Extracting Kinetic Parameters of Aniline Polymerization from Thermal Data of a Batch Reactor. Simulation of the Thermal Behavior of a Reactor

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ABSTRACT: A simulation model of the thermal behavior of a reactor during aniline polymerization is proposed. The model takes into account the polymerization mechanism together with heat production and dissipation. The temperature–time profiles can be simulated with different kinetic parameters. The model is used for two purposes: to extract kinetic parameters by fitting experimental temperature–time profiles of a cooled agitated batch reactor; and to estimate the temperatures changes occurring in a reactor under different experimental conditions to find the best conditions for industrial production of polyaniline. The rate equation used includes two rate constants: one in the absence of polymer (k_1) and another in the presence of polymer (k_2). The thermal factors, such as the heat transfer coefficient and the reaction enthalpy, are experimentally measured. A computer program is written that fits the experimental data using different kinetic parameters. The data analysis shows a temperature peak (T_{max}) whose magnitude decreases when k_2 decreases, whereas it is not affected by k_1. The time to reach the T_{max} is inversely proportional to k_1 and k_2. The model allows obtaining the kinetic parameters in different reaction media, e.g. varying the concentration of acid. The model is used to simulate the thermal behavior, to polymerize $1M$ of aniline: in one step the temperature of the reactor will increase till 82°C, such thermal runaway will cause polymer degradation, successive additions of portions of the total oxidant amount, paced at defined time intervals, is devised to maintain low temperatures while producing the same amount of polymer. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 39409.

INTRODUCTION

Conducting polymers have become interesting material for technological applications,[1–8] as it is evidenced by the awarding of 2000 Nobel Prize to A. Heeger, A.G. McDiarmid and H. Shirakawa.[9,10] Polyaniline (PANI) is the most studied intrinsic conducting polymer. In our days there are different ways to synthesize PANI, among them electrochemical polymerization and oxidation of aniline using a chemical oxidant.[11–14] It is accepted that the physicochemical characteristics of the polymer depend on the method of synthesis.[1,15–19] Chemical polymerization occurs with heat production,[20] and it is known that the high temperatures produce degradation of the polymer. Even in a cooled batch reactor, the production of heat and the end of the polymerization is observed as a peak in a temperature–time

(T–t) plot. Therefore, the temperature of the polymerization solution departs from that of the cooling bath, depending on the amount of heat produced and the heat transfer of the reactor. The polymer chain grows trough a redox process, where the growing chain is oxidized by the oxidant (e.g. persulfate ion) to its fully oxidized state (pernigraniline) and such state is nucleophilically attacked by aniline monomer with becomes attached to the chain end. The nucleophilic attack produces a chain in the reduced state (leucoemeraldine), which is then reoxidized by another oxidant molecule. When all the oxidant is used, the polymer is oxidized to the emeraldine state. If an excess of oxidant is used (e.g. more than 1.25 moles of persulfate per mole of aniline) the polymer remains in the fully oxidized state and is attacked by other nucleophiles present in the reaction media (water, chloride) causing polymer degradation. Therefore, it is

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advisable to polymerize under excess of aniline. In a cooled batch reactor, the temperature peak is only observed at the end of the polymerization process. At the beginning of the polymerization, there are no growing chains and the reaction follows a different mechanism, with a small rate constant.

The polymerization of aniline has been followed by different methods, such as measuring the concentration of aniline,[21] potentiometry,[22] and calorimetry.[23,24] Adiabatic calorimetry has also been used to obtain kinetic parameters of other kinds of polymerization.[25,26]

However, the calorimetric data obtained during polymerization of aniline has been analyzed only semiquantitatively by measuring the time for the maximum of the peak to occur, whose value is inversely proportional to the polymerization rate. In the best of our knowledge, there is no quantitative analysis on the effect of kinetic parameters on the shape, magnitude, and time position of the T–t peak.

