

# Physical Aging Behavior of 6F-PEEK and *m*-TPEEK Studied by Modulated Differential Scanning Calorimetry

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**ABSTRACT:** The aging behavior of two novel poly(ether ether ketone)s, 6F-PEEK and *m*-TPEEK, which were aged at 20°C below their glass transition temperatures, were studied by modulated differential scanning calorimetry (MDSC). The total, nonreversing heat flows and complex heat capacities of MDSC of the two kinds of materials were discussed. Similar total heat flows of MDSC to the ordinary DSC were achieved. They both grew in magnitude and moved to higher temperature as the aging time increased, which is associated with and characteristic of physical aging in heat flow. The complex specific heat capacity became sharper with aging time, which resulted in a higher  $T_{mid}$ . The relaxation time was calculated from the excess enthalpy. SAXS measurement added another proof that dense amorphous

phase formed in the metastable glass resulted from the rearrangement of molecular segments during aging. The increasing speed of dense amorphous phase fraction  $X_{DAP}$  of *m*-TPEEK was bigger than that of 6F-PEEK, which means the molecular segments of *m*-TPEEK are quicker to form dense amorphous phase than that of 6F-PEEK. This conclusion is consistent with their structures. The molecular chains of 6F-PEEK with bigger pendant group are more difficult to rearrange than those of *m*-TPEEK. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 312–317, 2005

**Key words:** poly(ether ketones); physical aging; MDSC; DSC; dense amorphous phase

## INTRODUCTION

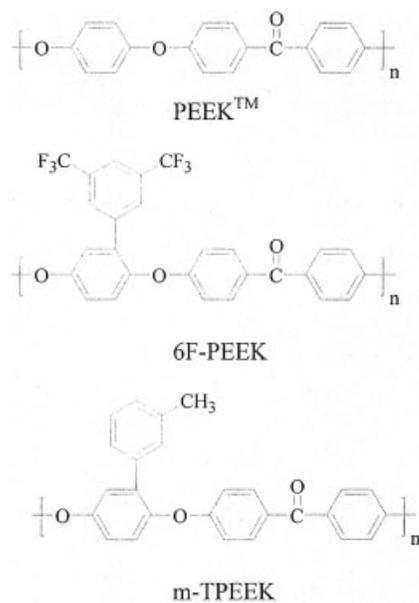
Aromatic poly(ether ether ketone)s (PEEKs) are a class of high-performance engineering thermoplastics known for their excellent combination of chemical, physical, and mechanical properties. This class of advanced materials has received considerable attention for potential applications in aerospace, automobile, electronics, and other high technology fields.<sup>1–3</sup> To improve the processability of conventional semicrystalline PEEK and develop the application in the optoelectronic field, novel soluble and amorphous 6F-PEEK and *m*-TPEEK were prepared by us recently.<sup>4,5</sup> The glass transition temperatures of 6F-PEEK and *m*-TPEEK are 149 and 148°C, respectively (Scheme 1). Because of their characteristic long-chain molecules, polymers are sensitive to the local environment, and the relaxation dynamics near  $T_g$  is essentially cooperative.<sup>6,7</sup> Changes in structure and material properties, such as specific volume, enthalpy, and entropy, occur in amorphous polymers upon annealing below and close to the glass transition temperature through the configurational rearrangement of polymer segments. Coupled with these changes, mechanical properties, dielectric properties, and microstructure of the sam-

ples also vary. This time-dependent behavior has been attributed to the nonequilibrium nature of the glassy state, which is often referred to as physical aging. The process of physical aging is a typical relaxation phenomenon.<sup>8–11</sup> Differential scanning calorimetry (DSC) and modulated differential scanning calorimetry (MDSC) have been extensively used to study the enthalpy relaxation process associated with the physical aging of polymers because they are convenient, sensitive, and highly reproducible.<sup>12–21</sup>

MDSC is a relatively new technique,<sup>22,23</sup> which adds a sample to a linear heating ramp of standard DSC with a superimposed low-frequency small-amplitude temperature oscillation resulting in a modulation in the heating profile. By deconvolution the total heat flow can be separated into a heat-capacity-related (reversing) component and a time-dependent nonreversing component. The reversing signal provides excellent resolution of the glass transition by separating the heat capacity from nonreversing processes. All exothermic behavior is detected only in the nonreversing heat flow signal. Therefore, MDSC is a good method for studying the glass transition process of polymers.

