Structure, Crystallization, and Properties of Poly(aryl ether ether ketone ketone)s Containing *meta*-Phenyl Links and Their Copolymers

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SYNOPSIS

Poly(aryl ether ether ketone ketone)s (PEEKK) containing *meta*-phenyl links and their series of copolymers were synthesized and investigated by both X-ray and differential scanning calorimetry (DSC) methods. Results showed that the heat properties of this kind of copolymer depended greatly on the content of *meta*-phenyl links in the copolymer system, in which occurred the lowest melting point. Results from X-rays showed that PEEKK containing *meta*-phenyl links had no (111) crystal face diffraction. These proved that *meta*-phenyl links had introduced asymmetrical factors, which had produced poor crystal structure and difficulty in crystallization. Even so, the modification of PEEKK by introducing the *meta*-phenyl links improved the polymer composite performances, e.g., the copolymer M_2, which kept performances close to PEEKK but better than PEEK. DSC results of M_2 showed that its Avrami number (n) was 1.5 and its crystal grew fibrously from isothermal crystallization of the melting state, while for the nonisothermal crystallization from the melting state, n was 4.4 to the spherical crystal growth, and the activation energy (ΔE) of crystallization was 184 kJ/mol, which was less than the ΔE of 296 kJ/mol for PEEKK crystallized from the nonisothermal melting state. When M_2 was isothermally crystallized from the rubber state, its n was 2 to the disklike crystal growth, while its n was 4.6 to the spherulitic crystal growth for the nonisothermal crystallization state of melting. The isothermal crystallization process was different from the nonisothermal process in the crystal nucleation and growth for M_2. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Nowadays, poly(aryl ether ketone)s as high-performance engineering plastics have attracted much attention.[1-6] In fact, their excellent mechanical properties, good resistance to acidity and alkali, high thermal and thermooxidative stability have made them very practical in our daily life and in industry. Some of them have been commercialized, such as PEEK (commercial name APC-2). Unfortunately, some others such as PEEKK, with a higher melting point, have made them difficult to process. The very poor flowing properties and the too high processing temperature (over 430°C) for PEEKK was even difficult for the processing capacity of the ZSK 30P 9P Lab extruding machine (from Germany). Due to this, their utility was limited and some modifications were made on PEEKK.[3,6-8] Also, the random and/or block copolymers of PEEKK–PES were obtained.[4,7] Successful results have been made on such modifications. To further extend these modifications, this article presents PEEKK containing *meta*-phenyl links and its copolymers. From the literature, it is known that Blundell[9] reported the crystal structure of poly(ether ketone)s containing *meta*-phenyl links (called PEEKmK; $m = meta$ phenyl links). The crystal structure of PEEKmK also was thought to be an orthorhombic crystal system with the *Pbcn* *D2H* space group. In this article, our studies cover the synthesis, crystal structure, crystallization, and properties of PEEKK containing *meta*-phenyl links and its copolymers.


EXPERIMENTAL

Materials

1,4-Bi(*para*-benzoyl)benzene (mp 219-221°C) was produced by the LongJin Organic Factory, China; diphenyl sufone (mp 128-129°C) was from the Yan Xi Chemical Factory, China; hydroquinone A.R. (mp 175-177°C) was imported from Japan; and iso-phathaloyl cloride (IPC, mp 37-43°C) was from the Jiang Xi Medicine Factory for Agriculture, China.

The catalysts used were commercialized from the Tian Jin Reagent Factory, China. Fluorine benzene (bp 78-81°C) was produced in ChangChun, China.

### Synthesis of 1,3-Bi(*para*-fluorine benzoyl)benzene

1,3-Bi(*para*-fluorine benzoyl)benzene (1,3-BPFBB) was prepared by an electrophilic route with anhydrous aluminum chloride as the catalyst. Fluorine benzene reacted with IPC at a temperature less than 5°C as follows:
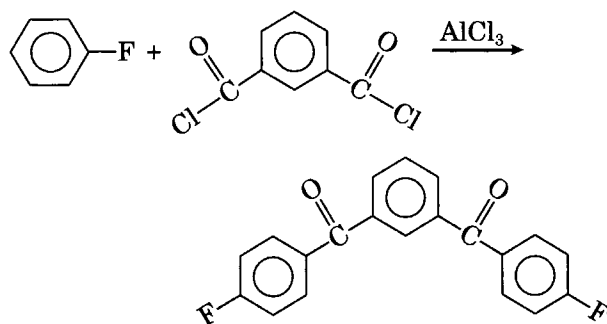
The product of 1,3-BPFBB was recrystallized from ethyl alcohol three times with a purity of 99%, yield of 82%, and mp of 180°C.