In this article, using the kinetic mechanism proposed in the literature[21,27] and the experimental measurement of T–t profiles (T–t) of PANI's polymerization, the reaction rate and the kinetic parameters of the reaction are measured. The experimental curve (T–t) is used to evaluate the overall heat transfer coefficient (U) of the reactor. The enthalpy of the reaction (ΔH) is obtained, in a separate experiment, from adiabatic calorimetry of the same reaction. Finally the temperature profile reaction is theoretically simulated and is compared with the curve obtained experimentally. The simulated T–t profiles fit the experimental data with kinetic parameters in agreement with reported rate constants data. In that way, the rate constants at different acid concentrations are measured.

Besides, the model allows to simulate the T–t profile of a reactor in other experimental conditions (e.g. aniline concentration = $1M$). The relatively high temperatures ($> 80^\circ$C), which could lead to polymer degradation, could be avoided by a sequence of oxidant additions. The simulation model is used to determine the optimal number of additions and the time span between them that maintains the temperature below a safe value.

EXPERIMENTAL

Kinetic Measurements. Synthesis of PANI

Kinetic measurements were carried out in a polymerization glass vessel reactor of 1 L of capacity (IVASA). The reactor was designed to allow the polymerization, with capacity of production of 5–100 g. The reaction mixture was stirred with a glass propeller with constant rotation speed (500 rpm.), driven by an adjustable stirrer (FBR). The speed of rotation was measured with a stroboscope (Cole-Palmer). The reactor was immersed in a glass container of 15 L of capacity to ensure that the temperature of the cooling fluid do not change during the experience. The container was filled with ice–water mixture agitated by a dual propeller driven by a motor of 1000 rpm and 0.15 HP. The temperature of the reaction mixture was measured using a digital thermometer (Hanna Instruments) with an accuracy of 0.1°C and time response of 1 s. Between experiments, the reactor and the glass helix were washed during 8 h, in a cleaning mixture prepared with equal parts of sulfuric acid and concentrated nitric acid.

The reactor was filled with a solution of aniline ($0.1M$) in aqueous acid (e.g. $1M$ ClH) at 0°C. An equimolar (compared to aniline) amount of ammonium persulfate (APS), dissolved in a minimum amount of acid is precooled (0°C) and added in one portion to the reactor which has reached thermal equilibrium with the bath. As it will be discussed below, 1.25 moles of APS are consumed per each mole of aniline. Therefore, the APS is always in defect. This is necessary because an excess persulfate will oxidize the polymer to the pernigraniline state, which is attacked by water producing chain scission and polymer degradation. The temperature is monitored by an electronic thermometer with storage capabilities (Hanna) during 1 h after oxidant addition. All the reagents used were of analytical grade.

The simulation of the concentration and the temperature profiles were performed using Matlab®.

Adiabatic Calorimetry

The adiabatic calorimetry experiment was performed in a 1 L Dewar flask immersed in a polystyrene foam insulator. The liquid inside was stirred using a magnetic bar and an external magnetic stirrer. The temperature inside the calorimeter was monitored with digital thermometer (CheckTemp) with 0.1°C resolution and 1 s time response. Before determining the reaction enthalpy, the calorimeter constant was determined using the heat of dissolution of concentrated sulfuric acid in water. The heat was calculated from the experimental profile T–t and the amount of added acid in the calorimeter.

In order to determinate the enthalpy of polymerization, the calorimeter was filled with $0.08M$ aniline in 250 mL of the $1M$ ClH solution, and the oxidant was dissolved in 5 mL of $1M$ ClH. The reaction mix and the oxidant solution were precooled to 0°C. The oxidant agent was incorporated to the aniline solution and the T–t profile was measured. The reaction enthalpy was calculated from this profile.

RESULTS AND DISCUSSION

The semi-empirical equations [eqs. (1–4)] used to study the kinetic of polymerization of aniline are based on the Tzou and Gregory work[21]:

$$[ANI]+1.25[Per] \rightarrow [PANI] \tag{1}$$

$$\frac{-d[ANI]}{dt} = \frac{d[PANI]}{dt} = \frac{-1}{1.25}\frac{d[Per]}{dt} = r \tag{2}$$

$$r = k_1.[ANI].[Per] + k_2.[ANI].[PANI] \tag{3}$$

$$\frac{-dT}{dt} = \frac{AU(T_a-T) + r\Delta HV}{VC_p} \tag{4}$$

where, [ANI] is the molar concentration of aniline, [PANI] is the molar concentration of polyaniline, [Per] is the molar concentration of ammonium persulfate, k_1 is the rate constant in absence of polymer,[21] k_2 is the rate constant in presence of polymer,[21,28] T_a is the temperature of the cooling fluid (0°C), V is the mixture reaction volume, r is the reaction velocity, C_p is the specific heat of reaction mixture, and ΔH is the enthalpy of the reaction.