In this paper, the physical aging behaviors of 6F-PEEK and *m*-TPEEK were studied by MDSC. The effect of aging time on the parameters, such as total heat flows, nonreversing heat flows, reversing heat flows, complex heat capacities, and other parameters, are illustrated. The aging phenomena of these two kinds

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Scheme 1

of PEEKs were also explained from the view of molecular activity.

## EXPERIMENTAL PROCEDURES

### Materials

6F-PEEK and *m*-TPEEK were synthesized according to the procedures reported by us.<sup>4,5</sup> The powder samples were pressed into films at 300°C on a laboratory thermal press machine, followed by quenching films at room temperature to erase their previous thermal history. The film samples were removed to a temperature-controlled oven and annealed at 128°C for *m*-TPEEK and 129°C for 6F-PEEK, respectively. The annealing temperatures are 20°C below their own glass transition temperatures.

### SAXS measurements

SAXS measurements were performed on a Regaku X-ray diffractometer instrument, Rint 2500/LC2, with a camera length of 520 mm. The operating conditions were a voltage of 45 kV and a current of 60 mA. Ni-filtered CuK $\alpha$  ( $\lambda = 1.542 \text{ \AA}$ ) was used. The path between the samples and the detector was evacuated to reduce air scattering and absorption.

### DSC and MDSC measurements

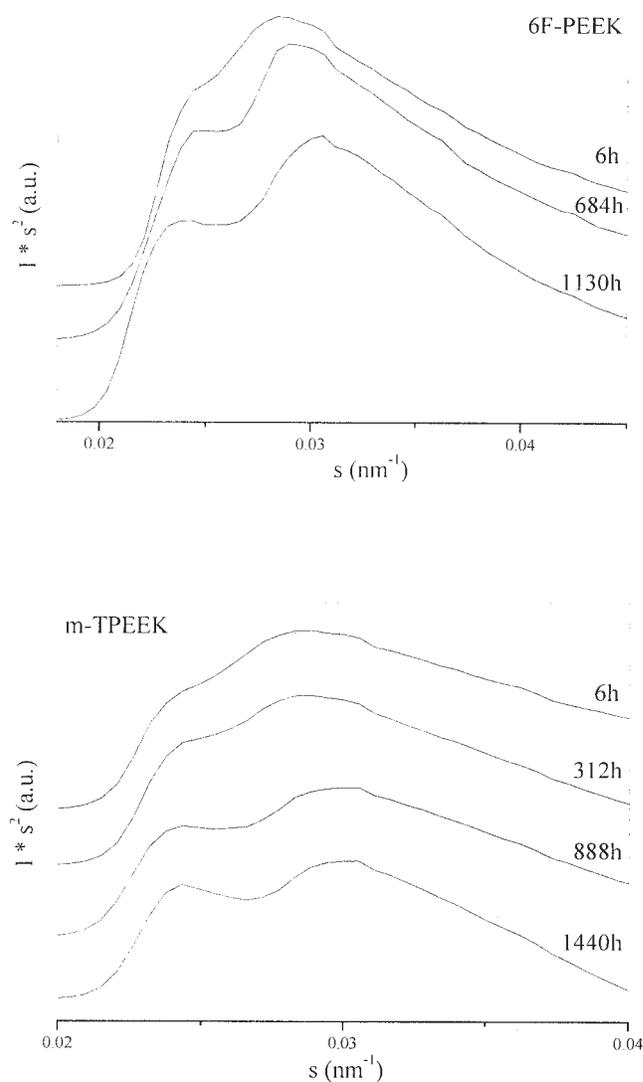
The DSC measurements were performed in a Mettler Toledo DSC 821<sup>e</sup> instrument with a scanning rate of 20°C/min. The MDSC measurements were performed with a TA 2920 MDSC. The conditions of the experiments utilized in MDSC were heating rate of 1°C/min with a modulation amplitude of 1°C and a period of

