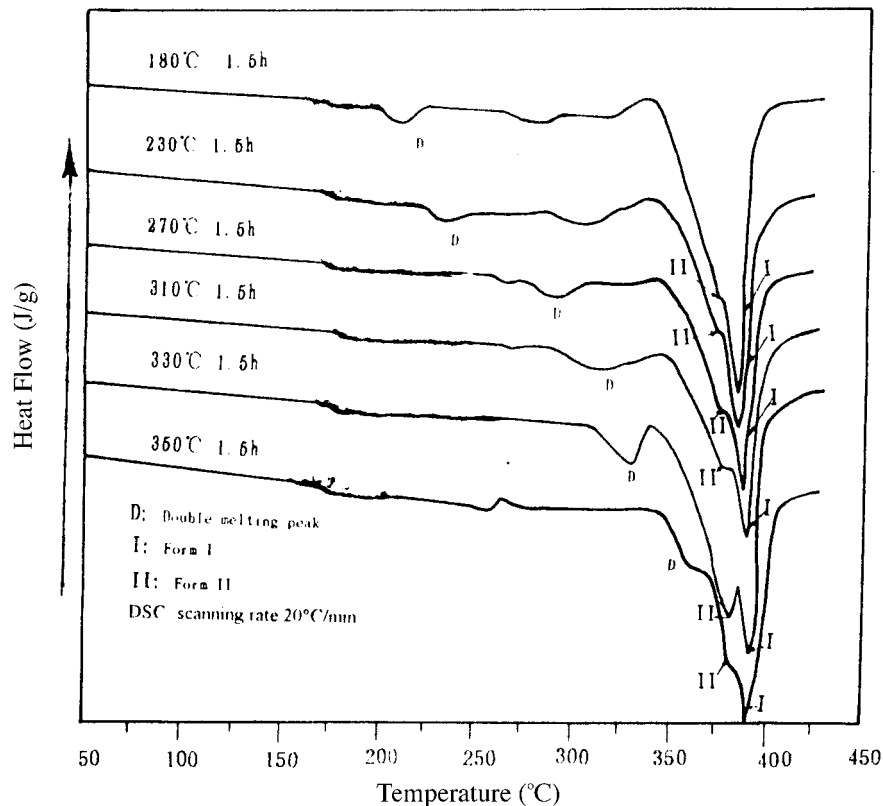


Figure 9 DSC scanning of PEKK samples crystallized at different temperature for 1.5 h from the glassy state.

forms of PEKK. Generally, all PAEKs crystallized resins have only one crystal form (form I) when crystallized from the melt state. Form I has characteristic peak positions at $2\theta = 18, 20, 22,$ and 28.5 (approximate position). Figure 7 has presented the WAXD patterns of PEKK crystallized in solvent at 60°C for different times. It clearly shows that the new crystal form has appeared (position of $2\theta = 15^\circ$ or so). This new crystal form

is indexed in Figure 7 according to model reported in literature.^{6,14} Peak (a) in Figure 7 ($2\theta = 20^\circ$ or so) is the residual diffraction pattern of form I.

Figure 8 has shown DSC scanning results of PAEKs samples, which have desorbed their solvents with residual solvent less than 0.5%. The DSC patterns of these polymers are basically similar to those crystallized from thermally annealing samples. Their glassy transition temperature

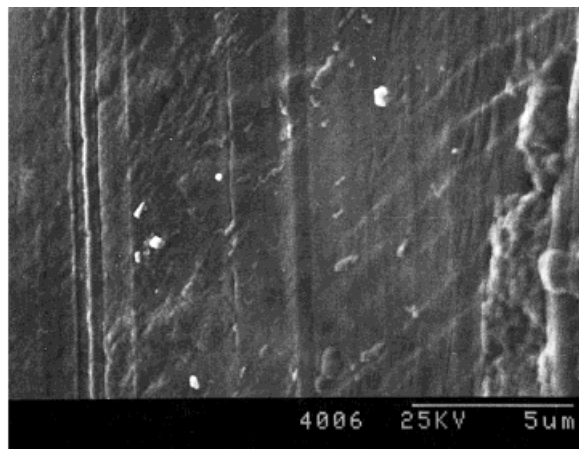
Table IV Crystallinity and the Glassy Transition of Samples of Solvent Crystallization Samples and Amorphous Samples for PAEKs Polymers

