

Physical Aging and Crystallization of Amorphous Poly(aryl ether ether ketone ketone)

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Received 16 July 1997; accepted 21 December 1997

ABSTRACT: Physical aging of poly(aryl ether ether ketone ketone) (PEEKK) was investigated. Heat flow responses were measured after annealing the amorphous samples that were obtained by quenching the melt into an ice-water bath at just below the glass transition temperature. Isothermal cold crystallization of the aged samples was carried out. The Avrami equation was used to determine the kinetic parameters, and the Avrami constant n is about 2. An Arrhenius form was used to evaluate the relaxation activation energy of physical aging and the transport activation energy of isothermal crystallization. The activation energy of physical aging was similar in magnitude to that observed for the temperature dependence of crystallization under conditions of transportation control. Results obtained were interpreted as purely kinetic effects associated with the glass formation process. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 907–912, 1998

Key words: physical aging; crystallization; PEEKK

INTRODUCTION

It is well known that changes in structure and material properties occur in amorphous polymers upon annealing at just below the glass transition temperature. This time-dependent behavior has been attributed to the nonequilibrium nature of the glassy state and is often referred to as physical aging. It is generally accepted that the change in dynamic mechanical properties arises from the densification that occurs in the glass on annealing. This relationship is usually expressed in terms of the free volume concept.¹ Physical aging is important in a narrow temperature range. Physical aging is characteristically accompanied

by a reduction in the level of free volume and the retardation of the molecular motion. Thus, a change in creep characteristics, an increased yield stress, and embrittlement of the polymer on impact are often experienced.² These features give rise to considerable interest in the physical aging phenomenon and the corresponding structural changes accompanying it. Recently, a number of experiments using different probes whose characteristics are sensitive to the glass transition or the free volume of their local environment have been reported in the literature.^{3–7}

Poly(aryl ether ketone)s (PEKs) are high-performance polymers used as engineering thermoplastics that have attracted much attention. Their excellent mechanical properties, solvent resistance, and high thermal stability have made them very practical in industry. Different PEKs have been developed by many large chemical corporations. Poly(aryl ether ether ketone ketone) (PEEKK) is a member of this PEKs family, which has a glass transition temperature of 150°C and a

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Contract grant sponsor: National Natural Science Foundation of China

Journal of Applied Polymer Science, Vol. 70, 907–912 (1998)

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CCC 0021-8995/98/050907-06

high melting temperature of about 360°C. The crystal structure of PEEKK has been reported by Zimmermann and Könnecke.⁸ A two-chain orthorhombic packing with $a = 0.775$ nm, $b = 0.600$ nm, and $c = 1.010$ nm and the $P_{bcn} - D_{2h}^{14}$ space group is one in which one chain is at the center of the ab projection in the unit cell and $4 \times \frac{1}{4}$ chains are at the corners. Chains in the crystals adopt an extended conformation with the phenylene rings alternating an angle of $\pm 37^\circ$ to the plane of the zigzag backbone. It has also been shown that the ether linkage and ketone groups are crystallographically equivalent. This crystal form is commonly observed in all members of the PEK family with minor dimension variations. The density of 1.385 g/cm³ and the heat of fusion of 124 J/g for the PEEKK perfect crystal were also determined by Zimmermann and Könnecke.⁸ Both crystalline and amorphous polymers can be obtained by a suitable choice of cooling rate from above the melting point. Accordingly, the polymers offer an excellent opportunity to study the effect of molecular structure on physical properties. It is especially interesting to determine whether there are simple temperature scaling laws for the rate of physical aging phenomena in such a system.

In this article we evaluate the role of physical aging in the cold crystallization of PEEKK. Thus, the effect associated with the glass formation process will be discussed.

EXPERIMENTAL

Samples used in this study were prepared from 1,4-bis(4'-fluorobenzoyl) benzene and hydroquinone. The inherent viscosity is 0.97 dL/g when measured in 98% H₂SO₄ (at 25°C, 0.01 g/10-mL concentration). The PEEKK powder was pressed at 400°C under 10 MPa pressure for 2 min, followed by quenching in an ice-water bath to form 1 mm thick amorphous sheets.

