Kinetic and Rheokinetic study of Dicarboxylic Fatty Acid Chain Extension Using a Dioxazoline Coupling Agent

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ABSTRACT: A kinetic and rheokinetic study of the condensation reaction of a dicarboxylic fatty acid, Pripol®1009 (C36), and a dioxazoline coupling agent (1,3-Phenylene)bis(2-Oxazoline) (OO) was made. The kinetic study showed a similar reactivity of the two acid groups of C36 and also a similar reactivity of the two oxazoline groups of OO. The reaction kinetics can be described using a second-order kinetic model. A kinetic constant $k = 16.1 \times 10^{-4} \text{ mol}^{-1} \text{ s}^{-1}$ at 156°C with an activation energy $E_a = 80.6 \text{ kJ}$ mol⁻¹ was calculated. A rheological evaluation of the reactants and the obtained polymers showed that the reactive system had Newtonian behavior during all the reaction times for shear rates lower than 100 s⁻¹. Using this kinetic modeling and measured viscosity evolution of the reactive system at different temperatures, rheokinetic models were proposed for viscosity evolution with the molar mass evolution of the synthesized polymer and the reaction time and conversion. Viscosity evolution of the reactive system during the first 10 min, corresponding to a typical mean residence time in reactive extrusion, were calculated using the proposed rheokinetic model. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 1017–1024, 1999

Key words: dicarboxylic fatty acid; dioxazoline; condensation; kinetic; rheokinetic; reactive extrusion

INTRODUCTION

Studies concerning flow mechanisms and modeling of a reactive extrusion process require information about the viscosity evolution in the different screw elements at different temperatures and shear rates.^{1,2} This type of rheokinetic modeling implies good control of the reaction conditions, side reactions, and kinetics. The estimation of viscosity evolution with molar mass, shear rates, and temperature is necessary for the rheokinetic modeling of a reactive extrusion process.

The addition of highly reactive coupling agents during the last steps of polymer synthesis by polycondensation leads to high molar mass polymers at a relatively low temperature, a short reaction time, and without the need for a vacuum.^{3,4} Dioxazolines were used as coupling agents of carboxyl terminated polyesters^{5–9} and polyamides.^{4,10} Dioxazoline can also be used to introduce oxazoline functions into a carboxyl-terminated polymer with the intention of synthesizing block and multiblock copolymers by reaction with other acid terminated polymers.

The aim of this study is to establish kinetic and rheokinetic models for a dicarboxylic fatty acid (C36) and a dioxazoline (OO) coupling reactions to use them to establish flow models of these reac-

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tions by reactive extrusion. Kinetic modeling will first be established, then using these kinetic and rheological models from nonreactive specimens having different molar masses, a rheokinetic model will be proposed. Viscosity evolution calculated using these models will be compared to the evolution of the experiments.

EXPERIMENTAL

Materials

The reactants used in this study were a fatty dicarboxylic acid (Pripol®1009 from Unichema International) containing 0.1% monomer (C18), 98% dimer (C36), and 1% trimer (C54). (1,3-Phenylene)-bis(2-Oxazoline) (OO) was supplied by Mikuni Chemical. Reactants were used as received without any further purification.

Apparatus

For the analysis of the C36/OO reaction, size exclusion chromatography (SEC) was performed using a Waters 510 device equipped with a 6000A pump, a U6K injector, and a double detector (UV at $\lambda = 254$ nm and differential refractometer R401). Tetrahydrofurane (THF) was used as a solvent at a 1.0 mL/min flow rate and a pressure of 3×10^3 Pa. Columns of Polymer Laboratories gel were used. Naphthalen was used as internal standard for the measurement of OO concentration during the kinetic studies.

Chromatograms of C36/OO standards were obtained using a Waters 410 device equipped with a Spectra Physics Isochrom pump, a R410 refractive index detector, and a Wyatt technology light scattering. A Waters linear column, with separation performance ranging from 5×10^2 to 2×10^6 g mol⁻¹ in a molar mass of polystyrene, was used. Tetrahydrofuran (THF) was used as a solvent, with a flow rate of 0.5 mL min⁻¹, at 23°C.

A Rheometrics RDA II viscoelastimeter equipped with a cone-plate tool having a diameter of 40 mm and a 50- μ m gap, in a steady-state mode, was used for the measurement of the viscosity of the specimens.