60 s. A N<sub>2</sub> purge was used for all measurements. The signal processing software was provided by the manufacturers. Careful baseline calibration is critical for these films and was performed regularly using indium. Careful calibration was also carried out by running a standard sapphire sample to obtain the accurate value of heat capacity.

## RESULTS AND DISCUSSION

### SAXS spectra

Figure 1 shows the SAXS spectra of 6F-PEEK and *m*-TPEEK annealed at 129 and 128°C for the times indicated against each curve, respectively. For the two kinds of materials, in addition to the main peak, there is a shoulder at lower  $s$  values, and its scattering intensity increased with aging. It shows that some



**Figure 1** SAXS plots of 6F-PEEK and *m*-TPEEK annealed at 129 and 128°C for the times indicated against each curve, respectively.

higher density phases formed during physical aging in the metastable glass.

### MDSC measurements

First, the heat capacity increase,  $\Delta C_p$ , was decided by the method reported by Cheng. et al.<sup>1</sup> In our MDSC measurements, the maximum differences ( $\Delta C_p$ ) in specific heat capacity between the glass and the liquid are  $0.216 \text{ J g}^{-1}\cdot\text{K}^{-1}$  for 6F-PEEK and  $0.259 \text{ J g}^{-1}\cdot\text{K}^{-1}$  for *m*-TPEEK, respectively.

For both kinds of materials, the experimental results agreed well with the predictions of an earlier theoretical model, such as the total heat flow and complex heat capacity.<sup>21</sup>

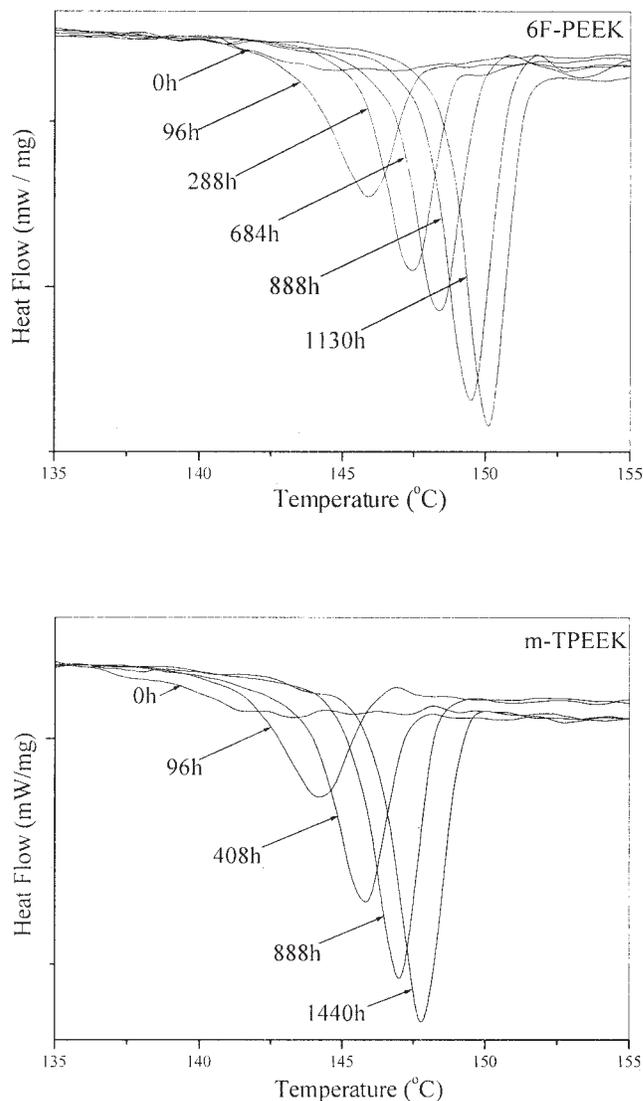
### Total heat flow and relaxation time $\tau$

