Effects of the Shear Flow on a Homogeneous Polymeric Reaction

Fan Xie, Chixing Zhou, Wei Yu

School of Chemistry and Chemical Technology, Shanghai Jiaotong University, 800 Dongchuan Road, Shanghai 200240, People's Republic of China

ABSTRACT: The reaction kinetics of the postamidation of polyamide 6 in the melt was studied by a new rheological method, and the reaction rate constant was calculated to be about 0.087 kg/mol min at 250°C. To study the effects of the shear flow on a homogeneous polymeric reaction, a more practical technique was used to select the data that responded only to the reaction without the effect of different shear flows. The experimental results showed that the reaction rate constant decreased with an increase in the shear rate. Moreover, the decreases in the rates were different under different shear modes: the reaction rate constant decreased slightly under oscillatory shear but strongly under steady shear. Possible reasons for these phenomena were examined. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 3056–3061, 2006

Key words: polyamides; rheology; viscosity

INTRODUCTION

As an effective means, the reactive process has been widely used to obtain desired properties. By the treatment of the extruder as a reactor, reactants with appropriate compositions are extruded with different types of reactions taking place under intensive flows. Mostly, the homogeneous polymeric reaction in the reactive process is polymerization.

The kinetics of polymerization have been studied for decades.[1–4] The most common methods for data acquisition are titration, Fourier transform infrared, and gel permeation chromatography. The influence of various reaction parameters, such as the temperature, catalyst type and concentration, and stoichiometric ratio of the monomers, have been well investigated in kinetic studies. However, generally less attention, if any, has been paid to the effect of the shear flow on the polymerization kinetics, and this can be attributed to the complexity of the flow. Macosko and coworkers[5–7] have extensively studied the polymerization kinetics of polyurethanes. They investigated the viscosity changes during various thermoplastic and thermosetting urethane polymerizations in Coutte rheometers and found that the shear rate had no significant effect on the extent of reaction. Other articles[8,9] have been published about the influence of the shear rate on the kinetics of curing of unsaturated polyester resins, using rheologi-cal and differential scanning calorimetry measurements. Despite the works mentioned previously, it seems that there are no systematic studies on the effect of the shear flow on the homogeneous polymeric reactions in melts. In addition, it is even more important to understand how the shear flow affects the reaction in a homogeneous system for its fundamental status.[10,11]

Recently, Bousmina and coworkers[12,13] reported that the interdiffusion coefficient between two polymer chains with a planar interface could be measured by the monitoring of the changes in the rheological properties under a small-amplitude oscillatory shear, which does not affect the diffusion mechanism. Once the rheological properties are related to the amount of *in situ* formed graft (or block) copolymers for a reactive blend, the reaction kinetics can be evaluated if one monitors temporal changes in the blends' rheological properties. Kim and coworkers[14,15] evaluated the kinetics of the reaction at the reactive end-functional monocarboxylated polystyrene (PS–mCOOH) and poly-(methyl methacrylate-*ran*-glycidyl methacrylate) (PMMA–GMA) polymer–polymer interface by putting samples under small-amplitude oscillatory shear. However, they did not give a very clear physical explanation for correlating the change in the rheological properties with the conversion of the *in situ* formed copolymers.

In this study, we investigated the reaction kinetics of polycondensation in a homogeneous melt and the effect of the shear flow on the reaction. Reactive polyamide 6 (PA6) was selected for the study. The end groups of this PA6 are not blocked, and each long chain has a carboxyl end group and an amino end group. The carboxyl end group can react with the amino end group in the melt and produce longer

TABLE I
Molecular Characteristics and Properties of PA6

Polymer	M_n (kg/mol)[a]	M_w/M_n[b]	Carboxyl groups per chain	Amino groups per chain
PA6	22	1.9	1	1

[a] Number-average molecular weight.
[b] Weight-average molecular weight/number-average molecular weight.

chains, which can be attributed to the polycondensation reaction. The reaction product is PA6 with a higher molecular weight, which is compatible with the reactants and keeps the system in a homogeneous state. The first step of this work consisted of characterizing the progress of the reaction in a homogeneous melt by a new rheological method and getting the reaction kinetic parameter. The second part of this work was devoted to studying the effects of different shear flows on the polymeric reaction in a homogeneous melt. By comparing the reaction kinetic parameters obtained under different shear flows, we investigated the effects of the shear flow on the polycondensation reaction rate constant and tried to give a reasonable explanation.