Synthesis of PEEKK–PEEKmK Copolymers

The homopolymers and copolymers containing *meta*-phenyl links were prepared by the reaction of 1,3-BPFBB and/or 1,4-BPFBB with the catalyst Na_2CO_3 and/or K_2CO_3 referring to the literature procedures[1,4-8]:
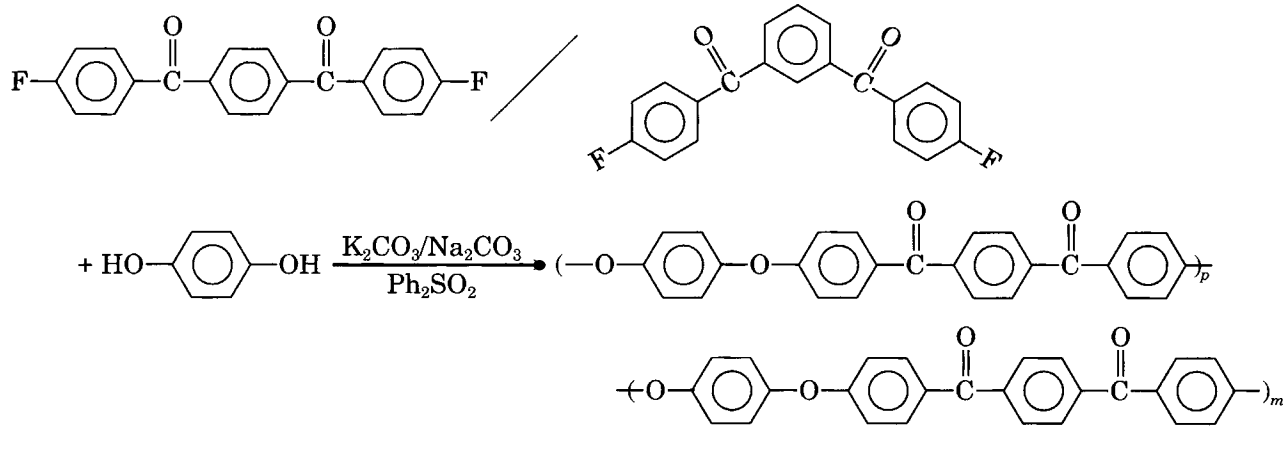
Sample Preparation

The powder of the samples from the above reactions were melted for 10 min at a temperature of 50°C above their melting points and molded into films with a thickness of 0.5-1.0 mm or so under the pressure of 10 MPa. Then, the films were quenched into amorphous samples in water. The amorphous samples were isothermally crystallized for different times at different temperatures or were put into a solvent of 1,2-dichlorine ethane to induce crystallization for 5 days (120 h).

Crystallization Dynamics

The methods of isothermal and nonisothermal crystallization dynamics, such as the Avrami equation,[10,11] was applied to describe the crystallization process of the above PEEKK–PEEKmK systems crystallized from both the rubber state (above the glassy state) and the melting state. These studies kept the sample weights fixed at 10.0 mg or so. In the isothermal crystallization process, samples were heated (or cooled) rapidly to the designated temperature to crystallize for 15 min from the rubber

or melting state. The crystallization curves of this process were recorded by the connected computer. But for the nonisothermal crystallization process, the samples were scanned by DSC at an increased (or reduced) rate (R) of 2.5, 5, 10, 20, and 40°C/min. The curves of this process were also recorded by the computer.

Measurement and Equipment

DSC measurements were made on DuPont TA-910 system with a N_2 gas flow, scanning rate of 10 or 20°C/min ranging from 50 to 450°C, and sample weight of 5–7.0 mg. The studies on crystallization dynamics were made on a Perkin-Elmer DSC-2C system. Thermogravimetric analysis (TG) was on an RG thermoelectronics balance of the Perkin-Elmer DSC with an increasing rate of 10°C/min, N_2 atmosphere at the flow rate of 40 mL/min, scanning scope ranging from 50 to 600°C, and sample weight of 5.0–7.00 mg. Infrared spectra were obtained on a Nicolet FTIR-5DX scanning from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1}. The hydrogen NMR spectra were measured on a Varian Unity-400 (MHz) with the mixture solvent of DMSO-d_6 and $CDCl_3$. The samples' inherent viscosities (η) of the copolymers were measured in a 0.1 wt % H_2SO_4 solution at 25°C.

RESULTS AND DISCUSSION

Results of Synthesis and Characterization

The IR spectra of the monomer 1,3-BPFBB was 1654.6 cm^{-1}, C$=$O stretching vibration of —Ar—CO—Ar— (Ar = phenylene); 1596.7 cm^{-1}, C$=$C stretching vibration of the aryl ring; 1501.9

cm^{-1}, C$=$C for asymmetric stretching vibration of the bisubstituted aryl ring; and 1155.2 cm^{-1}, C—F stretching vibration. The ^{1}H-NMR spectra of 1,3-BPFBB is shown below:
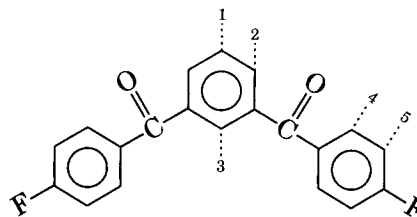
ANAL: Calcd: $\delta1$ = 7.60 ppm, $\delta2$ = 7.87 ppm, $\delta3$ = 8.44 ppm, $\delta4$ = 7.82 ppm, $\delta5$ = 7.12 ppm. Found: $\delta1$ = 7.65 ppm, $\delta2$ = 7.99 ppm, $\delta3$ = 8.13 ppm, $\delta4$ = 7.87 ppm, $\delta5$ = 7.18 ppm.

Also, both ^{13}C-NMR spectra of 1,3-BPFBB and 1,4-BPFBB were seen in our research. In the synthesis of the PEEKK–PEEKmK system, different molar ratios of 1,3-BPFBB to 1,4-BPFBB were taken to obtain the copolymers. But the sum of moles of 1,3-BPFBB and 1,4-BPFBB should be equal to that of hydroquinone, which would produce a high molecular weight according to the modified Carothers equation,[8] i.e., $Xn = (1 + r)/(1 - r)$, where Xn is the number-average degree of polymerization and r is the sum of the molar ratio of both 1,3-BPFBB and 1,4-BPFBB to hydroquinone. Results of the PEEKK–PEEKmK copolymers are in Table I and Figure 1.