Figure 2 shows the two families of curves of the total heat flow as a function of temperature for 6F-PEEK and *m*-TPEEK for different aging times, separately. It is obvious that the glass transitions of 6F-PEEK and *m*-TPEEK were characterized by marked endothermic peaks. The endothermic peaks indicate the familiar overshoot at the glass transition temperature, which grows in magnitude and moves to higher temperature as the aging time increases. This phenomenon is associated with and characteristic of physical aging in heat flow, as observed from the DSC trace when heating through their glass transition. It is a well-known effect displayed in conventional DSC scans.

Figure 3 shows the variations of total enthalpy with aging time of 6F-PEEK and *m*-TPEEK. The total enthalpy was calculated from the peak area using TA 2920 instrument software and the baselines before and after the glass transition, which are assumed to be linear in the region from room temperature to  $200^\circ\text{C}$ . There is a beginning point when the total heat flow curve began to depart from baseline and an ending point when the total heat flow curve began to superpose with another baseline. The total enthalpy is assumed to be the total area between these two points on the total heat flow curve. The experimental error is less than  $\pm 5\%$ . It is obvious that the enthalpies, in other words the extents of their endothermic process, of 6F-PEEK and *m*-TPEEK increase as a linear function of  $\ln t_a$  with different slope.

The excess enthalpy developed at aging time  $t$ ,  $\Delta H_t$ , could be obtained from the difference between the standard quenched glass and the aged glass between two fixed temperatures as outlined by others.<sup>10,24</sup> From the following scheme, we could get the maximum enthalpy change,  $\Delta H_{\max}$ , which corresponds to the equilibrium state that has been achieved at the aging temperature  $T_a$ .

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



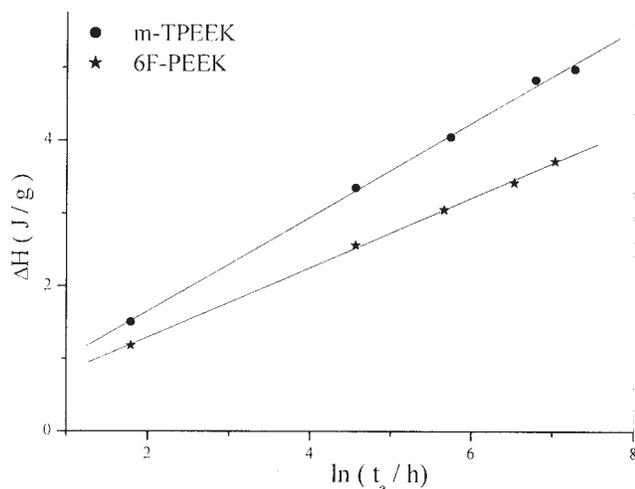
**Figure 2** Total heat flow versus temperature for 6F-PEEK and *m*-TPEEK annealed at  $129$  and  $128^\circ\text{C}$  for different times, respectively.

When the equilibrium amorphous glass is looked at as the reference state, the extent of physical aging at aging time  $t$  could be deduced as  $\Delta H_t/(\Delta C_p \Delta T)$  and the extent of the unaged part is  $[1 - \Delta H_t/(\Delta C_p \Delta T)]$ . The semi-logarithmic plots of the unaged extents with time of 6F-PEEK and *m*-TPEEK are shown in Figure 4, which gives the kinetic parameters of physical aging.

