Application of Time–Temperature Superposition Principle To Polymer Transition Kinetics

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ABSTRACT: The time–temperature equivalence equation is deduced simply in view of the transition kinetics of a polymer. The independent variables time and temperature are separated in the two sides of the resulting equation. Thus, a physical property of the polymer, which is temperature dependent, can be matched with the theoretical calculated curve from a supposed model of transition kinetics in which only time is involved as the independent variable. By comparing different models, one may judge which model is probably more correct. The procedure of data fitting is described. As an application example, the measured viscosity data at different temperatures for the coil–globule transition of poly(*N*-isopropylacrylamide) in aqueous solution is tested to judge its transition mechanism. A transition mechanism involving a two-stage reversible reaction fits the experimental data in a satisfactory way. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 1767–1772, 2006

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INTRODUCTION

Transition kinetics is one of the most important fundamental problems in polymer science. The conventional method to study transition kinetics is to measure the variation of the related physical properties with increasing time at a constant temperature. It is very difficult to ascertain the transition mechanism from a physical property, which is temperature dependent. However, at some time the transition process just takes place with temperature change, and the time-dependent property is difficult to measure; thus, the usual method seems to be useless for their kinetic study. Thus, it is significant to set up the relationship between time and temperature for the investigation of the transition mechanism directly from the temperature-dependent properties.

The time–temperature superposition or equivalency is a well-known principle in polymer physics. This principle was first proposed by Lenderman[1] in 1943,

in which time is equivalent to temperature for viscoelastic materials. Williams, Landel, and Ferry[2] subsequently proposed a semiempirical formula to describe the principle quantitatively known as the Williams–Landel–Ferry equation. Later, Seitz and Balazs[3] put forward another form of the equation that was suitable to semicrystallization polymers. Both equations could be deduced from the concept of free volume and the Doolittle viscosity formula. The superposition principle can be used to predict the creep and relaxation behavior and to construct a master curve. In the present article we initially show that the time–temperature superposition principle can be deduced in view of the transition kinetics of a polymer. Then, the procedures of how to match a theoretical kinetic curve, in which only time is the independent variable, with the temperature-dependent experimental physical property of the polymer are described. Finally, the viscosity data of the coil–globule transition of poly(*N*-isopropylacrylamide) (PNIPAM) in aqueous solution is utilized as an application example, which shows that a two-stage reversible transition is the most probable mechanism.

EXPERIMENTAL

Considering that a polymer in physical state *A* changes gradually into physical state *B* with a rate

constant k at a fixed temperature T, the physical property of the polymer in the intermediate stage should depend on how much initial polymer in the A state is converted to the B state. Consequently, any observable quantified physical property P is controlled by the relative amounts of both states presented in the polymer. Accordingly, we have

$$P = w_A \cdot P_A + w_B \cdot P_B \qquad (1)$$

where P_A and P_B are the corresponding quantified property of the polymer in states A and B, respectively, and w_A and w_B are the weight fraction of states A and B, respectively, in the gross polymer with $w_A + w_B = 1$.

If the transition from state A to state B follows first-order reaction kinetics,

$$A \xrightarrow{k} B \qquad (2)$$

the solution of the rate equation is

$$\frac{d}{dt} A = - k \cdot A \qquad (3)$$

and the amount of polymer in state A at time t is

$$A = A_0 \cdot e^{-k \cdot 1} \qquad (4)$$

where A_0 is the initial amount of the polymer. Thereby, the weight fraction of A at t will be

$$w_A = \frac{A}{A_0} = e^{-k \cdot 1} \qquad (5)$$

which depends both on t and the rate constant k, which is temperature dependent and is usually expressed by the Arrhenius equation:

$$k = Z \cdot \exp\left(\frac{-E}{R \cdot T}\right) \qquad (6)$$

where E is the activation energy and Z is a preexponential factor corresponding to the rate constant as the temperature approaches infinity.