The IR spectra of these copolymers were similar to those of PEEKK in that they all have a 1660 cm^{-1} stretching vibration for the C$=$O group, a 1600 cm^{-1} stretching vibration for the C$=$C bonds of the aryl ring, 1500 cm^{-1} for the C$=$C asymmetrical

Table I Physical Properties for PEEKK–PEEKmK Copolymers

| Sample	1,4-BPFBB (mol %)	1,3-BPFBB (mol %)	η_{iv} (dL/g)	T_m (°C)	T_g (°C)	T_g (Calcd)[a] (°C)
M_1	100	0	1.12	362	162	162
M_2	80	20	1.08	350	154	157
M_3	70	30	0.92	337	152	154
M_4	50	50	0.81	300	149	149
M_5	40	60	—	276	147	146
M_6	20	80	0.73	252	141	141
M_7	10	90	—	269	139	138
M_8	0	100	0.62	283	136	136

1,4-BPFBB, 1,4-bi (para-fluorine benzoyl)benzene. 1,3-BPFBB, 1,3-bi(para-fluorine benzoyl)benzene. η_{iv}, viscosity measured in concentrated H_2SO_4 (25°C).
[a] Calculated glassy transition temperature from Fox formula.
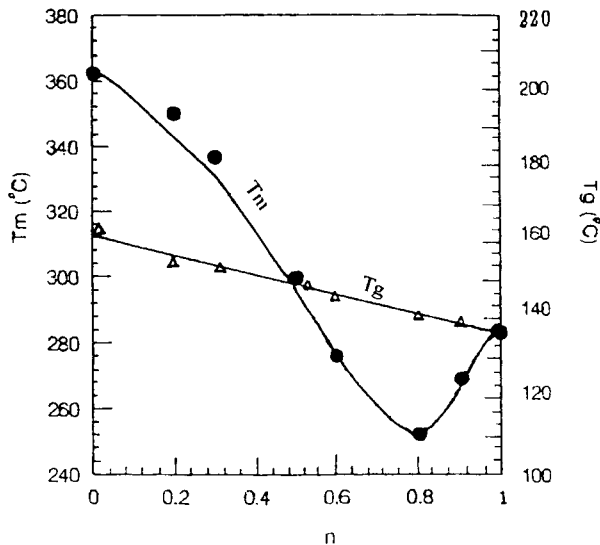
Figure 1   The relationship of heat properties (T_m, T_g) with the content of *meta*-phenyl links in PEEKK–PEEKmK copolymer system.

stretching vibration, and 1220 cm^{-1} for the ether group asymmetrical vibration of —Ar—O—Ar—, but there did exist a difference between PEEKK and PEEKK–PEEKmK copolymers, e.g., the vibration intensity at 931 and 1030 cm^{-1} were very strong, especially the former intensity which increased as the content of *meta*-phenyl links for the PEEKK–PEEKmK system increased, both of which were, we thought, characteristic peaks. From Table I and Figure 1, it is clearly seen that the heat properties of PEEKK–PEEKmK copolymers were influenced greatly by the *meta*-phenyl links, i.e., the melting point was reduced as the content of *meta*-phenyl links increased, and, finally, at the molar ratio of 20 for 1,4-BPFBB to 80 for 1,3-BPFBB, the lowest melting point was produced. This point is of significance to the processing technology because the copolymer at that point can be processed at 300°C or so; the only disadvantage of the sample at this point is that its melting point is so low as to limit its utility.
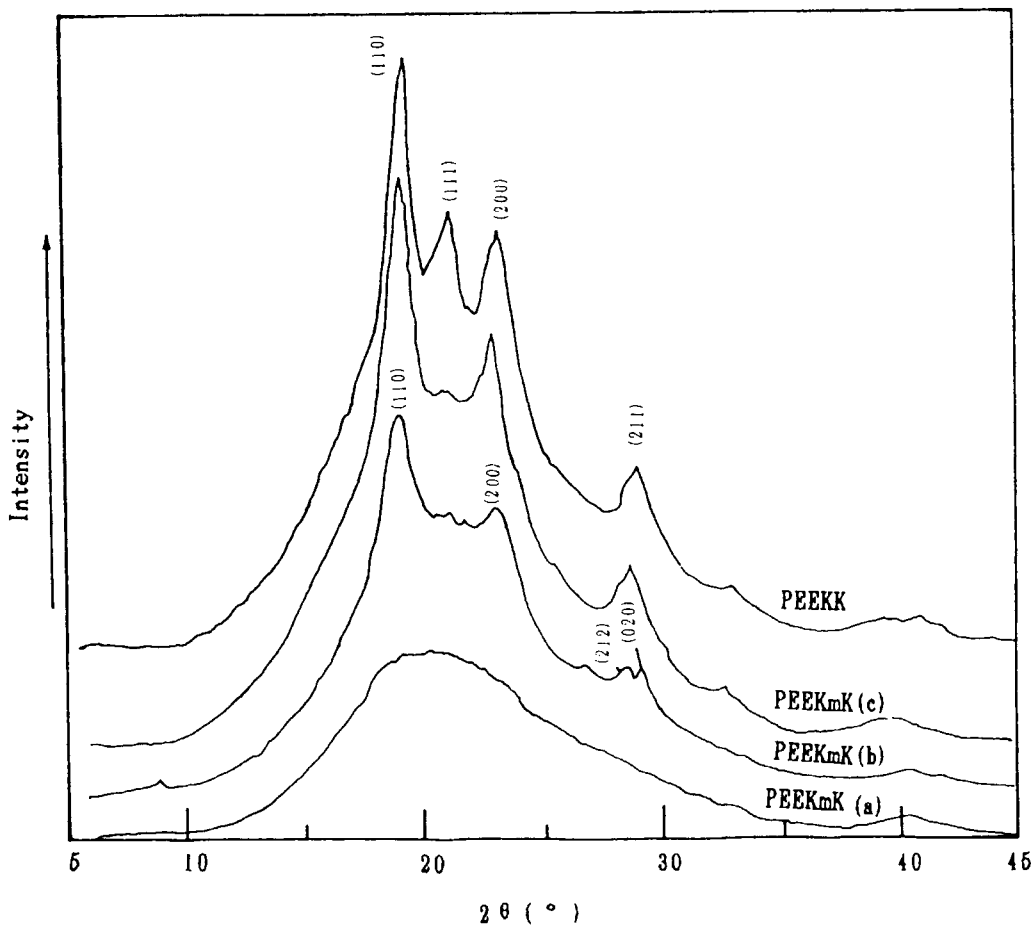

