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REVIEW ARTICLE

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Transition of polymers from rubbery elastic state to fluid state

Abstract On increasing the temperature of a polymer, the transition of the polymer from a rubbery elastic state to a fluid state could occur. The transition temperature is termed the fluid temperature of the polymer, T_f, which has a direct relationship with the polymer molecular weight. As one of polymer parameters, T_f is as important as the glass transition temperature of a polymer, T_g. Moreover, special attention to T_f should be paid for polymer processing. In research on the transition of a polymer from a rubbery elastic state to a fluid state, the concept of T_f would be more reasonable and more effective than the concept of $T_{l,l}$ because it is neglected in the concept of $T_{l,l}$ in that the molecular weight of a polymer may affect the transition of the polymer. In this paper the discussion on the fluid temperature involves the characters of polymers, such as the deformation–temperature curve, the temperature range of the rubbery state and the shear viscosity of polymer melt. From the viewpoint of the cohesional state of polymers, the transition of a polymer from a rubbery elastic state to a fluid state responds to destruction and construction of the cohesional entanglement network in the polymer. The relaxing network of polymer melt would be worthy to be considered as an object of study.

Keywords polymer, rubbery elastic state, fluid state, fluid transition temperature T_f, cohesional entanglement network

For an amorphous polymer in its solid state, the cohesional entanglements of molecules would be disrupted by heating or by the effect of solvent. The development of the disruption leads the amorphous polymer in a glass state to transition to its rubbery state, and then to its fluid state [1, 2]. The fluid state of a polymer used to be called “flow state” or “viscous flow state”. As a scientific term of a polymer state, the “fluid state” is more desirable than the “flow state” or the “viscous flow state” because “flow” means a physical phenomenon caused by the action of an external force, and there is no flow without any external force. T_g is called the glass transition temperature of a polymer, at which an amorphous polymer in a glass state changes to a rubbery state by heating up or a non-crystallizable polymer melt changes to a glass state from a rubbery elastic state by cooling down. T_g is an important parameter and it is a very familiar concept to polymer researchers. In another case, a crystalline polymer being heated would reach its melting point, T_m, at which the crystallites of the polymer break up and melt. The polymer melt may be in a rubbery elastic state or in a fluid state, and it depends on the molecular weight of the polymer and the temperature difference between the T_m and the T_g of the polymer in its amorphous state.

On increasing the temperature of a polymer, the transition from a rubbery elastic state to a fluid state could occur.

The transition temperature may be termed fluid temperature, T_f, to which there were quite frequent referrals in the former Soviet Union's literature. In Western literature the discussion about fluid temperature, T_f, can be rarely seen, and even then, it is a question that whether it is necessary to introduce fluid temperature, T_f, into polymer research as one of the important parameters of a polymer. The question is only based on the value that T_f possesses conditionally. Of course, T_f is a conditional parameter. It can be explained by taking a piece of erect glass used for windowpanes as a case in point. The window glass made of silicate is an amorphous glass according to both of its modulus and its hardness. Silicate glass has high softening temperature, but has no rubbery elastic state. The softening temperature is just its fluid temperature, T_f. If the time scale of observation is several decades, it would be found that the thickness of the upper end of the window glass is thinner than that of its lower end, and it results from the flowing of the glass in the gravitational field. In other words, the elongated time scale of observation could decrease the T_f of silicate glass down to room temperature. Moreover, the value of T_f would be affected by the sensitivity of instrument used to determining deformation.

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It should be noticed that the value of T_g depends on the time scale of observation, the sensitivity of instrument used, the increasing rate of temperature and so on. Therefore T_g is a conditional parameter, too. There is experimental evidence to show the conditionality of T_g as follows. The morphology of single chain particles of PMMA in the glass state has been studied by tapping mode atomic force microscopy (AFM) [3]. In this work, very dilute solutions of PMMA in good solvent, in poor solvent or in θ solvent were atomizer-sprayed on to a freshly cleaved mica surface. AFM image acquisition was performed at room temperature after natural evaporation of the solvent on the mica surface. At the initial period of observation, single chain PMMA particles sprayed onto the mica surface show very different morphological shapes, depending on the solvent used. However, it is interesting that those single chain PMMA particles, whether from a solution in a good solvent, in a poor solvent or in a θ solvent, all end up with a spherical shape in the course of storage at room temperature for six months. This means that even at temperature, some 80°C below T_g, the long range chain segmental motion in the PMMA particles still occurred at a very slow rate by cooperative internal rotations of chains in the single chain condensed state, leading to a change of particle morphology to that of the lowest energy. In other words, if the period of observation is long enough (in this work, it is six months) the T_f of PMMA can be decreased down to room temperature. The rubbery state of a polymer, in fact, is liquid to chain segments which are in motion without any displacement of the molecular center of mass. The character of chain segmental motion is the internal cause for the value of T_g has variability.