Fourier transform infrared spectroscopy was performed using a Nicolet Magna-IR 550 spectrometer. An Ever-GloTM source was used along with a KBr beam splitter and a DTGS-KBr detector.

Table I	Stoechiometric Ratio, Molar Mass, an	nd
Glass Tr	ansition of Each Standard	

Standards	r	$\bar{M}_n \\ (\text{g mol}^{-1})$	$\bar{M}_w \ ({\rm g\ mol}^{-1})$	$\underset{(°C)^{a}}{T_{g}}$
1	0.75	2300	4900	-30.5
2	0.77	2750	5600	-29.1
3	0.79	3600	6200	-25.2
4	0.84	4550	7500	-23.5
5	0.85	4800	8000	-19.2
6	0.89	5000	10,350	-14.7
7	0.92	7350	12,350	-8.9

 $^{\rm a}$ The $T_{\rm g}$ value is defined by the onset point of the transition.

A Mettler TA3000 was used for DSC analysis at a 10°C/min heating rate under nitrogen.

Thermogravimetric analysis (TGA) was performed in a TGA 2950 thermal analyzer from DuPont Instruments. Samples were analyzed under helium.

Kinetic Study

Reactions of C36 and OO were carried out in a four-neck flask equipped with a mechanical stirring apparatus and a nitrogen inlet, and heated in an oil bath. The C36 was first introduced into the flask and stirred until complete temperature stabilization. The OO was then added. A small decrease in the reactant temperature (usually 2°C) was observed before stabilization after 2 min. Samples were removed from the bath after selected time intervals and cooled rapidly in liquid nitrogen.

Rheological Studies

Standard samples with different molar masses were prepared to obtain the molar mass dependence of viscosity. They were synthesized using different OO to C36 stoichiometric ratios (r) in the reactor used in the kinetic study. All reactions were carried out at 160°C under nitrogen during 12 h. They were characterized by SEC and DSC (Table I).

For the rheological test of nonreactive specimens, the rheometer chamber and cone-plate equipment were preheated at the desired temperature. Samples were then placed on the plate. When the chamber temperature was completely stabilized, the gap between the cone and the plate was adjusted at 50 μ m.

For reactive systems, C36 and OO were mixed using a spatula for about 3 min at 60°C (r = 0.97). Then an equivalent procedure than for nonreactive systems was used.

RESULTS AND DISCUSSION

Kinetic Study

In a preceding article concerning the condensation reaction of this OO with a carboxyl terminated polyamide 12, it was found that the two oxazoline groups were similarly reactivity. Supposing that the two oxazoline groups and acid groups have a similar reactivity, the reaction scheme of OO with C36 becomes:

$$\mathbf{O} + \mathbf{A} \xrightarrow{k} \mathbf{E} \mathbf{A} \tag{1}$$

where O, A, and EA are respectively oxazoline, carboxyl acid, and esteramide groups.

The evolution of the different species are:

$$\frac{d[\mathbf{O}]}{dt} = \frac{d[\mathbf{A}]}{dt} = -\frac{d[\mathbf{E}\mathbf{A}]}{dt} = -k[\mathbf{O}][\mathbf{A}] \qquad (2)$$

Defining:

$$A = \frac{[A]_{t}}{[A]_{t=0}}, O = \frac{[O]_{t}}{[O]_{t=0}}, EA = \frac{[EA]_{t}}{[A]_{t=0}},$$
$$r = \frac{[A]_{t=0}}{[O]_{t=0}} \text{ and } K = k[O]_{t=0} \quad (3)$$

The differential eq. (2) becomes:

$$\frac{1}{r}\frac{dO}{dt} = \frac{dA}{dt} = -\frac{dEA}{dt} = -KOA$$
(4)

The relation between A and O is:

$$A = 1 + \frac{O - 1}{r} \tag{5}$$

Combining eqs. (4) and (5) leads to:

$$\frac{dO}{dt} = -KO[O + r - 1] \tag{6}$$

Equation (6) can be rearranged as:

$$\left(\frac{1}{0} - \frac{1}{0 + r - 1}\right) dO = -K(r - 1) dt \qquad (7)$$

Integrating eq. (7) one obtains:

$$\ln\left(\frac{rO}{O+r-1}\right) = -K(r-1)t \tag{8}$$

From eq. (8) we obtain:

$$O = \frac{(r-1)\exp(-K(r-1)t)}{r - \exp(-K(r-1)t)}$$
(9)

or for reaction conversion defined by (10):

$$p = 1 - \frac{[O]_t}{[O]_{t=0}}$$
(10)

we obtain (11).