Figure 2   WAXD results for the (a) amorphous sample PEEKmK and PEEKmK (b) crystallized in 1,2-dichlorine ethane for 120 h and (c) crystallized at 240°C for 8 h from the rubber state and compared with the amorphous sample PEEKK crystallized at 240°C for 8 h.
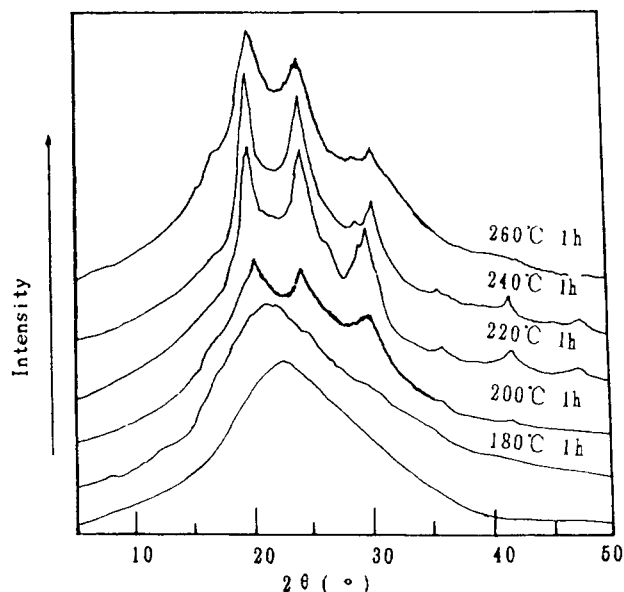
Figure 3 WAXD results of PEEKmK crystallized at different temperatures for 1 h from the rubber state.

From Table I and Figure 1, it is also known that the glassy transition reduced linearly as the content of the *meta*-phenyl links increased. The composition and the glassy transition approximately followed the formula of $1/T_g = M_A/T_{g_A} + M_B/T_{g_B}$,[4,6] where M_A and M_B stand for the molar percentage of compositions A and B, respectively, and T_{g_A} and T_{g_B}, for the glassy transition of compositions of A and B, respectively. These results still showed that the *meta*-phenyl links greatly influenced the properties of these copolymers; the reason for this resulted from that the *meta*-phenyl links introduced more disorder
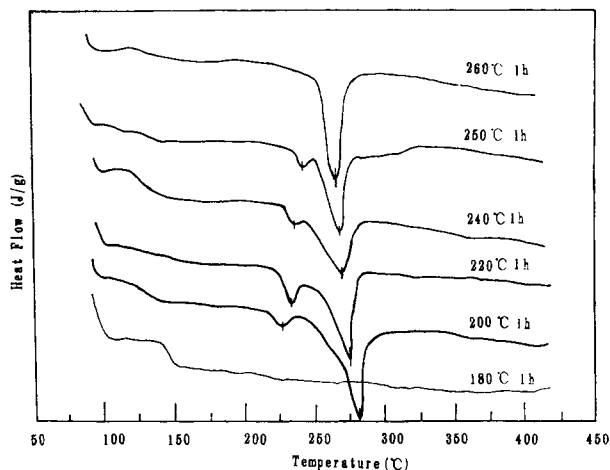
Figure 4 DSC scanning results for PEEKmK samples crystallized at different temperatures for 1 h from the rubber state (scanning rate: 20°C/min).

Table II Comparison of Properties of the Poly (aryl ether ketone) Family

	PEEK[5,6]	PEEKK	PEEKmK	M$_2$
T_m (°C)	334	362	283	350
T_g (°C)	143	162	137	154
T_d (°C)	> 520	> 520	561	552
T_{extr}	390	> 430	< 330	< 400

T_d, temperature at weight loss of 5%; T_{extr}, processing temperature for polymers in extrusion machine.

into the copolymer crystals and produced poor linearity in the copolymer molecular chains. The former caused the enthalpy (ΔH) to reduce and the latter was responsible for the increasing entropy (ΔS); both of these factors led to the decrease of the melting point (T_m) according to the formula $T_m = \Delta H/\Delta S$.

Crystal Structure for PEEKK Containing *meta*-Phenyl Links

The comparison results of between the amorphous PEEKmK and PEEKK samples by WAXD are shown in Figure 2. PEEKmK had three major characteristic peaks—(110), (200), and (212), which were similar to PEEKK which had four major diffraction peaks—(110), (111), (200), and (211). PEEKmK also kept nearly the same diffraction peaks when it was crystallized in a solvent of 1,2-dichlorine ethane [see Fig. 2(b)] or from the glassy state [see Fig. 2(c)]. According to the above diffraction comparisons, the PEEKmK crystal also had the orthorhombic *Pbcn* space group.[3,6,7] But a difference was seen in Figure 2 in that PEEKmK had no (111) face diffraction (peak position at 20.7°), which also revealed that incomplete crystals grew in the PEEKmK crystal. This was further proved by the PEEKmK crystallized at different temperatures for 1 h from the rubber state (see Fig. 3). According to the diffraction patterns above (also see Fig. 3), the d-spacings and parameters of crystals for PEEKmK and PEEKmK are given as follows:

For PEEKmK: d110 = 0.4786 nm,
d200 = 0.3874 nm,
d212 = 3.104 nm
a = 0.7747 nm,
b = 0.6086 nm,
c = 1.9869 nm.