EXPERIMENTAL

Materials

The molecular characteristics of the polymer employed in this study are listed in Table I. The PA6 used in this kinetic study of the polycondensation reaction was supplied by Jinlun Group Co. (Cixi City, Zhejiang Province, China) with an average of one —NH_2 end group and one —$COOH$ end group per chain. Therefore, it could also be called an active PA6 for the polycondensation reaction would reoccur at a higher temperature.

First, the active PA6 was molded into plates under 10 MPa at 240°C for 5 min. The thickness of the plates was about 1 mm. After that, the PA6 plates were cut carefully with a razor blade to form discs with a diameter of about 25 mm. Then, the PA6 plates were dried at 80°C *in vacuo* for 2 days and stored *in vacuo* to minimize the moisture sorption.
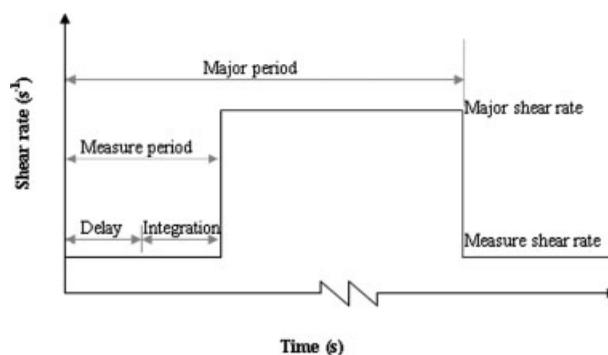
Rheological measurements

After a PA6 plate was put into a rotational rheometer (Gemini 200 HR, Bohlin Instruments, United Kingdom), the viscosity of the material was monitored with time at 250°C. To study the effects of the different shear flows, an oscillatory-shear mode and a steady-shear mode were employed. When the reactive system was under oscillatory shear, the strain amplitude was 0.1, which lay in the linear viscoelastic region, and the angular frequency was between 0.3 and 30 rad/s. When the reactive system

was under steady shear, the shear rate changed from 0.1 to 30 s^{-1}.

The viscosities of the reactive system under different shear rates were monitored. To correlate the apparent shear viscosity with the progress of the reaction, it is natural to choose a zero-shear viscosity as an indicator. Therefore, a new measurement technique should be employed to eliminate the shear effects on the material. The measurement method employed here is illustrated in Figure 1. As PA6 shows Newtonian behavior under low shear rates,[16] a relatively low shear rate would be chosen, and the viscosity measured under this low shear rate could be treated as the zero-shear-rate melt viscosity (η_0). First, the samples were sheared under a low shear rate (i.e., the measurement shear rate) for a measured period, and then the shear rate was raised to a high shear rate (i.e., the major shear rate). After that, the shear rate was reduced to the low shear rate again to measure the temporal viscosity and raised to the high shear rate again. The viscosity data obtained under the same low shear rate reflected the progress of the reaction, which happened mostly under the high shear rate.

Figure 1 shows that the measurement period was divided into a delay section and an integration section. On the one hand, as there is a relaxation for the polymer to reach a new equilibrium after a sudden change in the shear rate, the delay section should be set longer than the maximum relaxation time of the polymer. Experimental data prove that the relaxation time of PA6 is no more than 20 s at 250°C. On the other hand, the measurement period should be much shorter than the major period. Because the measurement period is much shorter than the total period, it is thought that the measurement period has little effect on the reaction at the high shear rate. The experimental parameters are shown in Table II.

After the samples were reacted for a given time, they were removed from the rheometer and then quenched for the end-group determination.

Figure 1 Schematic description of the measurement method used for the rheological measurements in this study.