$$p = \frac{1 + (r - 1)\exp[K(1 - r)t]}{r - \exp[K(1 - r)t]}$$
(11)

A TGA of OO showed an evaporation at 180°C. For this reason the kinetic study was made at temperatures lower than 175°C. This reaction was carried out at different temperatures. SEC evolution of specimens taken at different reaction times are shown in Figure 1. At the initial time, two peaks were observed. The first at elution time $t_e = 15.03$ min is attributed to C36 and the second peak at $t_e = 19.98$ min to OO. When the reaction progresses, these spectra show that the elution time corresponding to the dimer is close to the C36 elution time. This makes measurement of C36 concentration by SEC nonprecise. Using SEC, only the OO concentration was measured, because the two oxazoline functions have a similar reactivity, the O concentration is related to OO concentration by $O^2 = X$. Conversions were calculated using eq. (5); the chemical rate constants were calculated in each cases using the Newton-Raphson algorithm to fit the kinetic model to experimental data. Results are reported in Figure 2(a). It was found that $k = 16.1 \ 10^{-4} \text{ kg}$ mol⁻¹ s⁻¹ at 156°C. The kinetic constants have an Arrhenius temperature dependence. The activation energy (E_a) and the frequency factor (A) were calculated by the least squares method (A = 10.3 $\times 10^{6} \text{ kg mol}^{-1} \text{ s}^{-1}, E_{a} = 80.6 \text{ kJ mol}^{-1}$) These values are in good concordance with those calculated in a preceding article.¹¹ Comparing the ex-



Figure 1 SEC chromatograms at different reaction times for C36/OO reaction at 156° C and $[A]_{t=0} = 0.95 [O]_{t=0}$.

perimental data and the calculated evolution of the different reactants, a close correlation was observed [Fig. 2(a)]. This shows also that a similar reactivity hypothesis of the two oxazoline groups of OO and of the two acid functions was also realistic.

In reactive extrusion, the mean residence time is generally lower than 10 min. As seen in Figure 2, the reaction conversion at 156°C is 0.75. This shows that the reaction is too slow at this temperature to be realized by reactive extrusion. In a twin-screw extruder, if some precautions concerning the screw profile were taken, the reaction could be realized at a high temperature without evaporation of OO. Using this kinetic data, the kinetic rates and conversions with reaction time at high temperatures were calculated [(Fig. 2(b)]. Conversion higher than 0.95 is obtained at 230°C in 5 min. This shows that the reaction can be realized, from a kinetic point of view, by reactive extrusion for temperatures above 200°C.

Rheokinetic Study

The aim of this study was to establish the rheokinetic modeling necessary for reactive extrusion modeling. In the used twin-screw extruder (Clextral, BC 21 corotating intermeshing extruder), and under normal conditions, the maximum shear rate is approximately 100 s^{-1} . For this reason, the rheokinetic behavior will be only analyzed for a shear rate maximum of 100 s^{-1} . It is well known that polymer melts show a Newtonian limit and a region of diminishing viscosity with increasing shear rate. The Newtonian shear rate limit depends on the polymer structure and decreases with decreasing temperature and with increasing molar mass.^{10,12}

The rheological evolution with shear rate of the reactive system at initial time was made at 80°C (r = 0.97). At this temperature the reaction is very slow, and the conversion at the end of the measurements can be considered as zero. As shown in Figure 3, a Newtonian behavior is obtained for this reactive system for shear rates lower than 100 s⁻¹. Because the Newtonian limit increases with temperature, the reactants have also at initial time a Newtonian behavior at higher temperatures. Specimens that had completely reacted were also analyzed for temperatures above 130°C (Fig. 4). Here a Newtonian behavior was also observed.