The relaxation time,  $\tau$ , was defined as<sup>25,26</sup>

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

We could get the relaxation time of 6F-PEEK and *m*-TPEEK during their aging process by the slope and the intercept of the semi-logarithmic curves of the unaged extents with aging time. After calculation, we found the  $\ln(\tau/h)$  of *m*-TPEEK to be 7.92 and that of 6F-PEEK to be 8.64. The relaxation time of 6F-PEEK is

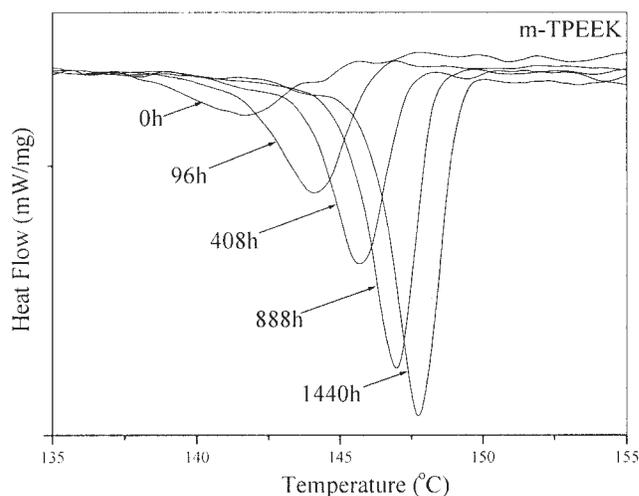
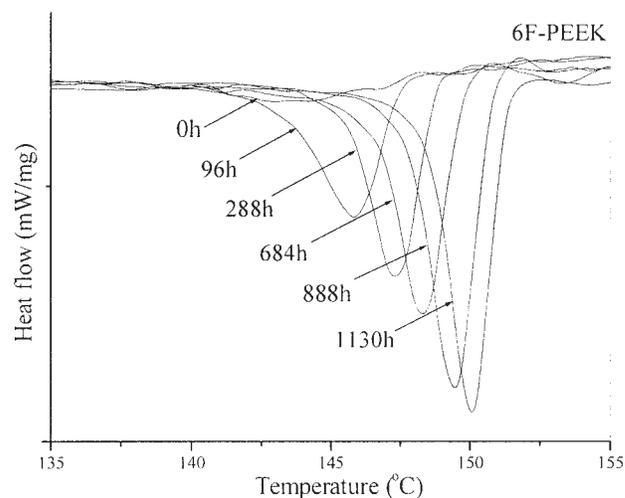


**Figure 3** Semi-logarithmic curve of the area under the total heat flow curves on aging time of 6F-PEEK and *m*-TPEEK annealed at 129 and 128°C.

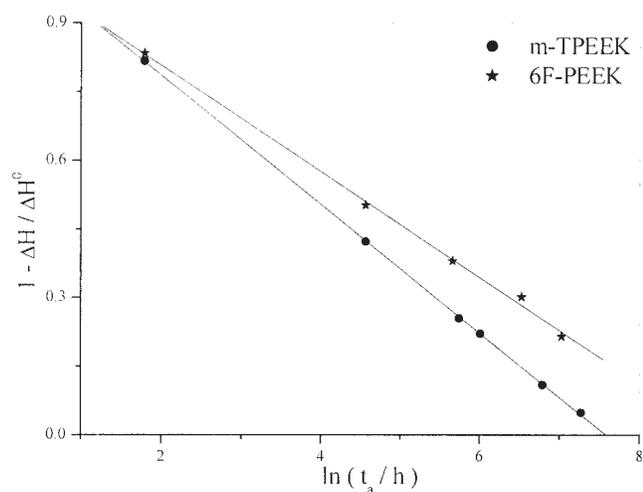
longer than that of *m*-TPEEK, which perhaps could be explained by the structure of the materials. 6F-PEEK has a comparable larger bulky side-chain [(3, 5-difluoromethyl)phenyl side group] than that of *m*-TPEEK [(3-methyl)phenyl side group]. Therefore, it needs more time to be relaxed.

#### Nonreversing heat flow and enthalpy loss

The curves of nonreversing heat flow as a function of temperature for 6F-PEEK and *m*-TPEEK for different aging times are shown in Figure 5. The overall effect of aging of both two kinds of materials is similar to that of total heat flow curves. There are also endothermic peak increases in magnitude and shifts to higher temperature with aging time.