To sum up, both of T_g and T_f are conditional parameters and in nature, glass transition is kinetic, analogous to fluid transition. T_f is the temperature at which some fluid deformation (non-reversible deformation) can be observed under the experimental conditions used, and T_g is the temperature at which some rubbery elastic deformation (reversible deformation) may occur under the experimental conditions used [4]. There is no reason that can be given to say that T_g is a important parameter and T_f is not. Moreover, T_f is necessary for determining the most appropriate temperature for a polymer processing or a polymer shaping.

1 Deformation-temperature curve

As early as the end of the 1940s the Kargin-Slonimsky schools in the former Soviet Union introduced the concept of polymer states based on the experimental results of the deformation-temperature curve. The polymer states are glass state, rubbery state and fluid state. This deformation-temperature curve, in fact, is the temperature spectrum of the mechanical properties of a polymer (Fig. 1).

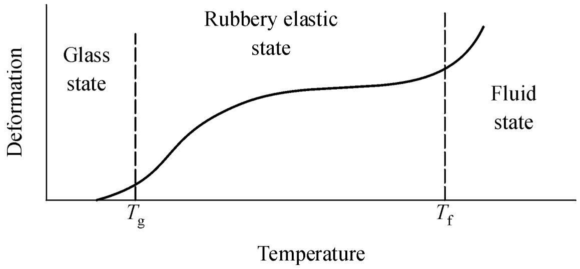

Fig. 1 The deformation-temperature curve of a polymer

In that experiment the deformation of a cylindrical sample of a polymer was observed with temperature scanning, and the sample is axially pressurized by a definite external force. The value of the modulus of an amorphous polymer in its glass state is 3–4 orders of a magnitude higher than that in its rubbery elastic state, leading to the jump in deformation to the zone of a rubbery elastic state from the zone of glass state when temperature scanning passes through T_g. In the rubbery elastic state, the value of the modulus has a small change with increasing temperature. According to the simplified theory about rubbery elasticity, the value of the modulus in a rubbery elastic state is directly proportional to the value of the absolute temperature. The temperature at the end of the rubbery elastic state, at the most, is 3 times higher than that at the beginning. The modulus of a polymer at the end of the rubbery elastic state, at the most, is 3 times higher than that at the beginning, too. Compared with the change of deformation, having 3–4 orders of a magnitude of change in the modulus near T_g, the change of deformation within a narrow range in the rubbery elastic state with increasing temperature can be neglected, leading to an almost horizontal region in the deformation-temperature curve, having no any deformation as shown in Fig. 1. When the temperature scanning passes through T_f, the polymer sample starts to flow, and the value of deformation goes up rapidly with increasing temperature (Fig. 1). As shown in Fig.1, the mechanical property of an amorphous polymer has three zones bounded by glass transition temperature (T_g) and fluid temperature (T_f). At beginning of the study of Kargin etc., an analytical balance was improved to obtain the data of the deformation-temperature curve and the improved analytical balance was called the Kargin balance in the former Soviet Union [5]. In the early 1960s, Slonimsky [6] was invited to give a series of lectures on polymer physics to Chinese researchers, and then Chinese researchers transformed a hardness tester to get a deformation-temperature auto record instrument fitted up with a linear rising temperature system, and the deformation was determined by a differential transformer. This kind of auto-recording instrument was widely used then in China.

If the molecular weight of an amorphous polymer is greater than M_c, which is a critical molar mass for chain entanglement, the value of glass transition temperature (T_g)

of the polymer becomes independent of its molecular weight, but the value of fluid transition temperature (T_f) of the polymer depends greatly on its molecular weight. The higher its molecular weight, the higher the T_f of polymer is. So that, the plateau region in the deformation-temperature curve of a polymer is widened with increasing the molecular weight of the polymer.

With increasing temperature, the behavior of a crystalline polymer is quite different from that of an amorphous polymer. The modulus of a crystalline polymer decreases rapidly near T_m. The crystalline region of the polymer melts at T_m. When the temperature of the polymer is over T_m, the polymer comes to a polymer melt, and the polymer melt may be in a rubbery elastic state or in a fluid state, depending on the difference between T_m and T_g at which the polymer is in its complete amorphous state (as mentioned above). Some hydrocarbon polymers, such as polyethylene and polypropylene, possess high crystallizability. To obtain samples of the polymers without any crystalline region is too difficult. So far, the exact value of T_g, at which this kind of polymer is in a complete amorphous state, still is unknown. There are different views on the value of the T_g of these polymers, but it is clear that the values of T_g are quite low below room temperature. The values of T_m of these crystalline polymers are over 100°C, so that ($T_m - T_g$) should be over 150°C. For a crystalline polymer with a normal molecular weight, the deformation-temperature curve is not much significant because the polymer becomes a fluid melt immediately after the melting of all the crystalline regions. There is a special case, for example, a nascent UHPE (nascent ultrahigh molar mass polyethylene) with very high molar mass of a few million. The macromolecular condensed state of nascent UHPE is a nematic liquid crystal state of nano-domains, and the T_m of nascent UHPE is over 140°C. The T_f of nascent UHPE is over 220°C, which is much higher than T_m [7]. It expresses that the high molecular weight and the high degree of orientation affect T_f greatly.