Inserting the Arrhenius equation into eq. (5) we get

$$w_A = \exp\left(- Z \cdot \exp\left(\frac{-E}{R \cdot T}\right) \cdot t\right) \qquad (7)$$

This indicates that the composition of the polymer physical states is a function of t and T. Because the physical property of the polymer is only dependent on its structural composition [eq. (1)], regardless of the

route it approached, if the composition of A (w_A) under T at t is equal to that under T_0 at t_0, the physical properties of the two polymers obtained via different routes should be identical. From eq. (7) we immediately have

$$\exp\left(\frac{-E}{R \cdot T}\right) \cdot t = \exp\left(\frac{-E}{R \cdot T_0}\right) \cdot t_0 \qquad (8)$$

Taking the logarithm for both sides of eq. (8) and then rearranging we have

$$\ln(t) - \ln(t_0) = \frac{E}{R}\left(\frac{T_0 - T}{T \cdot T_0}\right) \qquad (9)$$

Equation (9) is the simplest representation of the time–temperature super position principle. Its left side only contains t as a variable and its right side only depends on T. Arbitrarily choosing a reference temperature T_0, multiplying a constant $K = E/R$ to the reduced temperature $(T_0 - T)/(T \cdot T_0)$ is equal to adding a constant amount $S = -\ln(t_0)$ to the logarithm of t.

$$\ln(t) + S = K\left(\frac{T_0 - T}{T \cdot T_0}\right) \qquad (10)$$

The bridge between time and temperature as shown in eq. (10) has been set up. It provides the possibility that the transition kinetics could be investigated just from the temperature-dependent physical property by matching a theoretical kinetic curve in which only time is the independent variable.

RESULTS AND DISCUSSION

Principle of data fitting

Generally, if a certain physical property of a polymer is temperature dependent, one may ask whether a transition is involved and what the mechanism of the transition is. The principle of time–temperature super position as mentioned above provides a useful way to answer the question. We may use a supposed kinetic model to calculate the theoretical time dependency of the physical property of concern and then compare the theoretical curve with the experimental data. If they coincide well, we can confidently say that the assumed transition kinetics and mechanism are correct. However, a special data fitting technique must be used. It involves four main steps.

1. An arbitrary temperature T_0 is first chosen to serve as the reference. Converting the temperature to a reduced scale, a plot of the measured temperature-dependent physical quantity versus $(T_0 - T)/(T \cdot T_0)$ is constructed.

2. Set up and numerically solve the differential equations of the supposed transition kinetics with arbitrarily chosen fixed rate constants. Then, use a computer to easily calculate the variation of the weight fractions of the composing structural states with time. The results may be displayed in a separate diagram.

3. Calculate the variation of the desired physical quantity with time by the additive rule

$$P = \sum w_i P_i \tag{11}$$

with a presumed initial value of P_i. Superimpose the theoretical curve in the plot of experimental data versus $(T_0 - T)/(T \cdot T_0)$.

4. Match the calculated theoretical curve with the experimental data by first assigning a suitable value of constant S to move the theoretical curve horizontally until the two plots are located in the same region of the x axis, and then expand the width of the experimental data plot by choosing a suitable constant K until both ends of the experimental data fit the theoretical curve.

All of these operations can be manipulated easily on a computer. Comparing the goodness of fit with different mechanism and transition kinetics, we can decide which one is the most probable.

Application

The coil–globule transition of macromolecules is a very interesting topic both in theory and in applications.[4–10] The theoretical work on the kinetics of the coil–globule transition proposed a two-stage contraction process[11,12]: the first step is a rather fast crumpling of the unknotted polymer chain (crumpled globule), and the second step involves a subsequent slow knotting or rearrangement of thermal blobs of the collapsed polymer chain (compact globule). This prediction of the transition mechanism has been confirmed by Chu et al.[13] and Wu and Zhou[14] from experimental observations of the coil–globule transition of polystyrene and PNIPAM in solution, respectively, by the laser light scattering technique.

PNIPAM[4–6] is a kind of thermosensitive polymer in aqueous solution; the transition from a coil to a globule takes place when the temperature rises to its lower critical solution temperature at around 32°C. We studied the coil–globule transition and the reverse process globule–coil transition of single chain PNIPAM by viscometry[15,16] and differential refractometry.[17] It was shown that a mechanism involving two steps probably was still simplified because a hydration–dehydration process occurs simultaneously during the transition.[17] To reillustrate this viewpoint, we use the time–
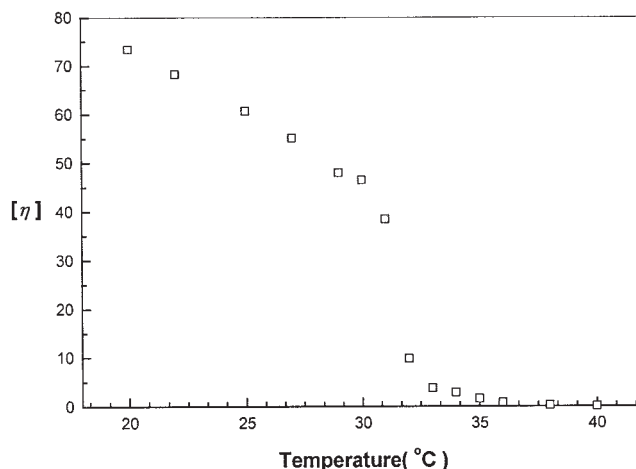