Equation (3) follows Tzou and Gregory,[21] notation. We change it to eq. (5), replacing the concentration of PANI (which could

enter the equation because it is a solid) for an equivalent polymer concentration which is directly the remaining concentration of aniline (1-[ANI]). While the calculation remains unaltered, the notation is clearer.

$$r = k_1 \cdot [ANI] \cdot [Per] + k_2 \cdot [ANI] \cdot (1 - [ANI]) \qquad (5)$$

To calculate the heat transference it is necessary solving the mass and energy balances [eq. (5)]. Therefore, the overall heat transfer coefficient (U), the area of transference of heat (A), the rate constants (k_1 and k_2), and specific heat at constant pressure (C_p), should be estimated.

Concentration Profiles

Figure 1 shows the concentration profile of the polymerization of aniline in an isothermal reactor at $T = 273$K. The profiles are built using the mole balances, eqs. (2–5), with the values reported by Tzou, $[ANI] = [Per] = 0.035M$, $k_1 = 0.001M^{-1}$ min^{-1} and $k_2 = 4.6M^{-1}$ min^{-1}. Considering that $E_a = 44.3 \pm 2.1$ KJ/mol is the activation energy of the reaction, previously reported by Genies and coworkers,[28] it is possible to calculate the Arrhenius constant for this reaction, which is $A = 2.59 \times 10^9 M^{-1}$ min^{-1}, and it is possible to express k_2 as function of the temperature as follows:

$$k_2 = 2.59 \cdot 10^9 \cdot e^{-\left(\frac{46400}{8.314 \cdot T}\right)} m^{-1} \text{min}^{-1}$$

The plots resemble the curves found experimentally by Tzou and Gregory,[21] using the aniline concentration measured by chromatography.

In this article we will show that both rate constants (k_1 and k_2) could be evaluated with a simpler method: by fitting the experimental T–t curve. In the case of an agitated batch reactor with external cooling, it is necessary to consider the heat transfer through the walls of the reactor, incorporating the energy balance [eq. (4)]. The temperature decay curve was used to measure the overall heat transfer coefficient [see Determination of the Overall Heat Transfer Coefficient (U)]. The reaction enthalpy was measured experimentally in an adiabatic reactor [see Determination of the reaction enthalpy (ΔH)].
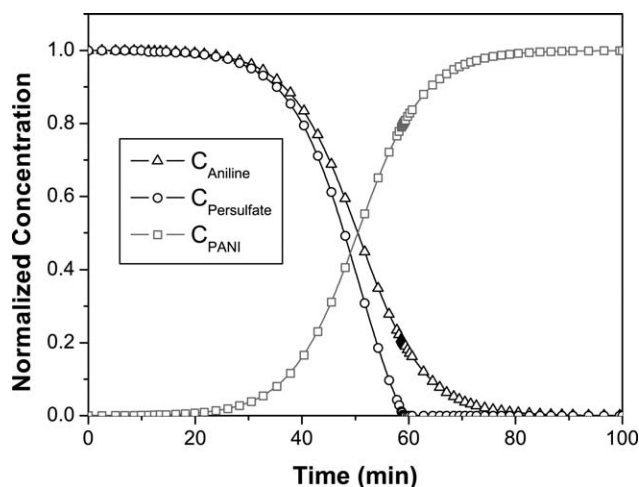