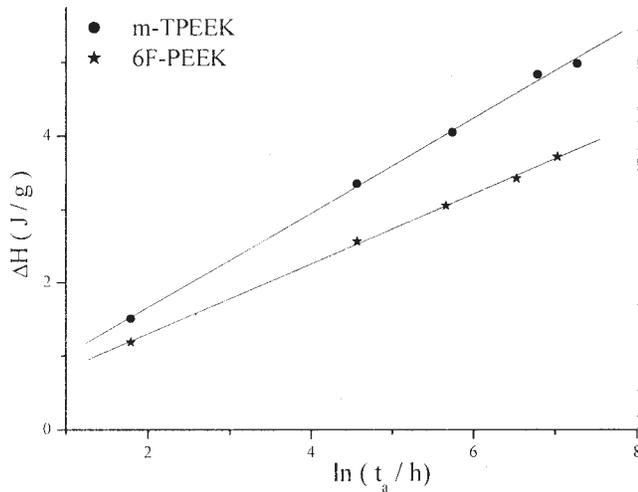
**Figure 5** Nonreversing heat flow versus temperature for 6F-PEEK and *m*-TPEEK annealed at 129 and 128°C for the times indicated against each curve, respectively.



**Figure 4** Semi-logarithmic plot of the unaged extent of 6F-PEEK and *m*-TPEEK with time.

Here, we just want to give a rough characterization of the variation of enthalpy loss after being aged. So, we adopt a proposed easy way<sup>12</sup> to calculate enthalpy loss during aging by the area under the so-called nonreversing heat flow, which argues that the difference between the reversible response of the sample and the total enthalpy change is a direct measure of enthalpy loss, although some authors<sup>13,16</sup> think it is not very exact, especially for long aging times.

Figure 6 shows the semi-logarithmic curves of relaxation enthalpy with time of 6F-PEEK and *m*-TPEEK. The relaxation enthalpy of the aged samples is strongly dependent upon the aging time. And we could also see that the curve of *m*-TPEEK has a bigger slope than that of 6F-PEEK, which means that the variation of relaxation enthalpy of *m*-TPEEK is more sensitive than that of 6F-PEEK to aging.



**Figure 6** Semi-logarithmic curve of the area under the nonreversing heat flow curves on aging time of 6F-PEEK and *m*-TPEEK annealed at 129 and 128°C.

### Complex specific heat capacity and dense amorphous phase fraction $X_{\text{DAP}}$

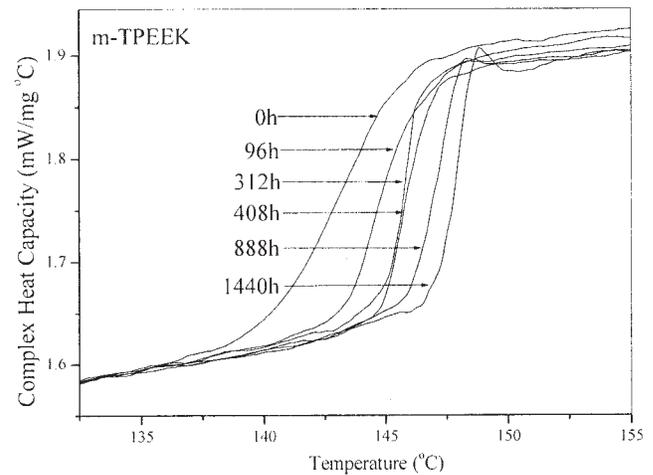
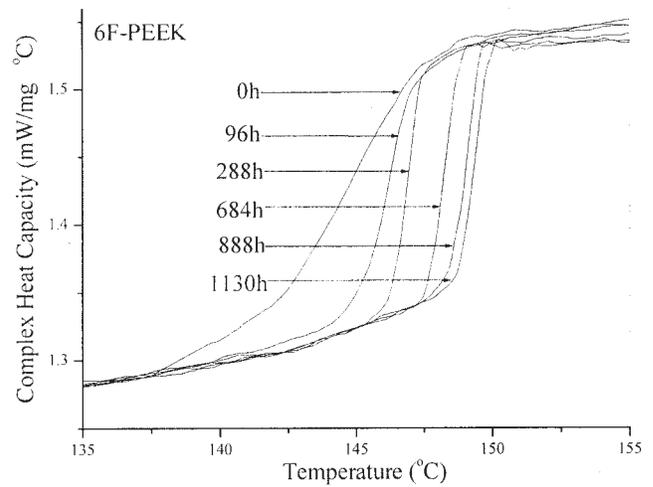
Figure 7 shows the effects of aging on the complex specific heat capacity for the aging times. The overall effect was that the transition became sharper as the annealing time increased by virtue of the onset moving toward higher temperatures and the endset remaining rather unaffected, which resulted in the midpoint temperature  $T_{\text{mid}}$  shifting toward higher temperatures upon aging.