TABLE II
Experimental Parameters for the Rheological Method

	Major shear rate	Measurement shear rate	Major period	Measurement period	
				Delay	Integration
Steady shear	0.1–10 s^{-1}	0.1 s^{-1}	300 s	20 s	20 s
Oscillatory shear	0.3–100 rad/s	0.3 rad/s	$\sim$ 300 s	20.9 s[a]	20.9 s

[a] The time at 0.3 rad/s was about 20.9 s.

End-group determination

The carboxyl contents of PA6 before and after the rheological experiments were determined by the Waltz–Taylor method.[17] The sample (ca. 0.5 g) removed from the rheological experiment was dissolved in 25 mL of benzyl alcohol heated to 100°C. After that, the pH value of the mixture solution was monitored by an electrolyte-type pH meter instead of titration with a 0.1N KOH/ethanol solution. From the pH value, the concentration of the carboxyl acid was obtained. The data were expressed as the means plus or minus the standard deviation for $n = 3$.

RESULTS AND DISCUSSION

Reaction kinetic analysis

There are three major reversible reactions in the kinetic scheme of PA6: ring opening, polycondensation, and polyaddition. These are shown in Table III. The polycondensation is most important because it determines the final degree of polymerization at equilibrium.[18] The parameters used for the reaction rate constant and equilibrium constant are given in Table IV.[19]

The viscosity (or complex viscosity under oscillatory shear) of active PA6 was recorded by a rheometer under steady shear and is shown in Figure 2. The shear rate was 0.1 s^{-1}. As the viscosity was measured under a relative low shear rate, it could be treated directly as η_0 because PA6 shows Newtonian viscosity behavior under this range.[16] η_0 is known to depend on the weight-average molecular weight (M_w) to 3.4 powers in the entangled system:

$$\eta_0 = K(M_w)^{3.4} \tag{1}$$

where K is the coefficient (its value for PA6 at 250°C is 9.5×10^{-14} Pa s).[20] M_w can be obtained as follows in the polycondensation reaction:[21]

$$M_w = M_0[(1 + p)/(1 - p)] \tag{2}$$

where M_0 is the mean molecular weight of a structural unit (the value for PA6 is 113 g/mol) and p is the extent of the reaction for the polycondensation. Then, we can correlate the viscosity with the extent of the reaction with eqs. (1) and (2). The extent of the reaction is also the conversion of the carboxyl end group (or amino end group) in this study. The plots of the conversion obtained from the viscosity by this new rheological method with time are shown in Figure 3.

The conversion of the reaction (x) was also obtained by carboxyl-end-group determination:

$$x = (c_a - c)/c_a \tag{3}$$

where c is the temporal concentration of the free carboxyl group and c_a is the total concentration of the carboxyl group, including amide linkages in PA6 chains (the value here is 8.85 mol/kg; see Fig. 3). The reaction conversions calculated according to the rheological method are close to the values obtained from the end-group determination method. This indicates that the aforementioned rheological analysis for the reaction conversion could be a useful method for the study of reaction kinetics.

Polyamidation, however, has been found to be second-order with respect to the functional groups throughout its course, in conformity with monofunctional amidations.[22] The forward reaction is a condensation reaction that increases the chain length

TABLE III
Kinetic Scheme for the Polymerization of PA6 in the Liquid Phase

Ring opening	$C_1 + W = P_1$
Polycondensation	$P_n = P_m = P_{n+m} + W$ (n = 1, 2, 3 . . .; m = 1, 2, 3 . . .)
Polyaddition	$P_n + C_1 = P_{n+1}$ (n = 1, 2, 3 . . .)

[a] C is caprolactam. P_n and P_m are polycaprolactam. W is water molecule.
[b] $P_n + P_m = P_{n+m} + W$.