Figure 1. Simulated plot of the concentrations of species during isothermal polymerization. $[ANI] = [Per] = 0.035M$, $k_1 = 0.001M^{-1}$ min^{-1}. $E_a = 44.3 \pm 2.1$ KJ/mol
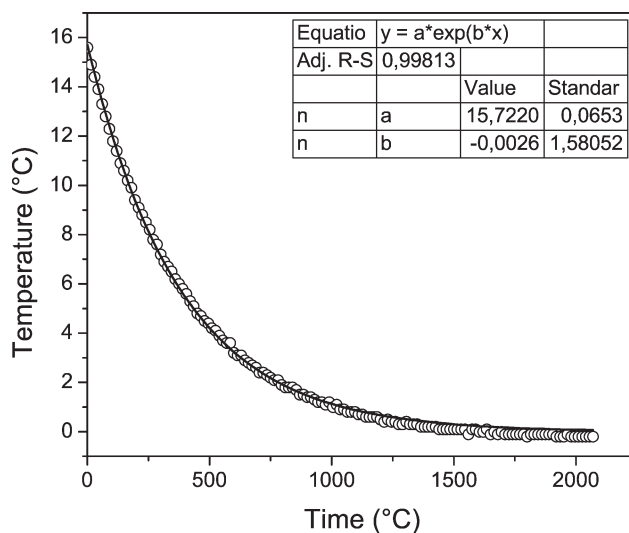

Figure 2. T–t profile of water, obtained using the same conditions of aniline polymerization.

Determination of the Overall Heat Transfer Coefficient (U)

To find out the overall heat transfer coefficient, 1 L of water at 25°C was mixed into the polymerization reactor immersed in 15 L of mixed water–ice bath. The obtained profile T–t is shown in Figure 2.

The reaction mixture is a very dilute solution (containing 0.1 mol of aniline + 0.1 mol APS, 1 mol ClH and ca. 55M of water) and it is possible to assume that it has the properties that are equal to the water. Taking this into account, it is possible to assume that the ratio of convective to conductive heat transfer and the ratio between kinematic viscosity and thermal diffusivity in the reaction mixture are the same to that of water.

The energy balance is shown in the following equation:

$$\frac{-dT}{dt} = \frac{AU(T - T_a)}{VC_{pv}} \qquad (6)$$

Integrating eq. (6) between $T = T_o = 15.6$°C when $t = 0$ s, and $T = Tr$ for $t = t$, eq. (7) is obtained

$$T = T_a - (T_a - T_o)e^{-\left(\frac{AU}{VC_{pv}}t\right)} \qquad (7)$$

Equation (7) reduces to

$$T = (T_o)e^{-\left(\frac{AU}{VC_{pv}}t\right)} \qquad (8)$$

Figure 2

Using eq. (7) and the values from the fit of the profile, the following equation is obtained:

$$\frac{AU}{VC_{pv}} = 0.0026s \qquad (9)$$

Since the effective area of interchange of heat of the reactor (A), was $A = 0.047$ m^2, the volume of water into the reactor $V = 1$
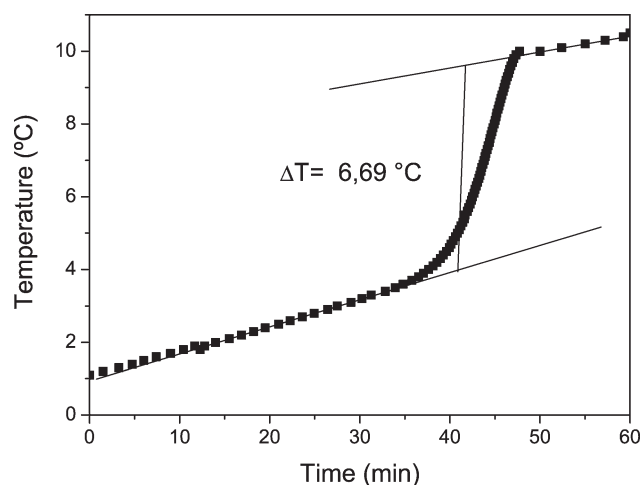
Figure 3. Experimental T–t profile for aniline polymerization in an adiabatic reactor.