2 The temperature range of rubbery state

As mentioned above the width of the temperature range of a rubbery state of a polymer, i.e. ($T_f - T_g$), depends on the molecular weight of the polymer. As early as 1949, Slonimsky *et al.* published an article [4] about the study of the viscoelastic properties of polymers. In the study, a single chain of a flexible polymer is represented by a model chain with a spring and a rigid ball connected alternately. Moreover, the influence of the interaction of chains in a multi-chain system on the displacement of the model chain under the action of an external force is considered by immersing the model chain in a viscous fluid with the same viscosity as the polymer. It is supposed that the viscous drag on the displacement of every ball obeys the Stokes' law, and the restoring force of every spring obeys Hookes' law. Moreover, there is another supposition that the temperature dependence of viscosity (η) of polymer obeys the Vogel equation [8],

$$\ln(\eta/\eta_0) = B/(T - T_0) \tag{1}$$

where η_0, B and T_0 are parameters, depending on the nature of substance.

The relaxation time of a viscoelastic element on the spring-ball model chain is τ, and $\tau = \eta/E$, where E is the modulus of the spring. The temperature dependence of E is much weaker than that of η in the temperature range of the rubbery elastic state. In the rubbery elastic state the modulus shows a slight change with increasing temperature (as mentioned above), so that the temperature dependence of τ mainly depends on the temperature dependence of η. Therefore,

$$\ln(\tau/\tau_0) = B/(T - T_0) \tag{2}$$

where τ_0 is a parameter of the substance. The temperature dependence ofτobeys the Vogel equation, too. In solving the equation, the displacement of the last ball in the dashpot is contributed by two parts. One part is from the displacement of the mass center of the chain, and the other part is from rubbery elastic displacement. The former results from viscous flowing, and this deformation is non-reversible. The latter is a rubbery elastic deformation with relaxation and it is reversible. The time dependence of the rubbery elastic deformation depends on the relaxation time (τ).

The temperature dependences of η and τ were introduced into the Vogel equations (1) and (2). Moreover, T_g and T_f were given, respectively, as follows. Under the effect of an external force for a definite time, the observable minima of the rubbery elastic deformation and the viscous flowing deformation appeared at T_g and at T_f, respectively. Then, the simple relation between ($T_f - T_g$) and the molecular weight of a polymer (M) is obtained as shown in Eq. (3):

$$\lg(M/M_c) = B'(T_f - T_g)/[C' + (T_f - T_g)] \tag{3}$$

where M_c is the critical molecular weight for the rubbery elastic deformation. Observably, there is $T_f = T_g$ if $M = M_c$. B' and C' are two parameters and independent of temperature, B' is dimensionless, and the dimension of C' is temperature. Eq. (3) expresses that T_f quite depends on molecular weight, and of course, on molecular weight distribution. So far there are no experimental data confirming the Slonimsky equation [Eq. (3)]. However, it is interesting that Eq. (3) is quite analogous to the form of the widely used WLF equation published by Williams, Landel and Ferry in 1955 [9] [Eq. (4)].

$$\lg[\eta(T)/\eta(T = T_g)] = -C_1^g(T - T_g)/[C_2^g + (T - T_g)] \tag{4}$$

where C_1^g and C_2^g are parameters of the WLF equation, taking T_g as the reference temperature. C_1^g and C_2^g are universal and are almost independent of the chemical structure of polymer chains. $C_1^g = 17.44$ (dimensionless) and $C_2^g = 51.6$ (in dimension of temperature). In 1963, Kovacs [10a] had first shown that the Vogel equation and the WLF equation are mathematically identical. The parameters of equations are related as follows:

$$C_1^g = B/2.303(T_g - T_0);\ C_2^g = T_g - T_0 \qquad (5)$$

Although the two equations mentioned above are quite analogous, the Vogel equation is more convenient for application than the WLF equation because the Vogel equation is not only simpler in form, but is also much easier to physically interpret than the WLF equation. According to Eq. (1) lg $\tau \rightarrow \infty$ as $T = T_0$, the relaxa-tion time goes to infinity, meaning that the molecular motion (cooperative internal rotation of chain) in the relaxation process will be stopped. As $C_2^g = 51.6$, so that $T_\infty = T_g - 51.6$. It means that the cooperative internal rotation will be frozen completely at 51.6°C below T_g. It conforms to the stopping of crystalline growth of the polymer at some 50°C below T_g.