TABLE IV
Parameters for the Reaction Rate[a] and Equilibrium Constant[b]

A (kg/mol h)[c]	E_a (J/mol)[d]	ΔH (J/mol)[e]	ΔS (J/mol K)[f]
1.8942×10^{10}	9.7365×10^4	-2.4877×10^4	3.9846

[a] $k = A \exp(-E_a/RT)$. R is gas content. T is absolute temperature.
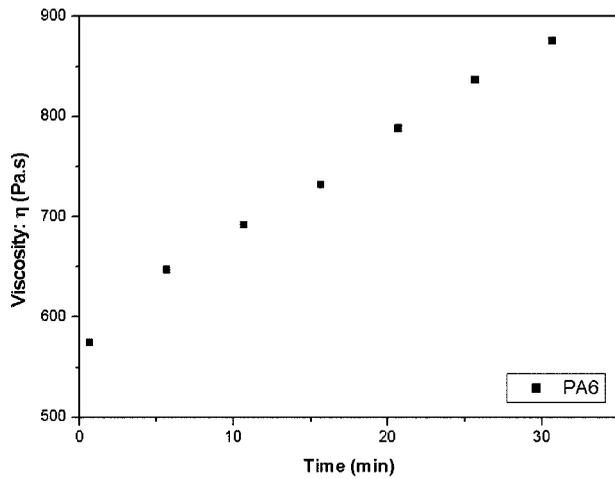[b] $K = \exp[(\Delta S - \Delta H/T)/R]$.
[c] Arrhenius frequency factor.
[d] Activation energy.
[e] Change in the enthalpy.
[f] Change in the entropy.

**Figure 2** Plots of the viscosity at 250°C versus the time for active PA6.

and produces water, whereas the reverse reaction is a hydrolysis reaction that breaks chains. As the initial concentrations of the carboxyl end group and amino end group are the same, the evolution of the carboxyl end group can be shown, as long as there is no leak of moisture from the rheometer:

$$-\frac{dc}{dt} = kc^2 - k'(c_0 - c)(c_a - c) \qquad (4)$$

where k and k' are the rate constants of the forward reaction and reverse reaction, respectively, and c_0 is the initial concentration of free carboxyl end groups (or amino end groups) in the experiment (the value is 0.0455 mol/kg). Then, the initial conversion (x_0) can be calculated as follows:

$$x_0 = (c_a - c_0)/c_a \qquad (5)$$

The value is 0.9949. If the right part of eq. (4) is 0, the equation for the equilibrium conversion (x_{eq}) is
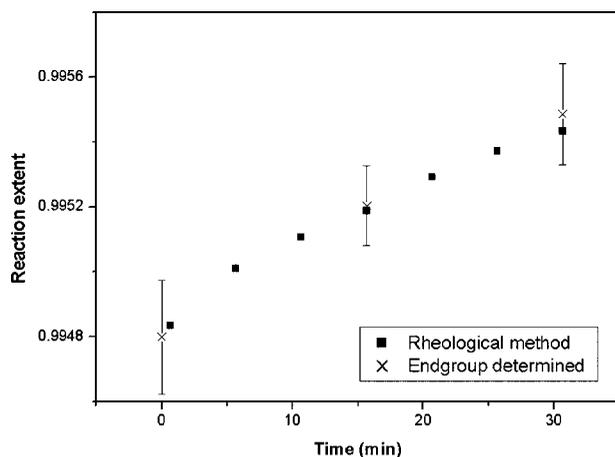
Figure 3 Plots of the reaction extent versus the time by different methods.

$$K = \frac{x_{eq}(x_{eq} - x_0)}{(1 - x_{eq})^2} \qquad (6)$$

where K is the equilibrium constant and its value is equal to k/k'. As K for the reaction between the carboxyl and amino groups has been calculated to be about 500 at 250°C, x_{eq} can be also calculated to be 0.9977.

Equation (4) can be written with x as follows:

$$\frac{dx}{dt} = kc_a\left[(1 - x)^2 - \frac{1}{K}x(x - x_0)\right] \qquad (7)$$

Rewritten for integration, the equation becomes

$$\frac{dx}{(1 - 1/K)(x - a)(x - b)} = kc_a dt \qquad (8)$$

where a and b are the roots of eq. (7) and their values are 1.0044 and 0.9977. Equation (8) is integrated with $x_{t=0} = x_0$, and yields

$$\frac{1}{c_a(1 - 1/K)(a - b)} \ln\frac{(x - a)(x_0 - b)}{(x - b)(x_0 - a)} = kt \qquad (9)$$

This is the equation for k based on the second-order reaction kinetics.