For PEEKK: d110 = 0.4728 nm,
d111 = 0.4246 nm,
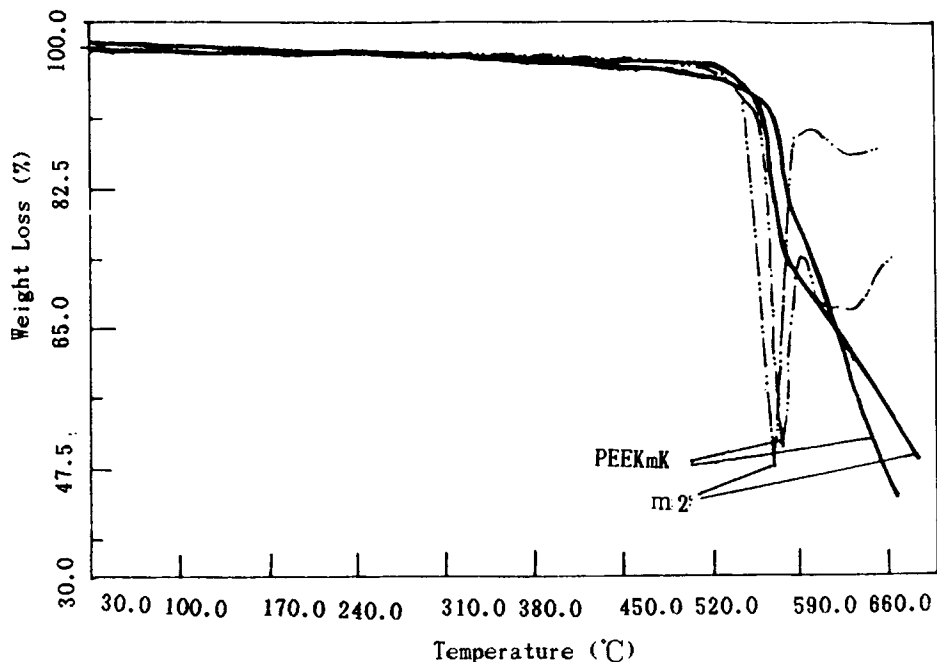
**Figure 5**   Weight loss curves for sample PEEKmK and M_2 subjected to thermogrametric analysis (scanning rate: 20°C/min).

$d200$ = 0.3831 nm,
$d211$ = 0.3067 nm
a = 0.779 nm,
b = 0.6025 nm,
c = 1.008 nm.

From these above results, it was thought that PEEKmK had four aryl rings in its crystal cell unit, while PEEKK had only two aryl rings in its repeated crystal unit.[3,7,13] This would also be seen in Figure 3 for WAXD results of PEEKmK crystallized at
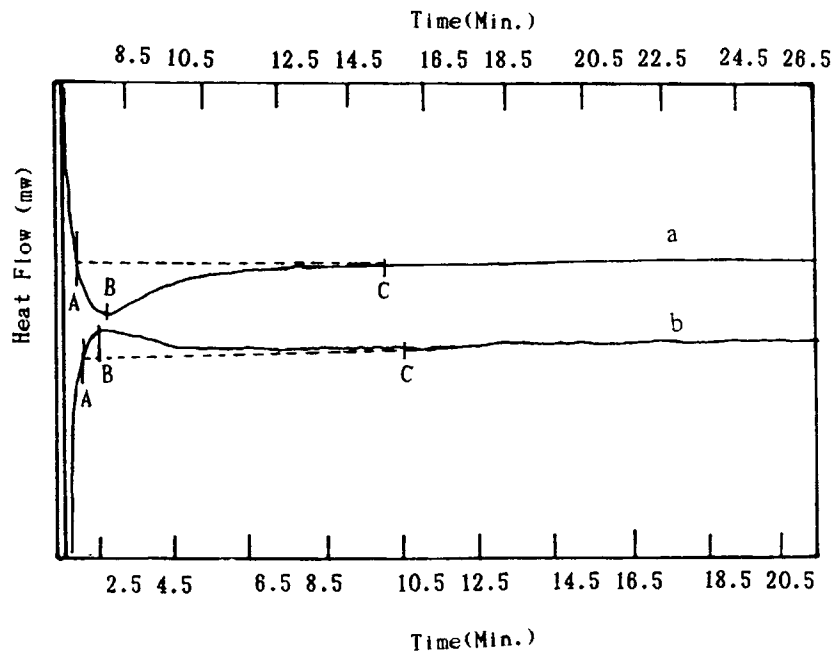
Figure 6   The DSC scanning curves for sample M_2 crystallized at different temperatures (a) from the rubber state and/or (b) from the melting state.
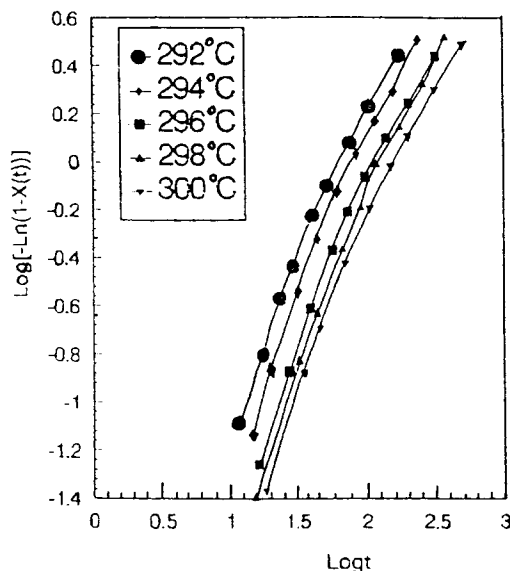
Figure 7 The Avrami plot for sample M_2 isothermally crystallized at different temperatures (292–300°C) from the melting state.