Figure 1 The plot of the intrinsic viscosity $[\eta]$ from experimental results to the temperature. The concentration of the normal PNIPAM solution was 6.65×10^{-4} g/mL. The intrinsic viscosity was calculated according to the formula[19] $[\eta] = [\sqrt{2}(\eta_{sp} - \ln(\eta_r))]/C$.

temperature super position principle to treat the intrinsic viscosity data at different temperatures reported earlier[15,16] as an application example. Figure 1 shows the variation of the intrinsic viscosity of PNIPAM in aqueous solution with the temperature. We assumed that the coil–globule transition followed first-order reaction kinetics. Three types of model transition mechanisms were tested: one-stage nonreversible, one-stage reversible, and two-stage reversible. The one-stage nonreversible transition is the following:

$$A \xrightarrow{k} C \tag{12}$$

The one-stage reversible transition is

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C \tag{13}$$

The two-stage reversible transition is

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B \underset{k_4}{\overset{k_3}{\rightleftharpoons}} C \tag{14}$$
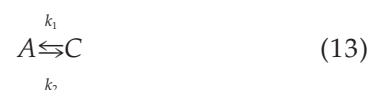
In eqs. (12)–(14), A, B, and C represent extended coil, crumpled globule, and compact globule, respectively. For calculating the theoretical curve of the variation of the intrinsic viscosity $[\eta]$ with time for a one-stage transition, we use

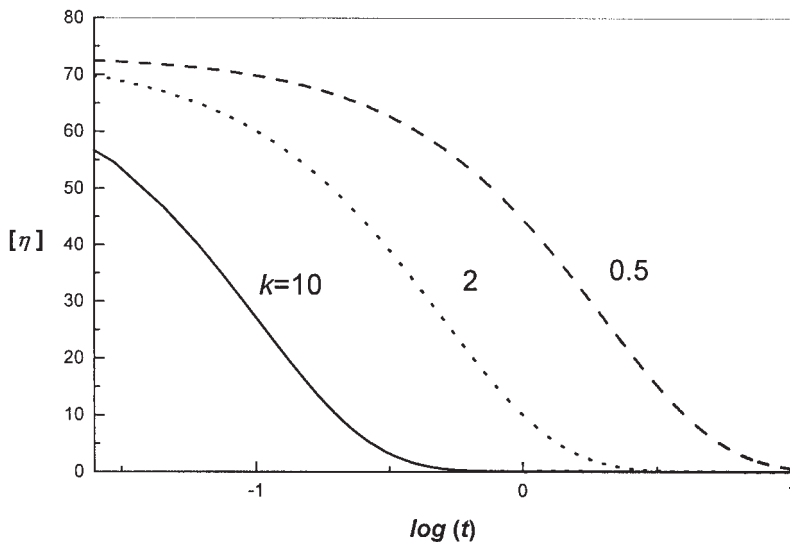$$[\eta] = w_A \cdot [\eta]_A + w_C \cdot [\eta]_C \tag{15}$$

Figure 2 The calculated intrinsic viscosity $[\eta]$ versus the logarithmic time curve for the one-stage nonreversible transition kinetics with various rate constants.

and presume

$$[\eta]_A = [\eta]_{20°C}$$

$$[\eta]_C = [\eta]_{40°C}$$

which are assumed to be the extreme intrinsic viscosity values at the two ends. As for the one-stage nonreversible transition as shown in eq. (12), the differential equation is written as

$$\frac{d}{dt} A = - k \cdot A \qquad (16)$$

By solving the kinetics equation with arbitrary chosen rate constants, the variation of the weight fractions of the composing structural states A and C with time could be easily attained. The theoretical intrinsic viscosity may be calculated in terms of eq. (15). Figure 2 shows the calculated curves of the intrinsic viscosity versus the logarithmic time for one-stage nonreversible transition kinetics with various rate constants. The location of the curve depends on the chosen rate constant. However, they are superimposed to one master curve by different shift factors S as shown in Figure 3. The experimental intrinsic viscosities versus the reduced temperatures are also plotted in this figure with the same numerical X axis. By regulating the constants K until the two ends match the theoretical curve, it can be seen that the major portion of the transition regions are apart from each other (Fig. 3). Evidently, the one-stage nonreversible transition kinetics are not suitable for describing this coil–globule transition.