Figure 4 shows plots of the conversion of the reaction with time based on the second-order reaction kinetics given by eq. (9). The experimental data can be well fitted by the second-order reaction kinetics. With eq. (9), k can be calculated to be 0.087 kg/mol min, which is close to the documented value of 0.06 kg/mol min in Table IV.[19]
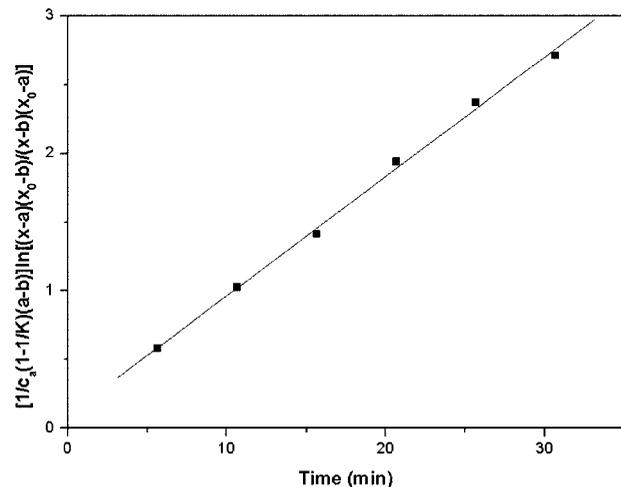
Figure 4 Plots of the conversion versus the reaction time based on the second-order reaction kinetics given by eq. (9).

Effects of the shear flow on the polymeric reaction

The apparent reaction rate constants in different shear modes are shown in Figure 5. The reaction rate constant decreases with an increase in the shear rate. This is not in agreement with the common wisdom. Many research studies have suggested that the reaction rate increases as the flow intensity increases, and Feng and Hu[23] studied how mixing increased the reaction rate of the complementary functional groups in detail. Although the reactive system in this study was different from that reported, the results of this experiment were unexpected nevertheless. The common point of view is that the shear flow increases the probability of collision of the functional groups in a heterogeneous reactive system by increasing the interfacial area. This obviously could not simply be applied to the homogeneous reactive system in this study.

A possible reason for the results of our experiment is that the reverse reaction of polycondensation was relatively raised by the shear flow. Welp et al.[24] showed that segments in the central sections are less mobile than those in the end sections. The functional group in the middle is more shielded by a backbone chain than that at the end. When the reactive system is under shear flow, the steric hindrance is reduced by the shear flow; this extends the chains, exposing the mid-functional groups. This implies that the functional groups in the middle will have a higher probability of meeting complementary functional groups in the shear flow, and this will increase the reverse reaction.

As the products of the reverse reaction, the two complementary functional groups stay nearby under quiescent conditions, and this provides a greater probability of meeting again for the forward reaction. This is different when the reactive system is under shear flow. The two complementary functional groups produced by the reverse reaction move away from each other under shear flow, and this greatly reduces the probability of meeting again for the forward reaction.

As the collision frequency of the complementary functional groups can also be increased by the shear flow,[23] there are two contrary effects of the shear flow on the reaction. A question should be asked here: which one is more dominant in the process under the shear flow? When two complementary functional groups approach within a capture radius (a), the reaction occurs.[25] However, if the collision frequency is increased, the distance moved by the functional group should be no less than an equilibrium radius of gyration (R). a is much smaller than R for polymer melts. That means when the complementary functional groups just move away from each other under shear flow, the forward reaction is greatly depressed because a is very small, and at the same time, the shear flow is not powerful enough to lead to more collisions of functional groups because R is bigger. Therefore, the forward reaction is depressed under the shear flow.