different temperatures for 1 h from rubber state, and corresponding to the samples in Figure 3, their DSC scanning results are also shown in Figure 4. It is seen that PEEKmK was more difficult to crystallize than was PEEKK or PEEK.[1-3,5-8]

Comparison of Polymer Properties

From Table I, all polymers containing *meta*-phenyl links had proper melting points, which would be practical in processing technology and, especially, M_2 still kept the high performances in both heat and processing properties. In fact, the extruding machine ZSK 30P9P had been used to test the processing properties of these polymers. The comparison results are listed in Table II. Also, the weight loss subjected to heat is seen in Figure 5, which shows the good thermostable properties for

PEEKmK and M_2. From Table II, it is shown that M_2 is still a good choice for high-performance plastics, which had attractive composite properties especially in processing temperatures.

Isothermal Crystallization Dynamics for M_2

For the isothermal crystallization process, the Avrami equation[10,11] is often used to described the crystallization dynamics of the polymers as below:

$$1 - X(t) = \exp(-kt^n) \tag{1}$$

where t is time; k, a constant of the crystallization dynamics rate; n, the Avrami number; and $X(t)$, the relative crystallization degree. Equation (1) can be changed into the following form:

$$\log[-\ln(1 - X(t)] = \log k + n \log t \tag{2}$$

In the experiment for the isothermal crystallization process, the curve of the heat of fusion–time was recorded by a computer, an example of which is shown in Figure 6(a) for M_2 isothermally crystallized at 298°C from the melt. In the isothermal crystallization process from the melt, different crystallization temperatures were recorded to obtain the Avrami plot of ($\log\{-\ln[X(t)]\}$) − log t shown in Figure 7.

It was apparent that all plots were close to a straight line. From these plots' extrapolation and their slopes, the values of log k and n were obtained; the results of these parameters are listed in Table III. It was found that the half-crystallization time ($t_{1/2}$) increased with the temperature of isothermal crystallization for M_2 crystallized from the melt, i.e., the crystallization rate ($1/t_{1/2}$) would be slowed as the crystallization temperature increases. The $t_{1/2}$ is given as below:

$$t_{1/2} = (\ln 2/k)^{1/n} \tag{3}$$

Table III Avrami Parameters for Sample M_2 Isothermally Crystallized from Melting State and Rubber State

C_{T_m} (°C)	n	K (S^{-n})	$t_{1/2}$ (s)	C_{T_g} (°C)	n	K (S^{-n})	$t_{1/2}$ (s)	$t_{1/2}^{-1}$ (s^{-1})
292	1.29	4.3×10^{-3}	51.4	173	1.81	4.4×10^{-6}	743.8	0.0013
294	1.31	2.8×10^{-3}	67.2	174	1.66	1.9×10^{-5}	560.1	0.0018
296	1.52	8.3×10^{-4}	83.6	175	1.99	7.8×10^{-6}	306.8	0.0033
298	1.53	6.6×10^{-4}	94.3	176	2.07	4.9×10^{-6}	307.8	0.00325
300	1.57	6.8×10^{-4}	82.4	177	2.10	7.4×10^{-6}	233.0	0.0043

C_{T_m}, isothermally crystallized from melting state; C_{T_g}, isothermally crystallized from glassy state; $t_{1/2}$, from $K = \ln 2/(t_{1/2})^{1/n}$.

Table IV Crystallization Rate Parameters for Sample M₂ at Different Increasing Rates (R) from Rubber State and at Different Reducing Rates (−R) from Melting State

R (°C/min)	T_{max} (°C)	t_{max} (s)	C_{max} (%)	$-R$ (°C/min)	T_{max} (°C)	t_{max} (s)	C_{max} (%)
2.5	183.0	175.2	46.3	−2.5	301.3	254.4	44.7
5.0	186.8	127.2	46.5	−5.0	296.8	158.4	45.2
10.0	191.0	70.8	52.1	−10.0	289.7	153.0	41.6
20.0	196.0	46.8	45.4	−20.0	281.9	78.0	46.0
40.0	201.3	24.0	45.4	−40.0	274.6	39.9	41.8

T_{max}, temperature at the maximum crystallization rate; t_{max} and C_{max}, time and relative crystallization degree; $[C_{max}(t)/C(\infty) \times 100\%]$ at T_{max}, respectively.

From the above crystallization process, it was obtained that n was 1.5, this corresponding to the fibrous crystal growth according to Morgan's theory.[14]

Nonisothermal Crystallization Process from the Melt

For this crystallization process, amorphous film of M₂ was melted at 380–390°C for 2 min and then scanned by DSC at the reducing rate ($R, R = -2.5$, −5.0, −10.0, −20.0, and −40.0°C/min). An example of these crystallization curves are also seen in Figure 6(b). Also, the equation to describe such a process was by eq. (4):

$$1 - C(t) = \exp(-Z_t t^n) \qquad (4)$$

Equation (4) can be changed into (5):

$$\log\{-\ln[1 - C(t)]\} = \log Z_t + n \log t \qquad (5)$$

where $C(t)$ is the relative crystallization degree, Z_t is constant of the crystallization rate, and n is still the Avrami number. According to the Avrami equation[10,11] and Jeziorny,[15] Z_t can be corrected as eq. (6):

$$\log Z_t = \log Z_c/R \qquad (6)$$

where R is the absolute value for an increasing or decreasing rate (°C/min). In this nonisothermal crystallization process, the temperature peak position at the maximum crystallization rate is expressed by T_{max}, at which the relative crystallization degree and crystallization time is described by eq. (7):

$$t_{max} = (T_{max} - T_A)/R \qquad (7)$$

where A is the crystallization starting point [see Fig. 6(a)]. From the recording values of $C(t)$ and t, and T_{max}, t_{max}, and C_{max} listed in Table IV, the Avrami plots were obtained as in Figure 8 for M₂ crystallized from the melting state. All results showed a quite good linear relationship between ($\log\{-\ln[1 - C(t)]\}$) and t. Also, the parameters obtained are listed in Table V, which shows that with increase of the reducing rate of R, Z_c and $t_{1/2}$ gradually decrease or the crystallization rate slows down. For this process, the Avrami number n was 4.4, corresponding to the spherical crystal growth according to Morgan's theory.[14] This crystallization process was quite different from that of the isothermal crystallization. It was thought that the high reducing rate of the tem-