For polymers, the specific heat capacity jump  $\Delta C_p$  is proportional to the amorphous weight fraction.<sup>1</sup> From our measurements of MDSC,  $\Delta C_p$  related to the glass transition decreased with aging, and its decreasing magnitude increased with aging time. On the other hand, from the SAXS scattering curves of 6F-PEEK and *m*-TPEEK, we could observe that, after aging, their scattering intensity in the  $Q$  range about from 0.0286 to 0.03 nm<sup>-1</sup> increased with aging time. Connected with the increasing enthalpy relaxation peak in the glass transition region with aging time and our SAXS measurements, we could conclude that higher density phases were introduced into the metastable glass during aging. So the form of "dense amorphous phase" (DAP) was introduced for the discussion of the aged materials.<sup>10,27,28</sup> The dense amorphous fraction,  $X_{\text{DAP}}$ , is defined as

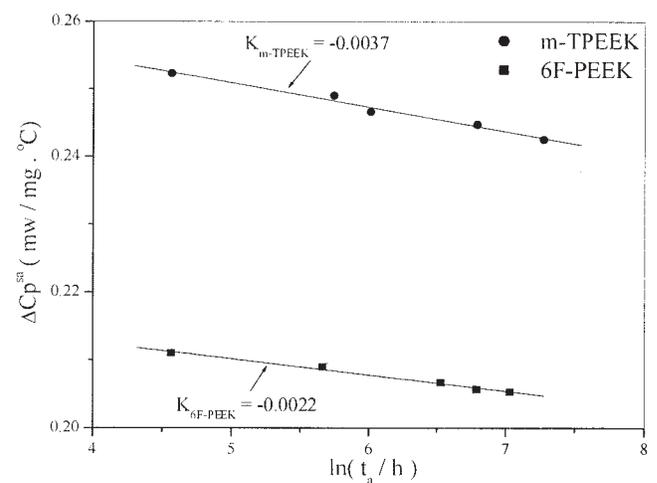
$$X_{\text{DAP}} = 1 - \Delta C_p^{\text{sa}} / \Delta C_p^{\text{a}}$$

where  $\Delta C_p^{\text{a}}$  is the specific heat jump at the glass transition temperature of a 100% amorphous sample and  $\Delta C_p^{\text{sa}}$  is defined as the specific heat jump of the aged sample.