Properties ^a	PEEK	PEEKK	PEKK	PEEKmK	PEBEKmK
ΔH (J g^{-1})	27.2	32.3	57.5	26.3	20.8
X_c (%)	21.0	25.3	41.1	14.6	—
T_g^b ($^\circ\text{C}$)	143	167	171	146	161
T_g^c ($^\circ\text{C}$)	152	181	183	157	>161

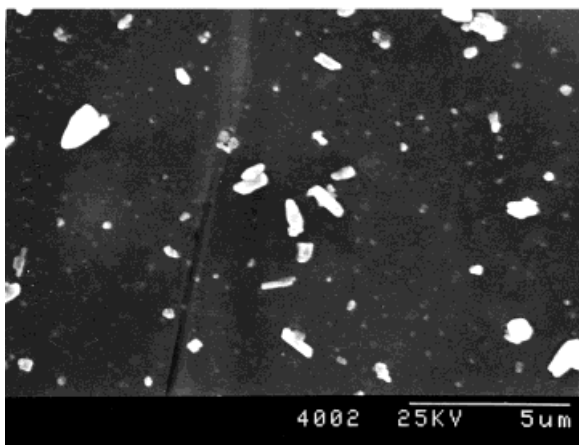
^a ΔH represents heat of fusion by DSC for solvent crystallization samples; X_c , and crystallinity degree.

^b Results from amorphous samples.

^c Results from solvent-crystallized samples.



(a)



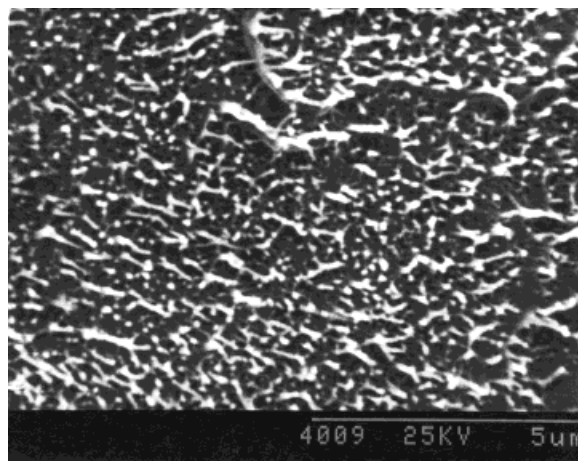
(b)

Figure 10 SEM of quench-fractured surface morphology for amorphous PEEKK film (a) and solvent-crystallized films (b). The tensile-fractured direction of the film is from the top to bottom of the picture.

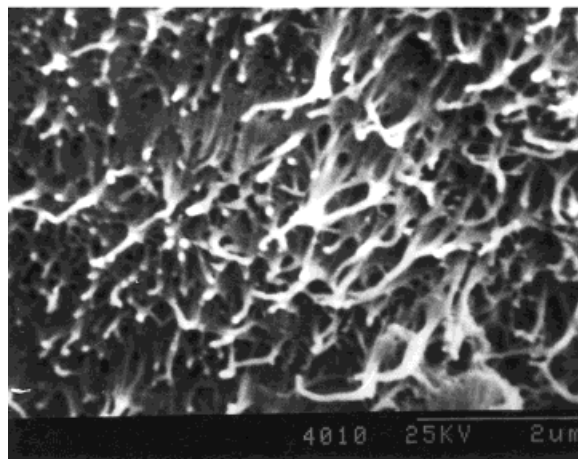
is detected by careful repeat scanning of the solvent-crystallized samples. But, for both PEB-EK_mK and PEKK, two melting transition temperatures had appeared, which is not the “double melting behavior” as often detected in samples crystallized from a thermally annealing state. In contrast, their two melting peaks correspond to the polymorphism in them; that is, the higher melting peak results from stable form I, whereas is the lower one forms the relatively unstable form II. It should be noted that the solvent-crystallized PAEKs have quite different DSC patterns in that their “double melting behavior” as the samples crystallized from thermally annealed state have disappeared completely. For PAEKs thermally

annealing samples, their double melting behavior has such common characteristics that the double melting peak position increases as the annealing temperature. This characteristics is detected in the sample crystallized from both the glassy and the melting state. For PEKK, this characteristics has been shown in Figure 9.