Kovacs called the polymeric chain with critical molecular weight (M_c) in Eq. (3) "segment", but did not have any discussion about it. The "segment" called by Kovacs must not be the Kuhn segment because the Kuhn segment characterizes the rigid strength, and the value of its rigid strength is much lower than that of the polymeric chain with M_c. In the deformation-temperature curve of a polymer, the appearance of the modulus plateau in the rubbery elastic state zone and the value of the modulus at the plateau are independent of the molecular weight of the polymer. It means that a cohesional entanglement network of molecular chains exists in the polymer sample used [10b]. The value of the modulus at the plateau depends on the molecular weight between two cohesional entanglement points and independent of the molecular weight of the polymer chain. The critical molecular weight, M_c, for the appearance of a rubbery elastic deformation is very close to the critical molecular weigh for molecular "entanglement" [10c], i.e., the critical molecular weight for forming cohesional entanglement network, so that they can be considered as the same numerical value. Further experimental investigation is expected to explain the relationship between the rubbery elastic deformation observed above T_g and the forming of the cohesional entanglement network.

When a liquid of small molecules is cooled, and the liquid has high viscosity near its T_m, the liquid would come to its glass state with further cooling because of the super cooling of the liquid. When a solid of small molecules is heated, it directly goes to a liquid state (fluid state) without any appearance of the rubbery elastic state at T_g. On the other hand, the behavior of the polymer is different from small molecules as follows: Over T_g, a polymer comes to a rubbery state, where polymeric chain elements have much free space for motion resulting from cooperative internal rotations. In other words, the polymer is liquid for its local segments, but the polymer still is solid because the motion of these segments does not result in any displacement of the mass center of the whole of polymeric chain. Above T_f a polymer comes to its fluid state resulting from the displacement of the mass center of the polymer chain. It shows the dual nature of the structure and the dual nature of the molecular motion of polymers [11]. The two dual natures are characteristic for polymers.

According to the above discussion, the viewpoint of authors' about $T_{l,l}$ and T_f is not difficult to understand. It is reasonable that $T_{l,l}$ called by Boyer [12–14] is just T_f because if $T_{l,l}$ is the transition temperature from "solid (solidified) liquid" (liquid for local segment and without any displacement of the center of mass of the segment) [14] to "fluid liquid" [15], then $T_{l,l}$ quite observably is identical with T_f, and the polymer changes to "true liquid" above T_f. In addition, a good evidence for authors' viewpoint is the fact that a chemical cross-linked polymer does not have T_f, and $T_{l,l}$ could be removed by chemical cross-linking of the polymer. It is known that the T_f of a polymer depends on the molecular weight of the polymer. So far, there are no experimental data confirming the molecular weight dependence of $T_{l,l}$. Before introducing the concept of T_f, the molecular weight dependence of $T_{l,l}$ is commonly neglected in polymer research, leading to a problem as follows: Some experimental regulations with $T_{l,l}$, such as $T_{l,l} = 1.2\ T_g$ and $T_{l,l}$ (K) = 49 + 1.041 T_g and $T_{l,l} = T_g + 76$°C and so on, lose their precision because $T_{l,l}$ neglects its dependence on molecular weight [10d].

In the temperature range of a rubbery elastic state, the relaxation time (τ) of polymers or viscosity (η) obeys the Vogel equation:

$$\begin{aligned}\ln(\tau/\tau_0) &= B/(T - T_0) = (BR/RT)(1 - T_0/T)^{-1} \\ &= (BR/RT)[1 + (T_0/T) + (T_0/T)^2 + \cdots] \qquad (6)\end{aligned}$$

where R is the gas constant and $T_0 / T < 1$. There is $\ln(\tau/\tau_0) = BR / RT = \Delta E_a / RT$ as $T \gg T_0$. The activation energy of molecular motion is ΔE_a, and $\Delta E_a = BR$. In other words, at a higher temperature the relaxation time (τ) and viscosity (η) of a polymer obey the Arrhenius equation, and the polymer comes to a fluid state. It means that after a polymer comes into its rubbery elastic state, the polymer gradually changes to an Arrhenius fluid from a Vogel fluid with further increases in temperature. If the Vogel equation is rewritten according to the form of an Arrhenius equation, then there is $\Delta E_{app}(T) = BR\ [1 + (T_0/T) + (T_0/T)^2 + \ldots]$, and an apparent activation energy (ΔE_{app}) of relaxation time (τ) is a function of temperature and gradually decreases with increasing temperature. The relationship between $\ln(\tau/\tau_0)$ and $1/T$ is non-linear. Usually, $R\ [\mathrm{d} \ln(\tau/\tau_0)/\mathrm{d}(1/T)]$ is taken as ΔE_{app}. However, Struik has pointed out that this way of treatment is not correct [15]. For a Vogel fluid, the following equation is established,

$$\ln(\tau/\tau_0) = \Delta E_{\mathrm{app}}(T)/(RT)$$

then

$$\Delta E_{\mathrm{app}}(T) = BR[T/(T-T_0)] \tag{7a}$$

but

$$\begin{aligned} R[\mathrm{d}\ln(\tau/\tau_0)/\mathrm{d}(1/T)] &= BR[\mathrm{d}(T-T_0)^{-1}/\mathrm{d}(1/T)] \\ &= BR[T/(T-T_0)]^2 \end{aligned} \tag{7b}$$