The one-stage reversible transition mechanism shown in eq. (13) was then taken into account. Its kinetics equations are

$$\frac{d}{dt} A = - k_1 \cdot A + k_2 \cdot B$$

$$\frac{d}{dt} B = k_1 \cdot A - k_2 \cdot B \qquad (17)$$

The theoretical curve was calculated similarly to that of the one-stage nonreversible transition. However, it
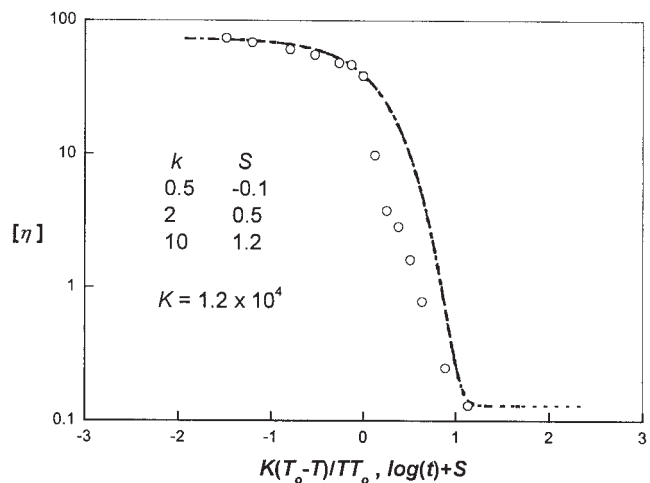

Figure 3 Superposition of the experimental data with the calculated intrinsic viscosity $[\eta]$ versus the logarithmic time curve for the one-stage nonreversible transition kinetics with $K = 1.2 \times 10^4$ and $T_0 = 304$ K. (○) The experimental data versus the reduced temperature and (- - -) the theoretical calculated data versus the logarithmic time.
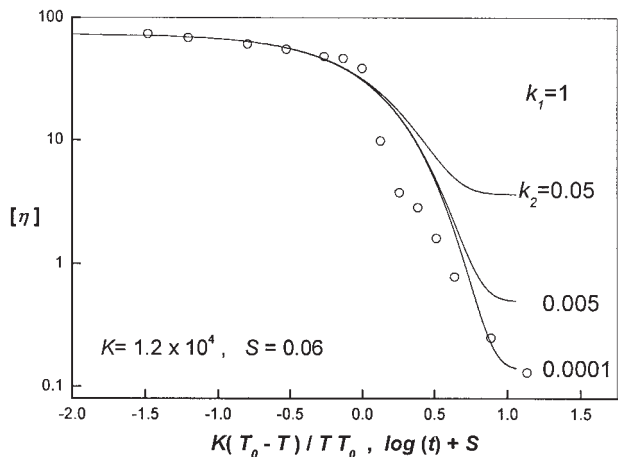
Figure 4 Superposition of the experimental data with the calculated intrinsic viscosity [η] versus the logarithmic time curve for the one-stage reversible transition kinetics with T_0 = 304 K and various rate constants. (○) The experimental data versus the reduced temperature and (- - -) the theoretical calculated data versus the logarithmic time.
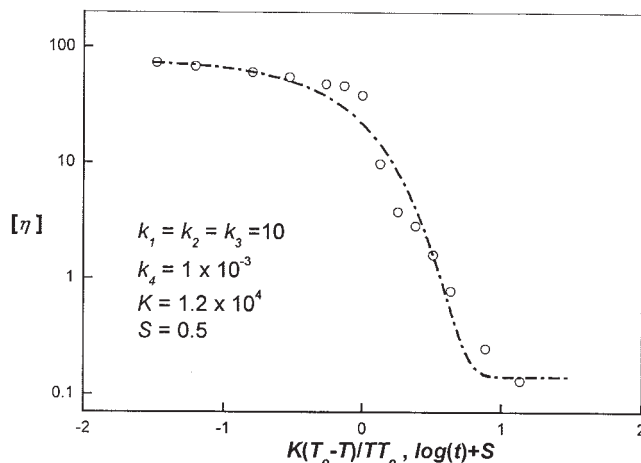
Figure 6 Superposition of the experimental data with the calculated intrinsic viscosity [η] versus the logarithmic time curve for the two-stage reversible transition kinetics with T_0 = 304 K. (○) The experimental data versus the reduced temperature and (- - -) the theoretical calculated data versus the logarithmic time.

