

AN INVESTIGATION ON THE LOW TEMPERATURE RELAXATION OF POLYETHERETHERKETONE*

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ABSTRACT

The temperature spectra of internal friction of polyetheretherketone (PEEK) are investigated from 130K to 250K with a multi-function torsion pendulum in the frequency range of 0.1 Hz to 5 Hz. A relaxation process, γ relaxation, appears in the temperature range of the measurement. Its relaxation time distribution in terms of a Gaussian distribution, and the relation between molecular motion mechanism and the distribution characteristic are discussed. The element process of γ relaxation is found to be a disordering one.

INTRODUCTION

The relaxation characteristic of polymer plays an important role in polymer science, which represents some structural features of polymer and is related to certain properties of polymer as well. A great number of researches have been done on polymeric relaxation process^[1-8], however, most of them tend to make qualitative description instead of quantitative study that helps to reveal the nature of relaxation. In this paper, the authors treat quantitatively the low temperature (130–250 K) relaxation in polyetheretherketone (PEEK) prepared under usual conditions with the theory of continuous distribution of relaxation time so as to determine some parameters of the relaxation process and discuss the relevant mechanism.

EXPERIMENTAL

Powdered PEEK kindly supplied by Jilin University was moulded into specimen strip with size of 60 mm $\times$ 5 mm $\times$ 1 mm and had the crystallinity of 36%. The internal friction measurements were carried out on an inverted torsion pendulum (MFIFA-1) made by Hefei Solid State Physics Institute of Academia Sinica. Temperature was increased automatically by step heating with a rate of 2K/min, and the time for temperature stabilization was 0.5 min. Internal friction was measured every 3K in the frequency order of 5, 1.357, 0.368 and 0.1Hz with forced vibration mode.

RESULTS AND DISCUSSION

The temperature T dependence of relative shear modulus G and internal friction

* Project supported by the National Natural Science Foundation of China

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Received September 9, 1991

Q^{-1} of PEEK is shown in Fig.1. It can be seen that there is an anelastic relaxation peak and relevant decrement of modulus in the range of 130 K to 250 K. Similar low temperature internal friction peak also can be observed in other polymers. As for the polymers without side groups, such relaxation is attributed to the local motion of some units in the main chain in general, even though its actual molecular mechanism is rather complicated. And the low temperature relaxation in PEEK used to be named γ relaxation and interpreted as due to the motion of aromatic rings, i.e. phenylene units^[4,5] on the basis of the study on low temperature relaxation behaviour of the polymers with similar segments such as polyarylsulfone (PAS), polyarylethersulfone (PES) and so on^[6,7].

In order to determine the peak height Q_m^{-1} and peak temperature T_m accurately, after the systematic background internal friction having been subtracted from the experimental curve, curve fit procedure would be necessary. As a result of tests, the following fifth order polynomial is found to fit the experimental data quite well:

$$Q^{-1} = \sum_{i=0}^5 a_i (T - 273.15)^i \quad (1)$$

where a_i is a coefficient independent of temperature and temperature T is in Kelvin scale. Thus the γ relaxation in PEEK can be described with the very polynomial. Once every a_i is determined, Q_m^{-1} and T_m can be derived easily.

According to the relaxation theory^[8-10], the dependence of oscillation frequency f on relaxation peak temperature T_m can be written in the form

$$f = f_0 e^{-H/kT_m} \quad (2)$$

where f_0 is the molecular characteristic frequency, H activation enthalpy, and k Boltzman constant. By making plots of $\ln f$ against T_m^{-1} , the activation enthalpy associated with γ relaxation is obtained with least-square method, i.e. $H = 48.9 \text{ kJ/mol}$. Because there are two phenylene units on the main chain: $-\text{CO}-\text{C}_6\text{H}_4-\text{O}-$ and $-\text{O}-\text{C}_6\text{H}_4-\text{O}-$, and moreover, every phenylene unit could move in various modes, thus the calculated activation enthalpy represents just an apparent value of statistical average in fact, although γ relaxation in PEEK has been assigned to the local motion of phenylene units.

The experimental data indicate that γ relaxation peak of PEEK broadens with increasing frequency, which suggests that it should not be associated with a single relaxation process but possesses a certain relaxation time distribution. Generally, the continuous distribution function $\Psi(z)$ of anelastic relaxation time τ is considered to follow a Gaussian distribution:

$$\Psi(z) = \beta^{-1} \pi^{1/2} \exp[-(z/\beta)^2] \quad (3)$$

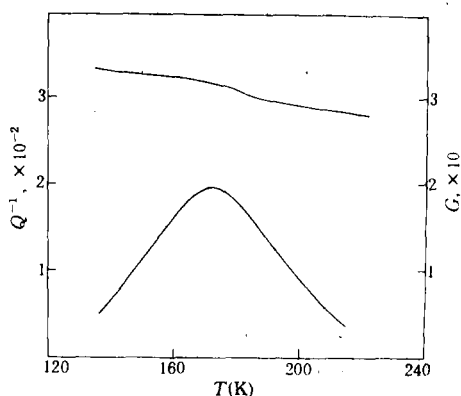


Fig.1 The temperature T dependence of relative shear modulus G and internal friction Q^{-1} of PEEK (frequency $f = 1.357 \text{ Hz}$)

with

$$z = \ln \tau / \tau_m \quad (3-a)$$

where τ_m is the most probable relaxation time and can be obtained from the peak where $\omega \tau_m = 1$, and β is the half-width of the distribution at the point where $\Psi(z)$ falls to $1/e$ of its maximum value $\Psi(0)$. The relaxation time distribution can be determined so long as the value of β is fixed. The treatment for determining β from temperature spectrum of internal friction has been set up by Seeger and coworkers^[10], the crux of which lies in a correction to temperature axis on the basis of Arrhenius equation, i.e. a variable x' is introduced:

$$x' = (1/T - 1/T_m) H/k \quad (4)$$

And then a normalized internal friction Q^{-1}/Q_m^{-1} vs. x' curve can be drawn instead of the temperature spectrum. By comparing it with a set of normalized $f_2(x', \beta)/f_2(0, \beta)$ vs. x' standard curves of various β (where $f_2(x', \beta)$ is a physical quantity in proportion to internal friction)^[11], and finding out a pair of coincident curves, one can confirm that the relaxation time distribution of the relaxation process follows Gaussian distribution and the value of β corresponding to the standard curve expresses the half-width of the unknown relaxation time distribution.

After the experimental data of γ relaxation in PEEK are treated according to the above-mentioned method, all the normalized Q^{-1}/Q_m^{-1} vs. x' curves measured at the four frequencies turn out to be coincident with the standard curve with $\beta = 2.75$ (refer to Fig. 2). That is to say, the relaxation times of γ relaxation in PEEK consist of a continuous distribution as shown in equation (3) with half-width 2.75.

The identity of β with one another corresponding to the relaxation time distribution measured under different frequencies means that the distribution of γ relaxation times of PEEK is entirely due to the existence of a distribution in τ_0 —the molecular characteristic relaxation time, i.e. the distinct phenylene units and their

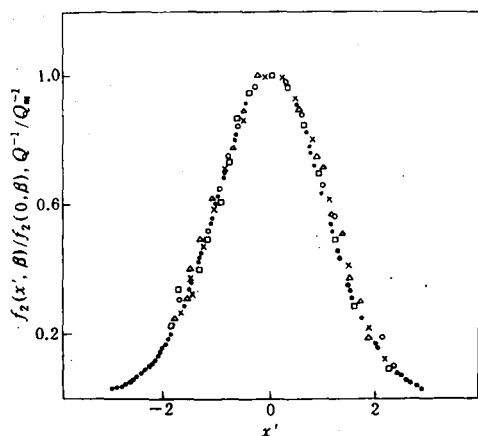


Fig. 2 Comparison of Q^{-1}/Q_m^{-1} vs. x' curves with the normalized $f_2(x', \beta)/f_2(0, \beta)$ vs. x' dotted curve with $\beta = 2.75$; ($\square$) 5 Hz; (Δ) 1.357 Hz; ($\times$) 0.368 Hz; ($\circ$) 0.1 Hz

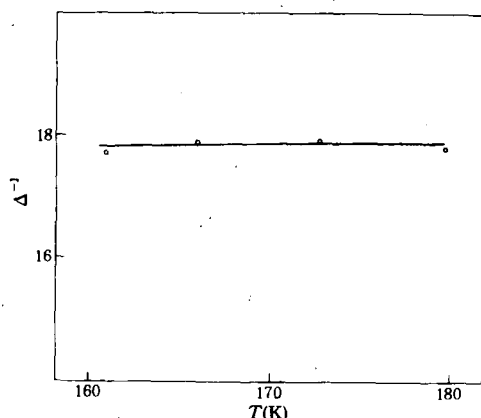


Fig. 3 The inverse relaxation strength Δ^{-1} as a function of peak temperature T_m

various modes of motion are concerned.

The relaxation strength Δ , which describes relaxation process quantitatively, is defined by:

$$\Delta = Q_m^{-1} / f_2(0, \beta) \quad (5)$$

By means of the internal friction peak height Q_m^{-1} and $f_2(0, \beta)$ for a series of values of β ($\beta = 2.75$ in the case of γ relaxation in PEEK) tabulated in Ref. 11, the relevant relaxation strength Δ can be obtained from equation (5). According to the relaxation theory^[9], if interactions exist between relaxation units or within a special ordering configuration of relaxation units, the temperature dependence of relaxation strength Δ will be analogous to the Curie-Weiss law: $\Delta \propto (T - T_c')^{-1}$, where T_c' is the critical temperature for a "self-induced" ordering. The interaction energy E_1 can thus be obtained from T_c' : $E_1 = kT_c'$. In addition, for relaxation involving an ordering process, the relaxation strength decreases as the temperature increases, and for relaxation involving a disordering process, the relaxation strength increases as the temperature increases or is independent of temperature. Fig. 3 exhibited a plot of Δ^{-1} against T_m . It is evident that the straight line does not intersect temperature axis above 0 K. Hence, it can be deduced that the element process of γ relaxation in PEEK is a disordering one. In other words, there is no limit of specific direction or position to the mode of motion of the phenylene units on PEEK main chain.

CONCLUSIONS

1. The γ relaxation of PEEK results from a continuous summation of the vibration of the phenylene units in multiple frequencies with an invariable activation enthalpy (48.9 kJ/mol).

2) The relaxation time distribution of the γ relaxation of PEEK can be described by a Gaussian distribution function, the half-width of which is 2.75.

3. Depending upon the structure of PEEK chain, the element process of the γ relaxation of PEEK is a disordering process.

In addition, by means of the temperature dependence of β and Δ , not only further information about the micromechanism responsible for the γ relaxation of PEEK and the influence of crystallinity, but also the details of interaction between different components at molecular level of the blends with PEEK can be obtained. The paper on these subjects will be submitted for publication in the near future.

Keywords:

Polyetheretherketone; γ relaxation; Gaussian distribution; Relaxation strength; Disorder element process.

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