Observably, $\Delta E_{\mathrm{app}}(T)$ shown in Eq. (7a) is quite different from R [d $\ln(\tau/\tau_0)$/d$(1/T)$] shown in Eq. (7b). A Vogel fluid with $T_g = 373$ K is taken as an example [10a]. As $T = T_g$, there are $T_g - T_0 = C_2^g = 51.6$ and $BR = 2.303RC_1^gC_2^g = 2072R = 17.2$ kJ/mol. The values obtained are introduced into equations of (7a) and (7b), respectively, and calculations are carried out as follows.

$$\begin{aligned} \Delta E_{\mathrm{app}}(T = T_g) &= BR[T_g/(T_g - T_0)] \\ &= 17.2(373/51.6) = 125(\mathrm{kJ/mol}) \end{aligned}$$

$$\begin{aligned} R[\mathrm{d}\ln(\tau/\tau_0)/\mathrm{d}(1/T)]_{T=T_g} &= BR[T_g/(T_g - T_0)]^2 \\ &= 17.2(373/51.6)^2 \\ &= 900(\mathrm{kJ/mol}) \end{aligned}$$

There is a great difference between the value (1900 kJ/mol) obtained from R [d $\ln(\tau/\tau_0)$/d$(1/T)$] and that (125 kJ/mol) from $\Delta E_{\mathrm{app}}(T)$. Usually the apparent activation energy $\Delta E_{\mathrm{app}}(T)$ obtained from R[d $\ln(\tau/\tau_0)$/d$(1/T)$] was used to explain the transition from a glass state to a rubbery elastic state on the level of molecular motions. Now it should be reconsidered.

3 Shear viscosity of polymer melt

As an important parameter the shear viscosity of a polymer is used for characterizing its molecular weight and for marking polymers with different molecular weights in the industrial field. However, it must be noted that a polymer melt may be in its rubbery elastic state or in its fluid state. In the industrial field, the measurement of the shear viscosity of a polymer is usually carried out by capillary viscometry. Under a given pressure and at a given temperature, the melt flows out of a storage hopper and passes through a capillary tube with known diameter and length. The amount of the melt flowing out of the capillary is measured within a definite time period and is defined as the Melt Flow Index. The Melt Flow Index is approximately proportional to the reciprocal of the melt viscosity. For a Newtonian fluid the shearing stress is directly proportional to the shear rate, and the coefficient of proportion is called shear viscosity.

For a viscous flow in a capillary, there is a flow rate gradient along the diameter direction of the capillary. The value of shear rate depends on the perpendicular distance from the central axis of the capillary. The shearing rate on the capillary wall is zero, and that at the central axis reaches a maximum value, showing a parabolic profile. For a polymer with high molecular weight, the viscosity of its melt or solution exhibits the shearing rate dependence, i. e. both of them are non-Newtonian fluids, leading to the complexity for treating the data of viscosities obtained by capillary viscometry [16]. Usually, the non-Newtonian behavior of a polymer melt or a polymer solution in its shearing flow is shear-thinning, i.e., the viscosity decreases down with increasing shear rate. According to the experimental data, the shearing flow of a polymer melt or a solution is Newtonian at a very low shear rate. Then, its apparent viscosity decreases down with increasing the shearing rate. Finally, at a high enough shear rate, the Newtonian flow zone appears again, which can be called the second Newtonian flow zone [16–21]. However, experiments at a very high shear rate are hard to carry out, so that to obtaining exact data is difficult. The experimental data of concentrated solutions of a cellulose derivative show the second Newtonian flow zone (Fig. 2) [17]. In Fig. 2, the figures on the curves represent the solution concentrations in percentage.

In Fig. 3 [18] the flow of polydiamethyl-siloxane (35°C, molecular weight of samples responding to curves of 1 to 6

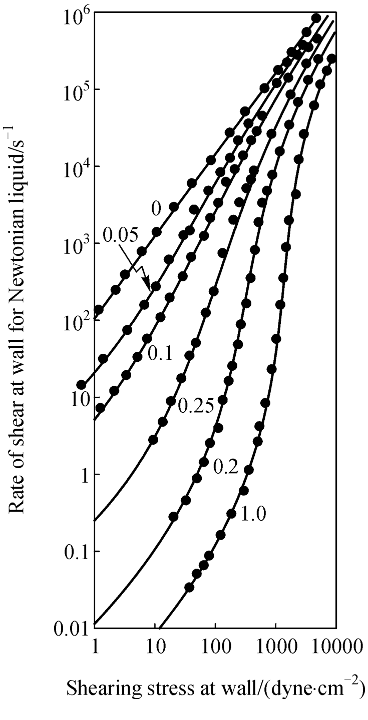

Fig. 2 Flow curves of cellulose trinitrate (13.7% N) in butyl acetate

as follows, 1: 160 000; 2: 64 000; 3: 31 000; 4: 14 500; 5: 5400; 6: 2400) is approaching the second Newtonian flow zone. While the flows of HD-polyethylene (curve 8, Melt Flow Index: 2, at 190°C) and polystyrene (curve 7, $\overline{M_w}$: 266 000, $\overline{M_w}/\overline{M_n}$: 3, at 190°C) cannot reach the second Newtonian flow zone [19a, 19b] because of unstable flowing or melt fracture at high shear rates.