Table V The Avrami Parameters for Sample M₂ from Nonisothermal Crystallization of the Melting State

R (°C/min)	T_{max} (°C)	Z_t (s⁻ⁿ)	n	Z_c (s⁻ⁿ)	$t_{1/2}$ (s)	$t_{1/2}^{-1}$ (s⁻¹)
−2.5	301.3	3×10^{-9}	3.70	3.9×10^{-4}	182.2	0.0055
−5.0	296.8	4.8×10^{-8}	3.23	0.034	164.7	0.0061
−10.0	289.7	2.2×10^{-11}	4.76	0.086	160.5	0.0063
−20.0	281.9	6.5×10^{-10}	4.76	0.347	78.8	0.127
−40.0	274.6	1×10^{-9}	5.44	0.596	42.2	0.0237

Z_t, rate constant for nonisothermal crystallization; Z_c, rate constant corrected by eq. (6).
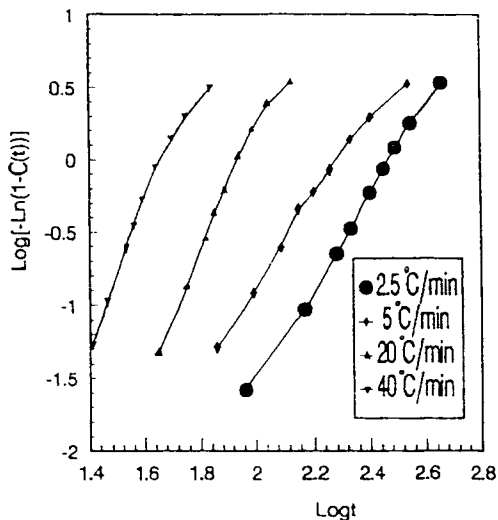
Figure 8 The Avrami plot for sample M_2 at different reducing rates ($R < 0$) of temperature from the melting state.

perature makes the crystal easy to form, which may greatly enhance the crystallization speed.
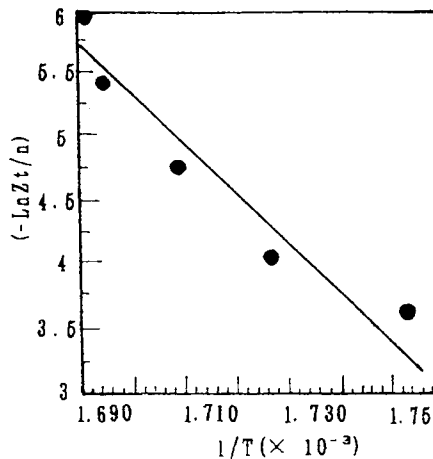
The Activation Energy

The activation energy for both isothermal and non-isothermal crystallization from the melting state is described by eq. (8):

$$(Z_t)^{1/n} = k_0 \exp[-\Delta E/(R_0 T)] \qquad (8)$$

where k_0 is the correction factor, and R_0, the constant of 8.31 J/mol K. Equation (8) was changed into the following form:
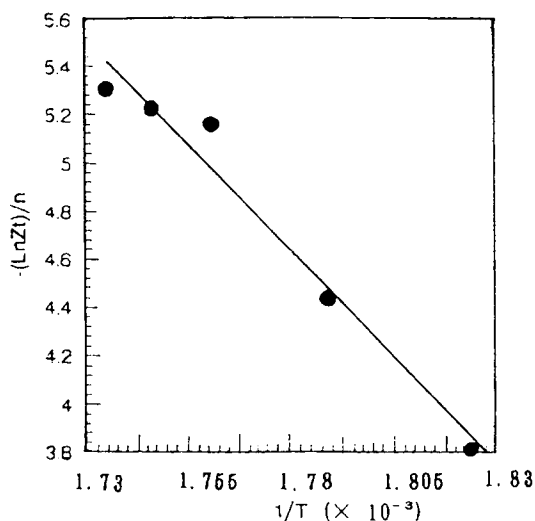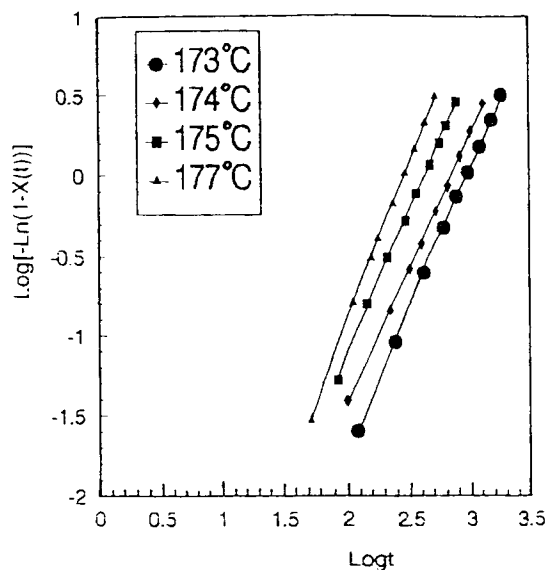

Figure 9 The $(-\ln k/n) - 1/T$ plot for sample M_2 crystallized from the nonisothermal melting state.