A Perkin-Elmer 7 series thermal analysis system (DSC-7) was used to measure the thermal properties of PEEKK. It was equipped with a Digital microprocessor that stored the calorimeter baseline as a function of temperature and automatically subtracted the calorimeter response to display heat flow as a function of temperature. The thermal response and the temperature were calibrated with the heat of fusion and the melting point of ultrapure indium and zinc. Over the range of thermal transition and over

limited temperature ranges, the heat capacity varied linearly with temperature. The extent of aging was determined using the method of Kemmish and Hay,³ which will be described in the following text. The crystallization of the aged samples was carried out by heating the aged glass rapidly to the crystallization temperature. Heat evolution rates were stored as a function of time and the data analyzed to determine initial points at which the sample equilibrated at the crystallization temperature. We assume that the extent of crystallinity that developed at time t , X_t , was

$$X_t = \int_0^t (dH_c/dt)dt / \int_0^\infty (dH_t/dt)dt \quad (1)$$

in which dH_c/dt is the heat evolution rate at time t due to crystallization. Figure 1 shows the heat flow change for those isothermal cold crystallizations just above the glass transition temperature (T_g).

RESULTS AND DISCUSSION

At first sight, ice-water quenched thin sheets of PEEKK were amorphous by WAXS, density, and DSC measurements. A minimum density of 1.266 g/cm³ at 25°C was obtained; and a maximum in the heat of crystallization of 24 J/g was observed at 175°C, which is immediately above the glass transition region. This heat of the maximum exotherm of crystallization corresponded with the development of 18% crystallinity as measured by density and X-ray diffraction. The maximum change in specific heat from the glass to liquid at the quenched glass transition, ΔC_p , was 0.275 J/g/K. These measurements were taken as an indication of the total amorphous nature of PEEKK and that a standard glass was formed equivalent to quenching into the ice-water bath. When amorphous PEEKK was heated at 20°C/min through the glass transition, it showed a well-defined crystallization exotherm in the 168–178°C region. Further heating resulted in the development of more crystallinity, and the subsequent melting above 360°C reflected this further crystallization.

Physical Aging of Amorphous PEEKK

The glass transition of PEEKK samples held at various temperatures that were close to but below