$\times\ 10^{-3}\ m^3$, the heat capacity of the solution ($C_{pv} = 4{,}187 \times 10^6\ J\ m^{-3}\ {}^\circ C^{-1}$), replacing into eq. (8), the value of U is calculated directly:

$$U = 231.62 \frac{J}{{}^\circ C.s.m^2} \qquad (10)$$

Determination of the Reaction Enthalpy (ΔH)

The T–t profile obtained in an adiabatic reactor for the polymerization of aniline is shown in Figure 3. From the profile, the enthalpy of the reaction can be evaluated.

As the reaction mixture is diluted, the specific heat capacity could be assumed to be that of water (4.187 J/g °C).

$$m_w \cdot Cp_w \cdot (T_f - To) + \Delta H_{rxion} + m_{eq} \cdot Cp_w \cdot (T_f - To) = 0 \qquad (11)$$

Where the water mass equivalent for this reactor, m_{eq} is 23.08 g, which is obtained by the heat of dissolution of the sulphuric
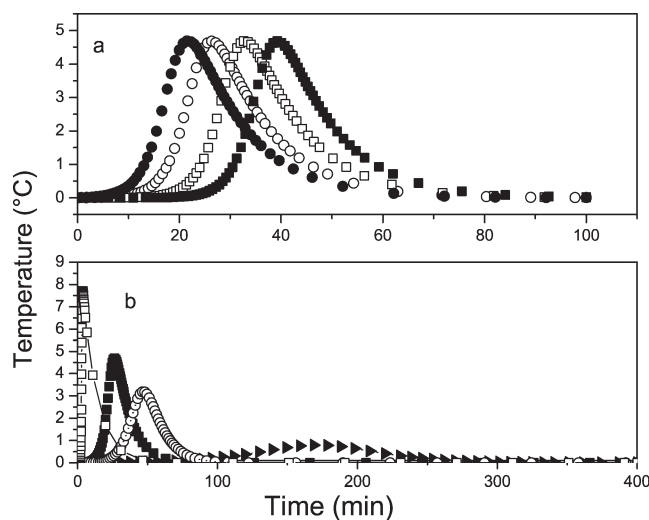
acid, and m_w is the mass of water, T_f is the final temperature reached in the polymerization, and T_o is the initial temperature of the reaction.

Using the temperature jump ($T_f - T_o = 6.69°C$), obtained from the plot, and using eq. (10), the enthalpy of the reaction can be calculated.

From eq. (11), ΔH will be

$$\Delta H = 228.7g \cdot 4.187 \frac{J}{g°C} \cdot 6.69°C + 23.08g \cdot 4.187 \frac{J}{g°C} \cdot 6.69°C$$

Thus, the enthalpy is

$$-\Delta H = 7052.62\ J$$

And the molar enthalpy is

$$\Delta H_{molar} = -440.78 \frac{kJ}{mol_{Aniline}}$$

This value is in close agreement with the value $\Delta H = -439$ kJ mol^{-1}, obtained by Fu and Elsenbaumer.[29]

Simulation of the T–t Profiles

Using the measured parameters it is possible to simulate the T–t profiles trough the appropriate differential eqs (1)–(5).To make the simulation of the polymerization it is assumed that k_2 is the function of the temperature as it is shown in the following equation:

$$k_2 = 2.59 \cdot 10^9 \cdot e^{-\left(\frac{46400}{8.314\,T}\right)} M^{-1} min^{-1} \qquad (12)$$

The changes of k_1 with the temperature are negligible, since k_1 is two or three orders of magnitude smaller than k_2. The value of k_1 is $0.001 M^{-1}\ min^{-1}$. In this way we propose define $\kappa_1 = a.\ k_1$ and $\kappa_2 = b.\ k_2$. Using the Matlab® program we explore the influence of κ_1 and κ_2 in the T–t profile (Figure 4).