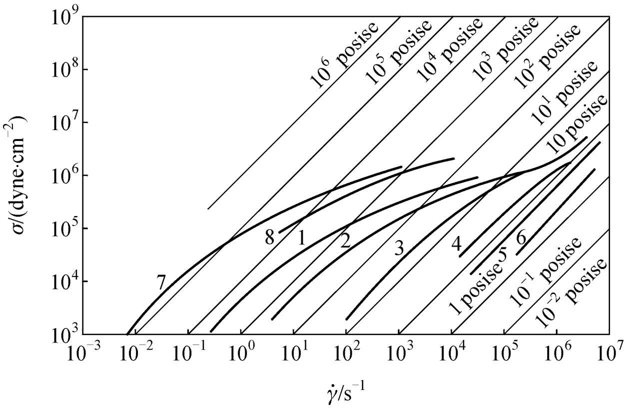

Fig. 3 Flow curves of polydimethyl-siloxane, HD-polyethylene and polystyrene

The fact that the concentrated solution and the melt of polymer have second Newtonian flow zone has important significance for understanding the non-Newtonian flow at the molecular level. When the viscosity of a polymer melt is measured by capillary viscometry at a temperature which is not much higher above T_g, the rubbery elastic deformation, which is a recoverable deformation, and the shear flow deformation, which is a non-recoverable deformation, exist in the deformation of the polymer melt flow at the same time. Moreover, the two parts of deformations in the melt flow can not be distinguished from each other in the measurement, so that the value of viscosity obtained from experimental data is not the exact shear viscosity, and it is difficult to obtain repeatable experimental results in this case. Until the experimental temperature increases up to some 50°C above T_g, the reliable shear viscosity of a polymer melt can be obtained because the temperature of the polymer is close to its T_f (normally, T_f is about 50–100°C above T_g and depends on the molecular weight of the polymer), at which the deformation of the polymer melt is mainly from shear flow. As the measuring temperature is too close to T_g, the measurement of the viscoelasticity of the polymer melt is difficult because of its very high viscosity. Based on the behavior of the polymer melt mentioned above, Ferry *et al.* [22] recommended "T_g+ 50°C" as the reference temperature for studying the temperature dependence of viscosity of polymer melt using the WLF equation and in that case, the applicability of the WLF equation can be studied in the range of about 20–30°C below T_f. Above T_f, the temperature dependence of a viscosity of polymer melt obeys the Arrhenius equation again, and does not obey the Vogel equation and the WLF equation. The transition temperature from the temperature region of viscoelastic flow, which does not obey Arrhenius equation above T_g, to the temperature region of viscous flow, which obeys the Arrhenius equation above T_f, can be taken as T_f. In addition, on the temperature spectrum (ln τ vs. $1/T$ plot) of dielectric relaxation time (dynamic measurements) obtained by Labanov *et al.*, the temperature, at which the Vogel relation of the relaxation merges with the Arrhenius relation of the relaxation, can be identified with T_f [10e]. The view on T_f mentioned above is expected to be confirmed by the observable dependence of $T_{l,l}$ on molecular weight, but no related experiments have been carried out so far.

When a polymer melt flows out of a storage hopper into a capillary tube, a contraction flow occurs at the entrance of the capillary tube, leading to a sudden jump of the flow rate in the flow direction along the central axial line of the capillary tube, and the flow becomes an extensional flow with the velocity gradient in the flow direction (For a shear flow the velocity gradient is in the direction which is normal to the flow direction). The viscosity of the extensional flow is called extensional viscosity, which is important for the spinning of polymer melts or concentrated solutions and film stretching. The extensional viscosities of polymers could not be obtained until recent years due to experimental difficulties.