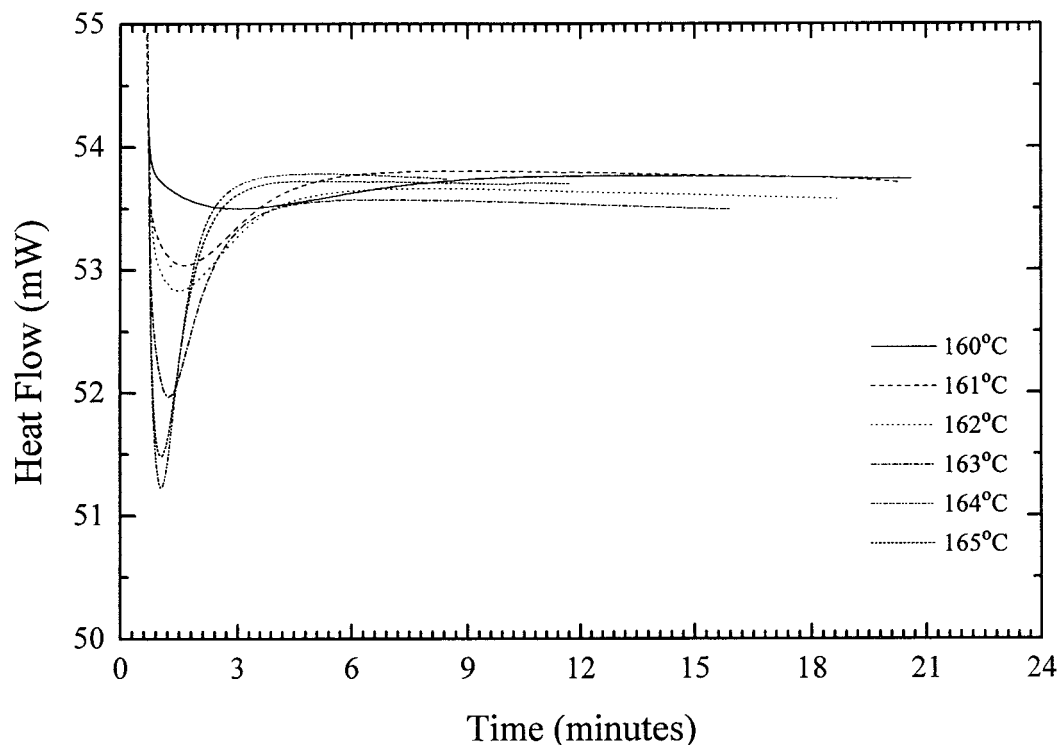


Figure 1 The time dependence of heat flow for the aged amorphous PEEKK.

the transition temperature exhibited marked endothermic peaks as observed from the DSC traces on heating through the glass transition. These thermograms of amorphous PEEKK subjected to aging from 110 to 140°C are shown in Figure 2. The endothermic peaks indicate the familiar overshoot of the glass transition temperature that are associated with and characteristic of physical aging. The relaxation enthalpy of the aged samples

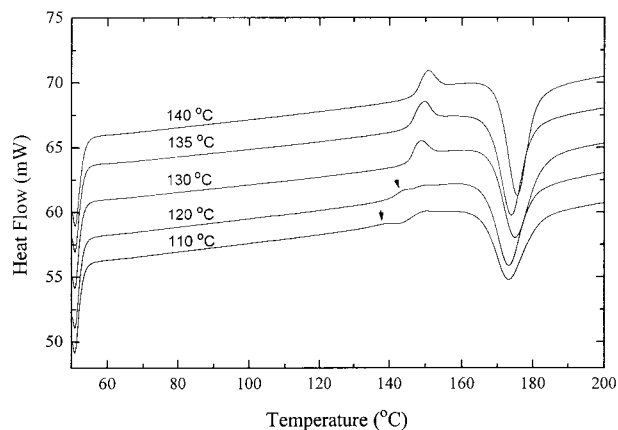


Figure 2 DSC curves of amorphous PEEKK samples subjected to physical aging at different temperatures.

is strongly dependent upon the aging temperature (T_a). As shown in Figure 3, the relaxation enthalpy of PEEKK decreased with the supercooling to T_g . This agrees with the chain segmental motion of macromolecules. Closer to the T_g , more energy used to transport may be obtained by the molecular chain.

The extent of the endothermic process increases logarithmically with time. The excess enthalpy de-

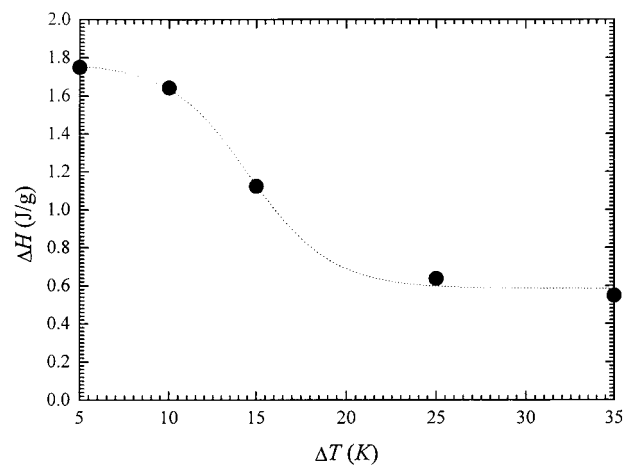


Figure 3 Dependence of the relaxation enthalpy (ΔH) of PEEKK on the supercooling to T_g .