As it can be seen [Figure 4(a)], decreasing κ_1 shift the peak to longer times without changing the shape or amplitude of the peak. On the other hand, when κ_2 decreases, both a delay in the reaction time reaction and a decrease of the temperature

Figure 4. Effect of the rate constants (κ_1 and κ_2) on the T–t profile. (a) $\kappa_2 = 1$ for all the simulations: close circle $\kappa_1 = 5$, open circle $\kappa_1 = 1$, open box $\kappa_1 = 0.1$, and close box $\kappa_1 = 0.01$. (b) $\kappa_1 = 1$ for all the simulations: close triangle $\kappa_2 = 0.1$, open circle $\kappa_2 = 0.5$, close box $\kappa_1 = 1$, and open box $\kappa_2 = 10$.
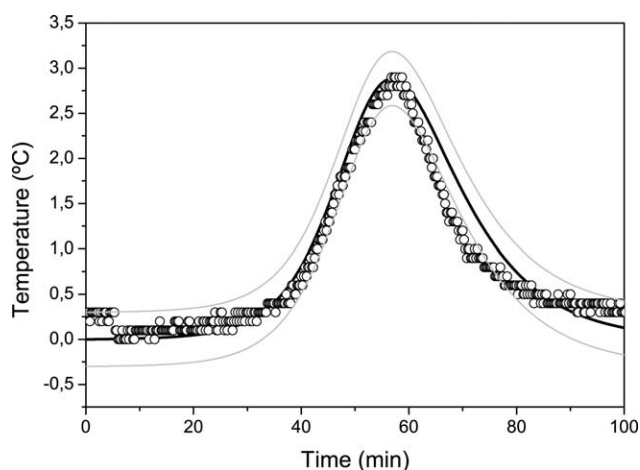

Figure 5. Simulated (line) and experimental data (dots) for aniline polymerization using $[ClH] = 0.25M$, $\kappa_1 = 0.0005$, $\kappa_2 = 1.98$ at 277K. The dotted lines show the range of residual errors in the measurement.

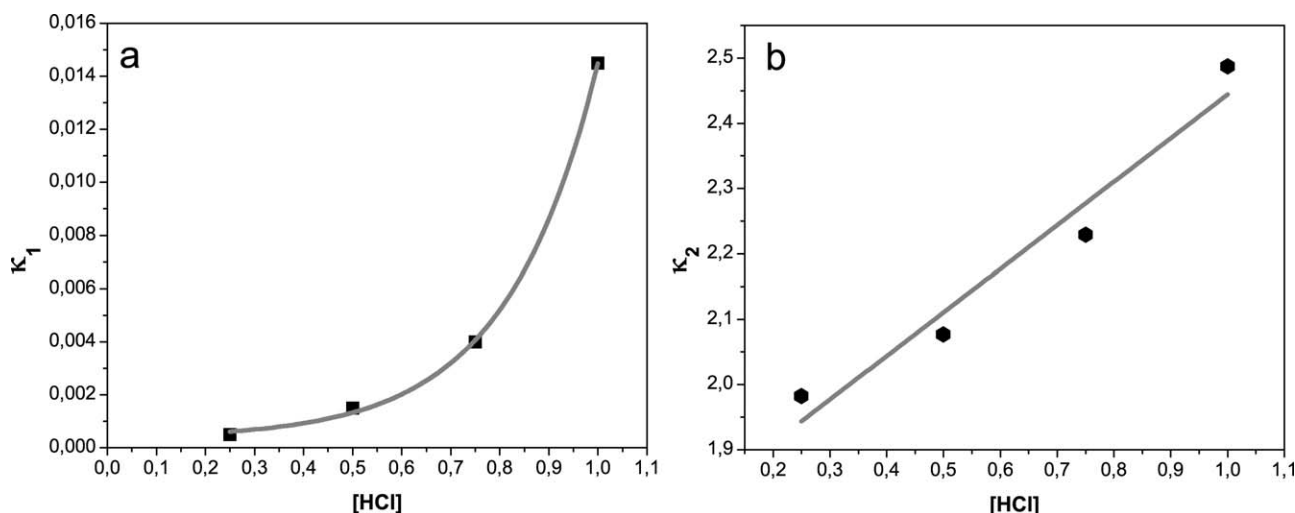**Figure 6.** Rate constant obtained by fitting experimental T–t profiles of aniline polymerization at different acid concentration: (a) κ_1 and (b) κ_2.

jump (with broadening of the peak) could be observed [Figure 4(b)].