Figure 10 The $(-\ln k/n) - 1/T$ plot for sample PEEKK crystallized from the nonisothermal melting state.

$$-\ln(Z_t)/n = \ln k_0 + \Delta E/(R_0 T) \qquad (9)$$

The plot of $[-\ln(Z_t)/n] - 1/T$ is seen in Figure 9, and from the plot extrapolation method and the plot slope, $\Delta E/R_0 = 22.142 \times 10^3$ (K) was obtained, i.e., ΔE, is 184.0 kJ/mol for M_2 isothermally crystallized from the melting state. The same nonisothermal crystallization process is also adopted for PEEKK[7]; from its plot of $[-\ln(Z_t)/n] - 1/T$ shown in Figure 10, $\Delta E = 35.62 \times 10^3$ was obtained, so $\Delta E = 296.0$ kJ/mol for PEEKK. The above comparison results strongly show that the introduction of *meta*-phenyl

Figure 11 The Avrami plot for sample M_2 crystallized at different increasing rates ($R > 0$) of temperature from the rubber state.

Table VI   Avrami Parameters for Sample M_2 from Nonisothermal Crystallization of the Rubber State

R (°C)	T_{max} (°C)	Z_t (s^{-n})	n	Z_c (s^{-n})	$t_{1/2}$ (s)	$t_{1/2}^{-1}$ (s^{-1})
2.5	183.0	3.0×10^{-9}	3.69	3.9×10^{-4}	184.8	0.0054
5.0	186.8	8.7×10^{-12}	5.18	6.1×10^{-3}	127.2	0.0079
10.0	191.0	4.0×10^{-9}	4.41	0.145	73.8	0.0136
20.0	196.0	6.0×10^{-10}	5.42	0.346	47.0	0.0213
40.0	201.3	2.8×10^{-7}	4.54	0.686	25.6	0.0391

links probably reduced the molecular regulations and rigidity, leading to the reduction of ΔE.
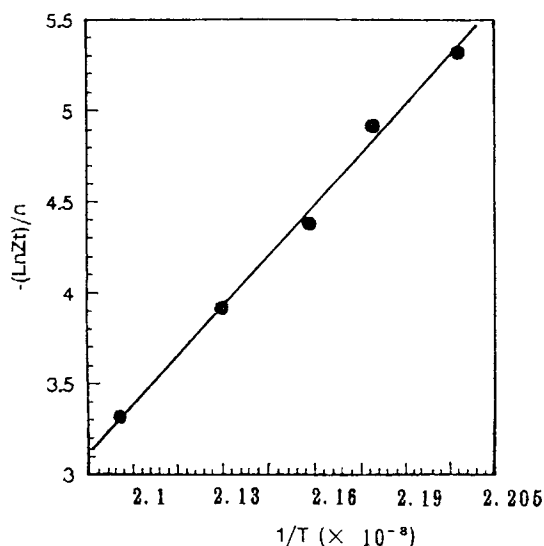
Crystallization from the Rubber State

When M_2 was isothermally crystallized from the rubber state, its amorphous film was scanned from the rubber state at different designated temperatures from 173 to 177°C. This process was also described by eq. (2), and its Avrami plots are shown in Figure 11, from which $n = 2.0$ and the $t_{1/2}$ listed in Table III were obtained. It is seen that the crystal was growing disklike.

Also, when M_2 was nonisothermally crystallized from the rubber state, the increasing rate (R, $R = 2.5$, 5.0, 10.0, 20.0, 40.0°C/min.) was changed to study the crystallization process. The relationship curves of the heat of fusion and time were similar to Figure 6(a). This crystallization process was also described by eq. (5). The T_{max}, C_{max}, and t_{max} calculated from eq. (7) is listed in Table VI, which shows that with

increase of R the T_{max} would increase. This was obviously opposite to its crystallization from the melting state (see Table V). But the relative crystallization degree kept nearly constant, which was similar to M_2 crystallized from the melting state. Based on the recording values of $C(t)$ and t, the Avrami plots are shown in Figure 12. From Figure 12, the results for the parameters of this nonisothermal crystallization process are listed in Table VI. From Table VI, it is shown that Z_c increased as the R increased, while $t_{1/2}$ reduced gradually. The Avrami number for this crystallization process was 4.4 to the spherical crystal growth for M_2, which was quite different from M_2 crystallized from the rubber state ($n = 2.0$). This further proved that the crystallization and crystal growth were quite different in the isothermal and nonisothermal crystallization processes either from the rubber or melting state.

CONCLUSIONS

The introduction of *meta*-phenyl links into the PEEKK molecular chain greatly influenced the properties as to their melting point, glassy transition, and molecular and crystal structure. Polymer PEEKK containing *meta*-phenyl links was difficult to crystallize compared with PEEKK itself. In the PEEKK-PEEKmK copolymer system, the glassy transition directly decreased with the content of the *meta*-phenyl links, but the melting point decreased with the content of *meta*-phenyl links at first, then decreased down to the lowest point at the content of 80% *meta*-phenyl links, and, lastly, the melting point increased with the content of *meta*-phenyl links. Results from this copolymer system also showed that the composite performances were enhanced to a practical extent, such as copolymer M_2, which had not only good properties but also composite properties as well. The study from the crystallization dynamics predicted that the way for crystals to grow for M_2 were greatly dependent on the crystallization process and starting state.

Figure 12 The Avrami plot for sample M_2 isothermally crystallized at different temperatures (173–177°C) from the rubber state.

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