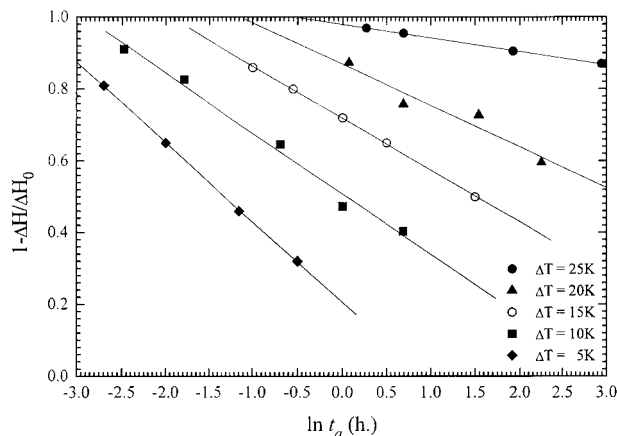


Figure 4 Ln–ln plots of the unaged extent with time, which shows the kinetic parameters of physical aging.

veloped at time t , ΔH_t , was measured from the difference between the standard quenched glass and the aged glass between two fixed temperatures as outlined by others.⁹ The maximum enthalpy change, ΔH_{\max} , is then

$$\Delta H_{\max} = \Delta C_p(T_g - T_a) = \Delta C_p \cdot \Delta T \quad (2)$$

corresponding to equilibrium having been achieved at the T_a . The extent of aging at time t is then $\Delta H_t/(\Delta C_p \cdot \Delta T)$ and the extent of the unaged portion $[1 - \Delta H_t/(\Delta C_p \cdot \Delta T)]$ decreased logarithmically with time at each aging temperature. Figure 4 represents the double logarithmic plot of the unaged extent and time. All data show good linearity with aging time. These were used to define a relaxation time, τ , as shown in the following equation:

$$(1 - \Delta H_t/(\Delta C_p \cdot \Delta T)) = A \ln(3t/2\tau) \quad (3)$$

Thus, the relaxation time during the aging process can be obtained from the slope and the intercept of the plot of $[1 - \Delta H_t/(\Delta C_p \cdot \Delta T)]$ versus $\ln t$. The relaxation time at a given value of supercooling was similar. This indicates that the shift in the T_g on aging results from the entropy term. This is in agreement with the theoretical predictions of Gibbs and DiMarzio.¹⁰

An Arrhenius form may be used to describe the relationship between the observed τ and the activation energy of aging (E_a) over the limited temperature range of the measurements (Table I). The plot of $\ln \tau$ versus $1/T$ is shown in Figure 5 and the corresponding E_a is 720 kJ/mol. This value is smaller than that reported by Kemmish

Table I Physical Aging Parameters of PEEKK

Supercooling (K)	Relaxation Time (h)	Activation Energy (kJ/mol)
5	3.78	720
10	30.56	
15	2.19×10^2	
20	2.94×10^3	
25	7.31×10^4	

and Hay³ and Ibadon.¹¹ The activation energy of aging of PEEK is 1.4 MJ/mol (determined by Kemmish and Hay); Ibadon reported a value of 2.14 MJ/mol for amorphous and semicrystalline isotactic polypropylene. In order to eliminate the probable and instrumental error, we repeated the physical aging experiments 3 times and found that the error was not beyond $\pm 5\%$. Compared with the other results reported by Kemmish and Hay³ and Ibadon,¹¹ it is clear that the chain rigidity takes an important role in the physical aging process of polymers.

Cold Crystallization of Aged PEEKK

A summary of crystallinity and time data for cold isothermal crystallization are listed in Table II. The time t_{\max} represents the time to reach the maximum rate of heat flow. Crystallization continuous until the time t_c , after which no further heat flow is observed. The relative amount of crystallinity is shown in Figure 6 for six crystallization temperatures. The Avrami equation as shown in eq. (4) can