Then, several curves are simulated and the T–t experimental profile for conditions similar to those used by Tzou and Gregory,[21] is fitted (Figure 5). As it can be seen, the agreement between the simulated curve and the experimental data is quite good. From the simulations, the rate constants obtained (for $0.035M$ of aniline and persulfate in $0.5M$ of hydrochloric acid), $\kappa_1 = 0.0015$ and $\kappa_2 = 2.1$ at ($T = 277$ K) agree quite well with those obtained by Tzou and Gregory[21] ($k_1 = 0.0009M^{-1}$ $\min^{-1}$ and $k_2 = 2.9M^{-1}$ $\min^{-1}$).

As it can be seen, the proposed method allows calculating the two rate constants, in a simple way only by measuring the temperature and reaction time, instead of the concentration measurements.

Determination of Kinetic Parameters of the Reaction and the Dependence of κ_1 and κ_2 with Acid Concentration

Using the fitting of the experimental data obtained at different acid concentrations (plots in supplementary information), it is possible to evaluate the dependence of κ_1 and κ_2 with ClH concentration [Figure 6(a)]. As it can be seen, κ_1 depends exponentially on the acid concentration [Figure 6(b)] on the other hand, κ_2 dependence with [ClH] is linear as it was proposed by Tzou and Gregory.[21]

Simulation of the Thermal Behavior of an Agitated Reactor During Aniline Polymerization

The kinetic model discussed above, allows calculating the temperature changes in the reactor during polymerization. While most of the polyaniline used in research has been produced at relatively low aniline concentrations (0.1–0.2M), in industrial production it is desired to use larger concentrations (1–2M) to reduce the separation operations (e.g. filtration), to reduce the amount of solvent used (mainly because of the cost of wastewater treatment) and increase the mass output of the reactor. However, in those conditions, the heat produced is large and a thermal runaway explosion has been reported.[30]

Therefore, we simulate the temperature changes occurring in a reactor where $1M$ aniline solution is treated with an equimolar amount of persulfate (in $1M$ ClH). The T–t profile is shown in Figure 7(a).

As it can be seen, the reactor temperature will reach ca. 83.2°C. At such temperatures, the polymer will degrade because of side reactions with water and acid. A simple way to avoid such problem implies pacing the addition of the oxidant during the experience. However, not only the addition should be small but also the reactor should cool down to the initial temperature after each addition. In Figure 7(b), it is shown that the simulation of one scenario where the persulfate is added in three equal portions at 10 min intervals (the time span ensures that all the persulfate is used in each step). As it can be seen, the maximum temperature is lower but still reaches 45°C, likely leading to polymer degradation.

On the other hand, using smaller portions and allowing the reactor to cool down to ca. 2°C after each addition, the temperature can be maintained below 12°C Figure 9(c)]

Therefore, the simulation of the thermal behavior of an agitated batch reactor can be used to control automatically a reactor producing polyaniline.

CONCLUSIONS

The T–t profiles of a cooled batch reactor during aniline polymerization can be simulated using a simple kinetic model, involving a rate constant (k_1) in the absence of polymer and another (k_2) operative in the presence of polymer. The simulation predicts that the magnitude of the temperature jump decreases and the time of the peak increases when k_2 decreases. On the other hand, only the time of the peak increases when k_1 decreases. The results agree with reaction mechanism proposed before.[31]