It is clearly seen that its double melting peak (*D*) moves toward higher temperatures, such as the crystallization temperature. The two melting transition peaks correspond to form I (upper) and form II (lower). Its glass transition temperature decreased slightly as the annealing temperature. Besides, it can also be found that the crystallinity



(a)



(b)

Figure 11 SEM of the impact morphology for amorphous PEEKK film (a) and solvent-crystallized films (b) with the same tensile-fractured direction as in Figure 10.

decreases in samples with metaphenyl links (for example, PEEKmK in Table IV).

Table IV has presented the physical properties for amorphous PAEKs films crystallized in solvents at room temperature. It is interesting that the glassy transition temperature of solvent-crystallized PAEKs have 9–13°C greater than that of samples crystallized from the annealing state. This phenomenon can be thought of as the results of morphology transition for PAEKs. The amorphous films will change its disordered state into an ordered state. The previously formed crystallized lamellae will exert obstacles on the residual amorphous areas on the core, which will help to form an interlayers between the ordered and crystallized hard shell near the film surface and the disordered amorphous core of the film, and which will delay the glassy transition correspondence in subject to the temperature. This interlayers from amorphous area will grow progressively and cause solvent-crystallized samples to have higher temperature relaxation than those crystallized from annealing state. Especially, the smaller and more tightly accumulated crystallites have formed in solvent-crystallization near this intermediate layers, which may be the major reason to explain the higher T_g of solvent-crystallized samples in Table IV. Meanwhile, recent years, Wolf et al.^{3,6,10} thought that the shorter long period distance for solvent-crystallized sample of PEEK than that for PEEK crystallized from annealing state is one of the main factors controlling the change of T_g .

Crystallization Morphology

Figure 10(a) and (b) show the SEM morphology of PAEKs solvent-crystallized films [Fig. 10(a)] compared with that of the amorphous samples [Fig. 10(b)]. The pictures are taken on the fractured surface near the film plane surface. The amorphous PEEKK has shown nearly no crystallites near the film surface [Fig. 10(a)], and the solvent-crystallized PEEKK has shown some aggregated crystals [big bright one in Fig. 10(b)] and a lot of condensed and homogeneously distributed smaller crystallites, which is contrast to that of PEEKK crystallized from annealing. It is interesting that the solvent-crystallized PEEKmK has much more condensed crystals scattering on the fibrillar part near the film surface, which has led PEEKmK to become crispy, the proofs of which has been shown in Figure 11(a). Meanwhile, the

very condense crystals help to form the intermediate layers and produce the difference of the mechanical properties between amorphous film and solvent-crystallized films of PAEKs samples. Figure 11(a) has shown the morphology on the near center part (or core) of PEEKmK films induced crystallization by the solvent of dichloroethane. From Figure 11(b) the toughened fibrillars are clearly seen, which is quite different from that shown in Figure 11(a).

The fractured patterns of these samples are quite different from the amorphous ones, the morphology of which has helped to explain that the solvent adopted has made films less toughened to some extent.

CONCLUSIONS

In the article, different PAEKs absorption and desorption behavior have been investigated. It has shown that the maximum equilibrium absorption (M_∞) depends on the experimental temperature. At 60°C, the M_∞ is 46% for PEEK, 50% for PEEKK, and 55% for PEKK, and the pseudo-Fickian diffusion coefficients show that the initial absorption rate is greatest at 60°C. Desorption experiment shows that the quantity of residual solvents depends on the desorption time and temperature and on the ketone content of polymer chains.

The ketone content or chain rigidity is related to the absorption experiment, and it has been shown that the solvent interacts with the polymer chains in the sorption process, which induces the polarization of polymer chain and the crystallization. The solvent-induced crystallization has produced a higher glassy transition (or relaxation) temperature than that crystallized in annealing state; but the solvent-crystallized samples often change their colors and become creeped and crispy. These will occur heavily when metaphenyl links are introduced, the main reason of which is probably the formation of the intermediate layers between the film surface exposed to the solvent and the film core area.

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