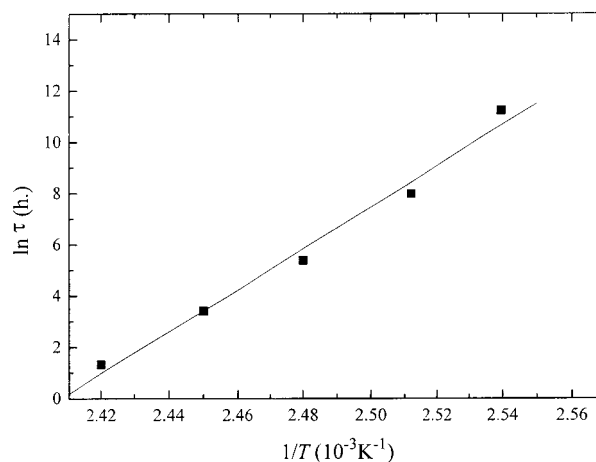


Figure 5 Plot of the $\ln \tau$ versus $(1/T)$, which gives the relaxation activation energy.

Table II Crystallization and Time Data for Isothermal Cold Crystallization from Aged Amorphous State of PEEKK

T_c (°C)	t_{\max} (min)	t_c (min)	ΔH_c (J/g)	X_c (%)	t'_{\max} (min)
160	2.28	9.39	7.2	6	3.08
161	1.17	6.48	12.0	10	1.37
162	1.03	5.19	10.4	8	1.31
163	0.73	4.86	12.9	10	0.93
164	0.53	3.54	14.2	11	0.67
165	0.52	3.24	12.4	10	0.70

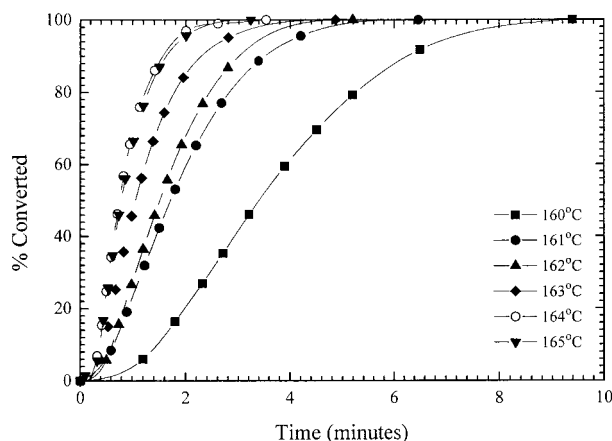
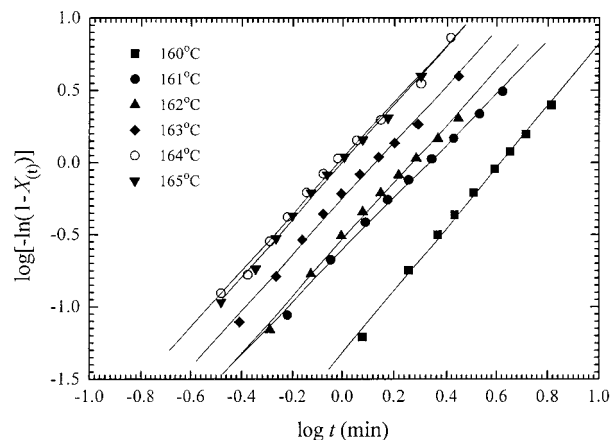
be used to describe the development of the relative crystallinity:

$$X_t = 1 - \exp(-kt^n) \quad (4a)$$

or

$$\ln(1 - X_t) = -kt^n \quad (4b)$$

where n is a constant whose value depends on the mechanism of nucleation and on the form of crystal growth and k is a constant containing the nucleation and growth parameters. Plots of $\log(-\ln(1 - X_t))$ versus $\log t$ are shown in Figure 7. Each curve shows a good linearity with time. From the fitting slopes and the intercepts of the linear regression for these experimental data, we can determine the Avrami parameters n and k from eq. (4). The values are listed in Table III.


Figure 6 The relative degree of crystallization for PEEKK as a function of crystallization time.

Figure 7 The Avrami plot for PEEKK isothermally crystallized at different temperatures from the aged glassy state.