The simulated curve fit the experimental T–t profile for aniline polymerization and provides rate constant values that are in
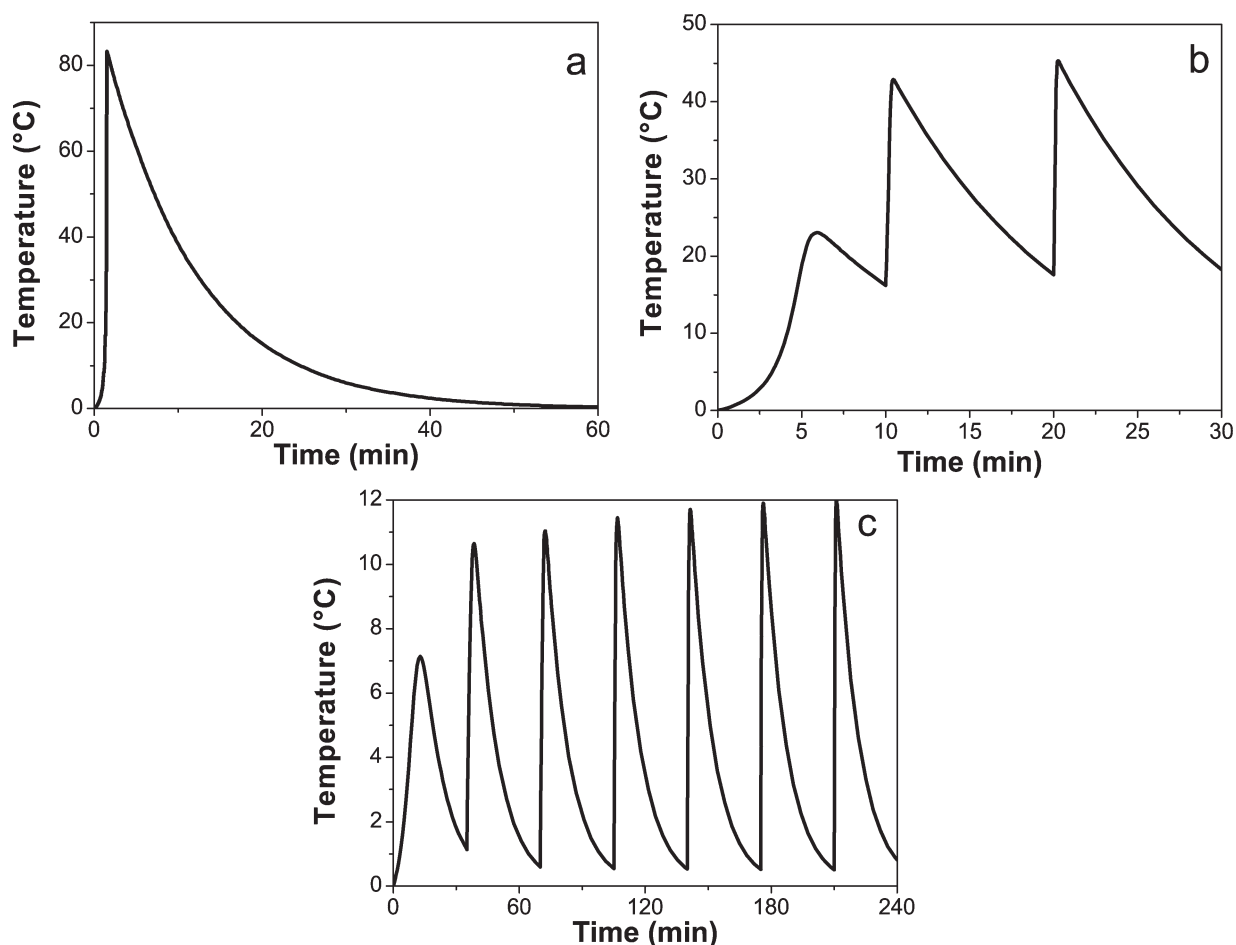
Figure 7. Simulation of the thermal behavior of a cooled batch reactor during aniline (1M) polymerization with the oxidant (equimolar to aniline) added as: (a) one portion; (b) three portions waiting only for the reaction to complete after each addition; (c) seven portions waiting after each addition until the reactor temperature decreases to 2°C.

agreement with those obtained by Tzou and Gregory.[21] The method also allows measuring the rate constants at different ClH concentrations. Whereas k_1 depends exponentially on [ClH], k_2 shows a nearly linear dependence on [ClH].

Ongoing research in our laboratory uses the method to determine the effect of different acid concentrations and counterion nature on aniline polymerization kinetics.

The thermal model of the reactor is used to evaluate different methods of oxidant addition, allowing to control the maximum reactor temperature. In that way, not degraded polymer can be obtained in relatively high (e.g. 1M) aniline solutions.

ACKNOWLEDGMENTS

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