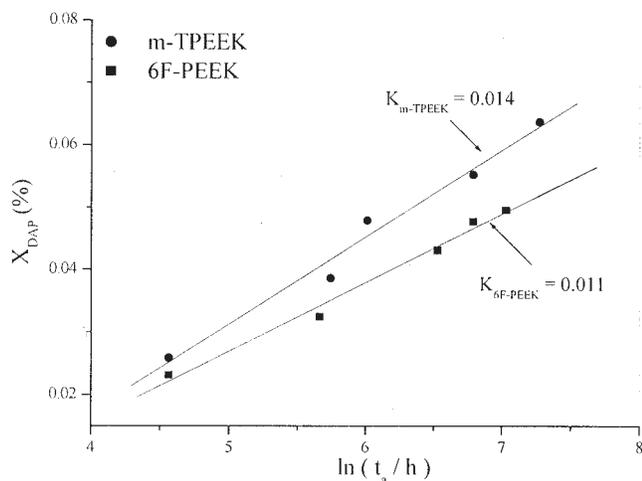
Figure 8 shows the semi-logarithmic plots of  $\Delta C_p^{\text{sa}}$  with aging times of 6F-PEEK and *m*-TPEEK. It could be observed the  $\Delta C_p^{\text{sa}}$  value of *m*-TPEEK is always



**Figure 7** Complex specific heat capacity as a function of temperature for 6F-PEEK and *m*-TPEEK annealed at 129 and 128°C for the times indicated against each curve, separately.



**Figure 8** Semi-logarithmic plots of the  $\Delta C_p^{\text{sa}}$  with aging times of 6F-PEEK and *m*-TPEEK.



**Figure 9** Semi-logarithmic plots of the  $X_{DAP}$  with aging time of 6F-PEEK and *m*-TPEEK.

bigger than that of 6F-PEEK. At the same time, the values of 6F-PEEK and *m*-TPEEK both decreased with the aging time, which means the value of  $X_{DAP}$  increased with aging time.

The semi-logarithmic plots of  $X_{DAP}$  with aging times of 6F-PEEK and *m*-TPEEK are shown in Figure 9. The data are compared with the anticipation: the dense amorphous fraction  $X_{DAP}$  of *m*-TPEEK and 6F-PEEK tended to increase with aging, which indicates that the microstructure of the samples did change upon physical aging even when the aging temperature was below their glass transition temperatures.

From Figure 8, we could also obtain the slopes of 6F-PEEK and *m*-TPEEK as  $-0.0037$  and  $-0.0022$ , separately. In Figure 9, the slopes of the curves of 6F-PEEK and *m*-TPEEK are 0.014 and 0.011, respectively. The slope values in Figure 9 indicate the speed of the dense amorphous phase's formation. In other word, it gives information about the rearrangement speed or the moving speed of molecular segments of the two kinds of materials. *m*-TPEEK has a greater slope than 6F-PEEK, which means that the molecular segments of *m*-TPEEK are a little easier to move.

On the other hand, from the structures of these two kinds of materials, we could also see that 6F-PEEK has a larger pendant group than *m*-TPEEK. There are (3, 5-difluoromethyl)phenyl side groups on the main chain of 6F-PEEK, while the side group of *m*-TPEEK is (3-methyl)phenyl, which is smaller in stereo volume than 6F-PEEK. The difference in the pendant group of these two kinds of materials perhaps results in the varied rearranging speed of molecular segments and also their different relaxing times.

## CONCLUSION

The physical aging behaviors of two novel kinds of PEEKs, 6F-PEEK and *m*-TPEEK, were studied by MDSC. The total heat flow of MDSC was similar to that of

conventional DSC. They both grew in magnitude and moved to higher temperature as the aging time increased, which is associated with and characteristic of physical aging in heat flow. The complex specific heat capacity became sharper with aging time, which resulted in higher  $T_{mid}$  with aging. The relaxation times of the two kinds of materials were calculated, and the relaxation time of 6F-PEEK is longer than that of *m*-TPEEK. On the other hand, there are dense amorphous fractions produced in the metastable glass that resulted from the rearrangement of molecular segments during aging. The variation speed of dense amorphous phase fraction  $X_{DAP}$  of *m*-TPEEK, which was derived from the  $\Delta C_p^{sa}$ , was larger than that of 6F-PEEK. This means that the molecular segments of *m*-TPEEK are quicker to rearrange into dense amorphous phase than that of 6F-PEEK. This conclusion is compared with their molecular structures. The molecular segments of 6F-PEEK with larger pendant group are more difficult to rearrange. Therefore they need longer relaxing times.

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