The half-life, $t_{1/2}$, is an important parameter for discussion of the crystallization kinetics, which can be expressed as eq. (5):

$$t_{1/2} = (\ln 2 / \ln k)^{1/n} \quad (5)$$

The calculated $t_{1/2}$ values are also listed in Table III.

As shown above, we obtained the t_{\max} directly from the experimental curves. According to the theoretical background, t'_{\max} is the solution of $d^2X/dt^2 = 0$. Equation (6) can be used to calculate t'_{\max} in terms of the Avrami parameters n and k , obtaining the following expression:

$$t'_{\max} = ((n - 1) / nk)^{1/n} \quad (6)$$

In terms of crystal growth rates G , the temperature dependence is determined by the activation energy of mass transfer across the phase bound-

Table III Avrami Parameters for PEEKK Isothermally Crystallized from Aged Amorphous State

T_c (°C)	n	k (s^{-n})	$t_{1/2}$ (s)	E (kJ/mol)
160	2.14	0.08×10^{-2}	23.59	
161	1.81	0.42×10^{-2}	16.80	
162	1.96	0.48×10^{-2}	12.64	599.38
163	1.95	0.93×10^{-2}	9.12	
164	1.95	1.78×10^{-2}	6.54	
165	1.99	1.67×10^{-2}	6.50	

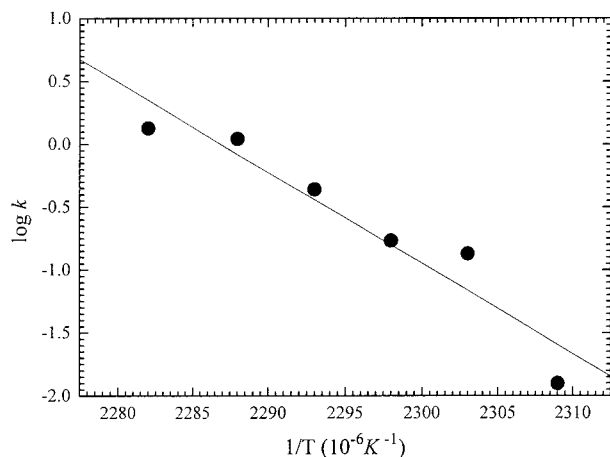


Figure 8 Arrhenius plot for the crystallization of PEEKK from the aged amorphous state.

ary ΔE and the free energy for the formation of the critical size nuclei ΔG_c^* ,

$$G = G_0 \exp(\Delta E/RT) \exp(-\Delta G_c^*/RT) \quad (7)$$

At high supercooling, crystal growth depends only upon ΔE , and a measure of ΔE was obtained from the overall crystallization rate constant k . According to an Arrhenius plot of $\log k$ against reciprocal temperature (see Fig. 8), an activation energy for mass transfer of 599 kJ/mol can be obtained.

Summarizing the results above, we obtained the Avrami index $n = 2$, which corresponds to lamellar growth by the heterogeneous nucleation of PEEKK. The activation energy of crystallization is very similar in magnitude to that of aging, which shows a kinetic nature of chain relaxation and crystallization from the glassy state. The crystallization energy obtained in this work is smaller than that reported by Chen et al.,¹² which implies that the nucleation may be reached by physical aging and that the barrier of crystallization is reduced through the prenucleation that accelerates the crystal growth process. By comparing our results to the results reported by Ibhaddon¹¹ and Kemmish and Hay,³ we concluded that the barrier of enthalpy recovery for polymers

through aging is effected by the rigidity of polymer chains.

CONCLUSION

Physical aging in PEEKK is accompanied by small aging peaks that are associated with the kinetic nature of glass formation. The extent of aging is related to the supercooling from the glass transition temperature and to the aging time. The activation energy of the aging process was similar in magnitude to that obtained for the temperature dependence of the cold crystallization for the aged samples. Physical aging improved the nucleation process and thus reduced the total barrier energy, which accelerated the growth rate of crystallization.

Financial support from the National Natural Science Foundation of China is gratefully acknowledged.

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