This phenomenon is also seemingly supported by the dynamics of polymer chains.[24] Because of highly anisotropic friction with the neighboring chains, the relaxation (or snakelike motion) of the long chain is a slow process in the static state. If the system is put under shear flow, the relaxation of the long chain is quickened. As such, when two complementary functional groups are located within a under the shear flow, the probability for them to collide is lower than that in the static state because the quicker relaxation process of the long chains makes them close to one another for a shorter period of time than that in the static state. The forward reaction is more susceptible to the relaxation of long chains because the reactants are two large molecules, and the reverse reaction is insusceptible because there is a small molecule (a water molecule) involved. Therefore, the shear flow can reduce the forward reaction by shortening the relaxation time of the long-chain reactants.

Another possible explanation for the phenomenon is that phase separation occurs. In many publications, the polydispersity of a polymer in a polymerization-induced phase-separation process has been studied in the presence of flow.[26–28] The shear flow shifts the thermodynamic state of a reactive system and leads to phase separation. Then, the homogeneous reactive system translates to the heterogeneous system. The phase-transition phenomenon caused by the elongation and orientation of macromolecules in a shear flow field reported in these studies might lead to a reduction of the reaction rate.
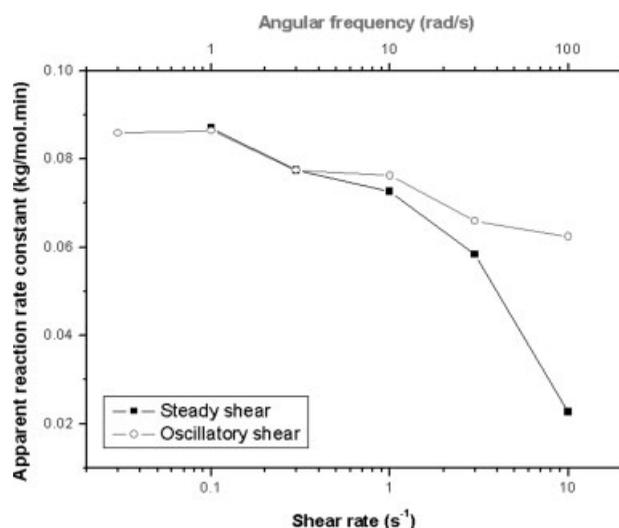
Figure 5 Plots of the apparent reaction rate constant versus the shear rate for the steady-shear mode and the angular frequency for the oscillatory-shear mode.

The shear rate of oscillation ($\dot{\gamma}$) is given by

$$\dot{\gamma} = \dot{\gamma}_0 \cos(\omega t) = \omega \gamma_0 \cos(\omega t) \qquad (10)$$

where $\dot{\gamma}_0$ is the maximum shear rate of oscillation, γ_0 is the strain amplitude, ω is the angular frequency, and t is the time. When the results obtained under oscillatory shear were compared with those obtained under the corresponding steady shear, we saw that the reaction rate constants were exactly the same under a low shear rate in different shear modes, as shown in Figure 5. However, with an increase in the shear rate, the decrease in the reaction rate constant under steady shear was much greater than that under oscillatory shear. This can be attributed to the difference in the morphology of the long chains under different shear flows. As mentioned previously, the shear flow extends the chains and exposes the mid-functional groups, especially under steady shear. Although the system is under high-frequency oscillatory shear, the morphology of the long chains is not much changed because it is mainly affected by the strain amplitude. Therefore, with an increase in the frequency under oscillatory shear, the morphology of the long chains does not change much, and the reaction rate constant does not decrease much.

CONCLUSIONS

In this study, the effects of the shear flow on a homogeneous polymeric reaction have been studied by a comparison of the reaction kinetics of the postamidation of PA6 under different shear flows. A new rheological method has been used to correlate the change in the rheological properties of the reactive system with the extent of the reaction to study the reaction kinetics of the polycondensation of PA6. The reaction rate constant has been calculated to be 0.087 kg/mol min at 250°C, which is close to the documented value. A new practical technique has been used to study the effects of the shear flow on a homogeneous polymeric reaction. In contrast to common wisdom, the reaction rate constant decreases with an increase in the shear rate. This phenomenon can be attributed to the simultaneous increase in the rate of the reverse reaction and decrease in the rate of the forward reaction. In addition, the reaction rate constant decreases slightly under oscillatory shear but strongly under steady shear. This result can be attributed to the different morphologies of the long chains under different shear modes.

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