Because of the shear rate gradient of the sample flow in the capillary as mentioned above, using a cone-plate viscometer is more suitable than using a capillary viscometer for a basic study. The cone-plate viscometer consists of a cone and a round plate. The cone is concentrically set on the round plate, and the surface of the cone makes a very small angle with the surface of the plate, bringing a gap for filling fluid sample. The shear rate of the sample fluid in the gap is almost uniform throughout all of the sample fluid and increases with increasing the relative rotation velocity of the plate to the cone. The shear viscosity can be obtained by calculation from the shear stress and the shear rate. The shear stress and the shear rate can be obtained from the rotation moment applied to the cone-plate and from the rotation velocity, respectively. Moreover, for a viscous elastic fluid sample, the upward push force during rotation can be measured for calculating the normal stress of the fluid. If an oscillatory torque is applied to the cone-plate viscometer, the dynamic measurements can be carried out in order to obtain the dynamic elastic modulus and the dynamic viscosity of a polymer melt. At a given temperature, the frequency spectrum of the dynamic viscoelasticity can be obtained by changing the frequency of the oscillatory torque. At a given frequency, the temperature spectrum of the dynamic viscoelasticity can be obtained by changing temperature. According to the time-temperature correspondence principle the data of the relaxation time of molecular motion of polymer melts obtained at frequencies of 3–4 orders of a magnitude and at different temperatures can be converted extendedly into a spectrum in a range of about 10 orders of magnitude of frequency. Onogi *et al.* [23] gave the frequency spectrum of the dynamic viscoelastic modulus and the dynamic viscosity $[\lg G - \lg(\omega_{a_T})]$ using polystyrene samples with different molecular weights and narrow-distributions (Fig. 4). The experimental measurements of viscoelastic properties were carried out with a concentric cylinder type rheometer. The value of the modulus is directly proportional to the reciprocal of the deformation under a given external force. The numbers and the molecular weights $(\overline{M_w})$ of the samples in Fig. 4 are as follows: L9: 8900; L12: 14 800; L14: 28 900; L34: 46 900; L16: 58 700; L37: 113 000; L27: 167 000; L15: 215 000; L22: 275 000; L5: 315 000; L19: 513 000 and L18: 581 000.

According to the two relationships that an increase in the modulus corresponds to a decrease in deformation, and an increase in frequency corresponds to a decrease in temperature, the ordinate G' in Fig. 4 can be changed to deformation, and the abscissa lg (ω_{a_T}) in Fig. 4 can be changed to temperature. For the convenience of observation, the Fig. 4 as modified above is rotated by 180° to get the deformation-temperature curves as shown in Fig. 5. The curves in Fig. 5 are qualitatively similar in running to the deformation-temperature curve in Fig. 1. There are three temperature zones corresponding with the glass state, the rubbery state and the fluid state, respectively. Besides, a modulus plateau appears in the temperature zone of the rubbery elastic state, too. The modulus value of the plateau is independent of the molecular weight of the polymer samples and is only dependent on the structure of the cohesional entanglement network of the polymer samples in the rubbery elastic state. The molecular weight of sample L14 in Fig. 5 is 28 900, which is very close to the critical molecular weight for cohesional entanglement, M_c. It was proven again that the critical molecular weight for the appearance of modulus plateau corresponds to the critical molecular weight for cohesional entanglement, M_c, which is normally obtained from the viscous behavior of polymer melts.

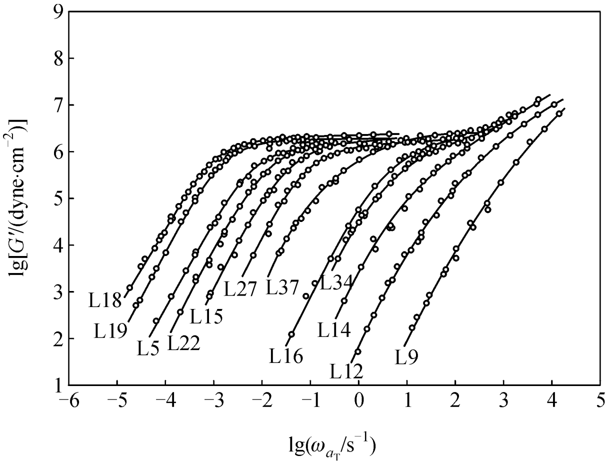

Fig. 4 Master curves of G' for narrow-distribution polystyrenes having different molecular weights (reference temperature 160°C)