was also not suitable for describing the transition, as shown in Figure 4. In this case, only when $k_2 \ll k_1$ does the high temperature end of the theoretical curve match the experimental data.

Finally, we attempted to test a reversible transition model with two stages as provided in eq. (14). Its kinetics equations are

$$\frac{d}{dt} A = -k_1 \cdot A + k_2 \cdot B$$

$$\frac{d}{dt} B = k_1 \cdot A - k_2 \cdot B - k_3 \cdot B + k_4 \cdot C$$

$$\frac{d}{dt} C = k_3 \cdot B - k_4 \cdot C \qquad (18)$$

For calculating the theoretical intrinsic viscosity, the additive equation

$$[\eta] = w_A \cdot [\eta]_A + w_B \cdot [\eta]_B + w_C \cdot [\eta]_C \qquad (19)$$

was used with
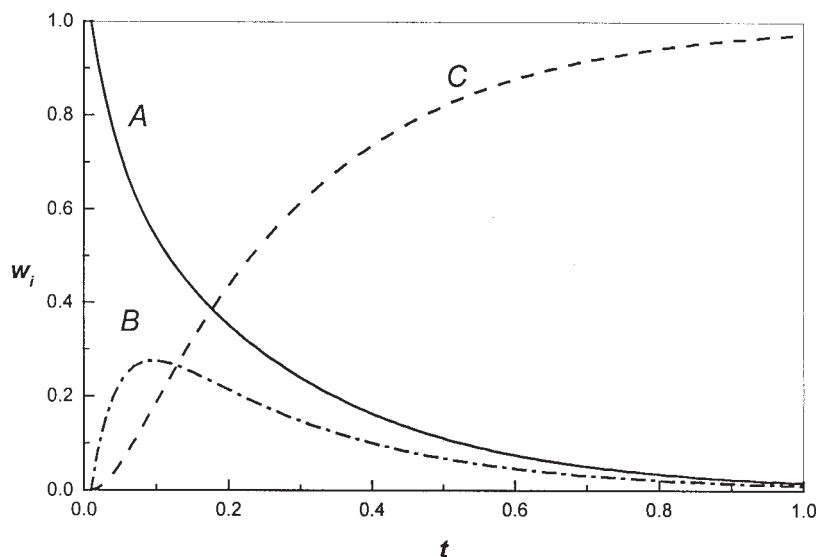
$$[\eta]_B = [\eta]_\theta \qquad (20)$$

Figure 5 The calculated weight fractions of extended coil (A), crumpled globule (B), and compact globule (C) versus the logarithmic time curve for the two-stage reversible transition kinetics.

where $[\eta]_\theta$ is the intrinsic viscosity at the θ temperature of 31°C. The results of the numerical solution of the differential equations of this model are provided in Figure 5. It includes the variation of the weight fraction of the intermediate state B (w_B) with time. The best fit of the theoretical kinetic curve with the experimental data will be obtained if the chosen value of k_4 is less than the others, as shown in Figure 6. This means that the reverse reaction (globule–coil transition) should be retarded, and the experimental facts[15,16,18] confirmed this prediction. Thus, we can conclude that the coil–globule transition of PNIPAM in aqueous solution is essentially a two-stage process. However, if we look more closely at Figure 6, discrepancies still exist, especially in the region where the transition starts. It is probably due to the fact that the process of hydration and dehydration are not considered.

CONCLUSION

We gave a new perspective on the time–temperature super position principle in terms of the transition kinetics of polymers, and a new method to judge the transition mechanism was provided from the temperature-dependent physical properties. Based on this knowledge, the coil–globule transition of PNIPAM in aqueous solution was studied. It confirmed the theoretical prediction that the coil–globule transition would involve two steps.

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