Because the reactive system is Newtonian at initial and final conversion it can be deduced that the reactive system, at the studied temperatures,



Figure 2 (a) Comparison between the experimental values and the calculated values (full curves) at 131, 146, and 156°C ($[A]_{t=0} = 0.95 \ [O]_{t=0}$). (b) Extrapolation at 230, 260, and 290°C of the C36/OO reaction ($[A]_{t=0} = 0.95 \ [O]_{t=0}$).

has a Newtonian behavior for all the reaction time when conducted at a shear rates lower than 100 s^{-1} . This greatly simplifies the rheokinetic modeling.

Viscosity related to weight molar mass (\bar{M}_{w}) is given in eqs. (12) and (13) for molar mass,¹² respectively, lower and higher than the critical molar mass (M_{c}) , which is about 6800 g mol⁻¹ for this system.



Figure 3 Evolution of the shear stress vs. the shear rate of C36/OO blend at initial time (*T*: 80°C and $[A]_{t=0} = 0.95 \ [O]_{t=0}$).

$$\eta_0 = B_1 M_w^{n_1} \tag{12}$$

$$\eta_0 = B_2 \bar{M}_w^{n_2} \tag{13}$$

 M_w expressed as a function of the reaction conversion (*p*) is (13):

$$\bar{M}_{w} = M_{0} \frac{\left(1 + rp^{2} + \frac{4r}{r+1}p\right)}{1 - rp^{2}}$$
(14)

Where

$${M_0} = rac{{{M_{{
m{OO}}}} + {M_{{
m{C36}}}}}}{2}$$

Replacing p from eq. (11) in eq. (14), M_w can be expressed as a function of reaction time.

$$\bar{M}_{w} = M_{0} \frac{\begin{pmatrix} 1 + r\left(\frac{1 + (r - 1)\exp[K(1 - r)t]}{r - \exp[K(1 - r)t]}\right)^{2} \\ + \frac{4r}{r + 1} \frac{1 + (r - 1)\exp[K(1 - r)t]}{r - \exp[K(1 - r)t]} \end{pmatrix}}{1 - r\left(\frac{1 + (r - 1)\exp[K(1 - r)t]}{r - \exp[K(1 - r)t]}\right)^{2}}$$
(15)

 M_w from eq. (15) can be introduced in eqs. (12) and (13) for a viscosity evolution modeling.

The viscosity evolution of the reactive system were measured for reactions at different temperatures. Using eqs. (12), (13), and (15), η was expressed as a function of the calculated molar mass. Results are given in Figure 5. For these experiments, $n_1 = 1.4$ and $n_2 = 3.3$ were measured.

 B_1 and B_2 have an Arrhenius temperature dependency, activation energy (E_{aB}) is independent of molar mass:

$$B_1 = 1.56 \ 10^{-6}$$
 at 160°C,
 $B_2 = 7.74 \ 10^{-14}$ at 160°C,
 $Ea_B = 56 \ \text{kJ g}^{-1} \ \text{mol}^{-1}$

Also using eqs. (6), (7), and (9), viscosity evolution with reaction time can be calculated. Examples of calculated evolution are given in Figure 6. Compared to experimental data, good agreement was obtained. It is also interesting to note that a polyester amide having a molar mass higher than M_c were quickly obtained; for this reason, and



Figure 4 Evolution of the shear stress vs. the shear rate of the C36/OO polymer at the final time at the same temperature as the rheokinetic measurements. $([A]_{t=0} = 0.95 [O]_{t=0} \text{ and } \bar{M}_w = 30,000 \text{ g} \cdot \text{mol}^{-1}$.

with a good approximation, it can be considered that viscosity evolution with reaction time can be modeled using only eqs. (13) and (15). All these results show that the kinetic and rheokinetic models and data are correct, and that a secondary reaction, if any, had no perceptible



Figure 5 Effect of molar mass on Newtonian viscosity at 150, 160, and 170°C.



Figure 6 Comparison between the experimental and the calculated viscosity (full curves) at 150°C (at a shear rate: 10 s⁻¹ and $[O]_{t=0} = 0.97 [A]_{t=0}$).

effect on the viscosity evolution of the reactive system.

CONCLUSIONS

High molar mass polyester amides were prepared by reacting small molar mass dicarboxylic fatty acid and a dioxazoline. A second-order kinetic model was proposed. Kinetic constants and activation energy were measured. Using these models and data, the kinetic evolution was calculated at a high temperature. This showed that the reaction could be realized with a reaction time compatible with reactive extrusion. Rheokinetic models were proposed and verified.

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