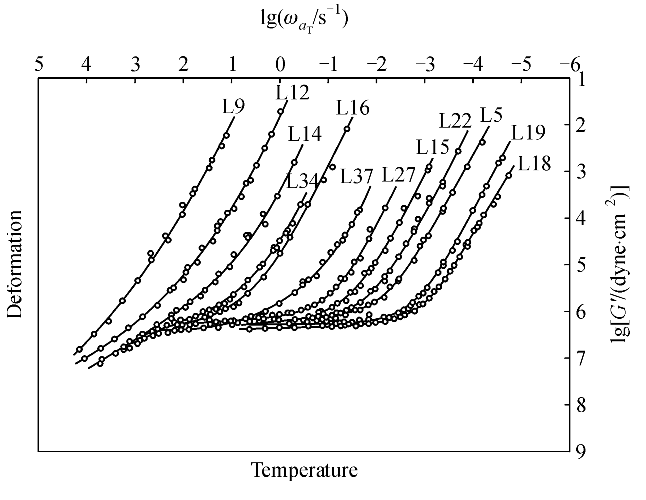

Fig. 5 The curves of deformation vs. temperature from Fig. 4

4 The viewpoint of cohesional entanglement network on the transition from rubbery state to fluid state

It is a conclusion from the viscoelastic behavior of polymer melts, that a physical cross-linked network exists in polymer melts above T_g and this network is normally called the “cohesional entanglement network of chains”. As mentioned above the network is not topological, and it results from the local cohesional entanglement of chains. On decreasing temperature, a polymer melt goes to its rubbery state from its fluid state and even to its glass state, i. e. becomes a solid polymer. However, the cohesional entanglement network in the polymer would not be disrupted in this cooling process, so that there is a cohesional entanglement network even in the glass state of the polymer [10b]. Moreover, some new cohesional entanglement points would appear with the slow decreasing temperature from the rubbery elastic state. It takes long time to form new cohesional entanglement points below T_g. Tens or hundreds hours are needed for the formation of new cohesional entanglement points below T_g. The increase in cohesional entanglement points would influence the physical properties of the polymers in the glass state. They became brittle. This phenomenon is usually called the physical aging of polymers. The term, “physical aging”, has been used for a long time, but it is not quite reasonable because “aging” normally means the changes in chain structure and physical properties of polymers, as a result of a irreversible chemical change. However, the physical aging mentioned above results from a reversible change in the structure of the cohesional entanglement network. Above T_g, the molecular weight of segments between two cohesional entanglement points, undoubtedly, is over that needed for its rubbery elastic deformation. After cooling a polymer sample from a temperature above T_g to its glass state followed by heating the sample, the new cohesional entanglement points formed in the cooling process would affect the T_g value and the heat effect related with its glass transition. This phenomenon is called the "thermal history effect". Usually, a solid sample is pretreated by heating at a temperature about 20–30°C above T_g and kept at that temperature for over 20 mins, followed then by quenching to get its glass state. In this way the cohesional entanglement points formed above T_g can be frozen in the sample in order to avoid the thermal history effect on determining T_g. Using samples as treated above, the experimental values of T_g with good repeatability can be obtained.

A polymer with a permanent network, such as a network with chemical cross-links, cannot flow. However, polymer melts can flow. It means that at least in a twinkling, the cohesional entanglements in a polymer melt can be ruptured, making a possibility for the flowing of the polymer melt. As mentioned above, the cohesional entanglement points of the network in a polymer melt are cohesive points between local chain segments and could be disrupted by heating over T_g. In fact, the disruption of cohesional entanglement points existing in a network and the formation of new cohesional entanglement points both occur at any moment, and a dynamic balance is formed. Either of the disrupting cohesional entanglement points and the formatting of new cohesional entanglement points is a relaxing process of molecular motions. Statistically, in a not much very high temperature range above T_g, the cohesional entanglement points may stay in their cohesive state for a much longer time period than in their disrupting state. With increasing temperature the time period of cohesional entanglement points in the disrupting state would become longer and longer, and that in the cohesive state would become shorter and shorter. When the temperature reaches up to a high temperature, the cohesional entanglement points in their disrupting state is long enough for the occurrence of the observable displacement of the mass center of molecular chains in the direction of a external force by means of cooperative internal rotations of molecular chains. This high temperature is just the fluid transition temperature, T_f. At a temperature above T_g the cohesional entanglement network in a polymer melt is a relaxing network. The cooperative internal rotations of a long enough molecular chain and the apparent activation energy over 100 kJ/mol are necessary for rubbery elastic deformation (as mentioned above). At T_f the transition of a polymer from an elastic state to a fluid state is quite different from its glass transition. A flow of polymer does not demand cooperative internal rotations of very long molecular chains. The flow activation energy is about 18–85 kJ/mol and independent of the molecular weight of the polymer. For example, the activation energy for a linear alkane with 20–25 carbon atoms in its chain length reaches 25–29 kJ/mol [24], which is the limit value for linear alkane and would not increase with increasing molecular weight. The activation energy for polyethylene (100% linear chain) is 25 kJ/mol [19b], which can be seen as the same value as that for a linear alkane with 20–25 carbon atoms. It means that the flow of polymeric molecular chains results from the displacement of the segments of molecular chains, i.e. the snake crawling as it is usually called. The model for the polymer flow is established on the study of viscosity of the linear alkanes, so that snake crawling does not result from the cohesional entanglement because a linear alkane with 25 carbon atoms does not have any possibility for chain entanglement. It should result from the excluded volume effect of molecular chains.

In fact, the study on the relaxing network of a polymer melt in its fluid state does not start yet. A possible experimental approach is to use the cone-plate viscometer. At a given shear rate of a steady flow, a sinusoidal oscillation with a small amplitude is superimposed parallel to the flowing direction between the cone and the plate of the cone-plate viscometer. Then, the dynamic response is measured. For example, the network structure of a fluid in flow can be characterized by measuring the dynamic modulus. Moreover, it is hopeful that the useful information about the relaxing network of a polymer melt in a wide range of flowing conditions can be obtained by changing the experimental temperature or changing the shear rate of the steady flow or changing oscillation frequency. The information would be helpful to more profoundly understand the shear rate dependences of the polymer flow and the viscosities of polymer melts. This method was first found in Booij's work [25] 30 years ago. The study of the relaxing network in a polymer fluid would be worthy to be considered as an object of polymer research, and so far the study has not been carried out with the viewpoint that the dynamic data of a polymer may give an insight into the structure of the relaxing cohesional entanglement network in the polymer.

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