In Situ Determination of Aniline Polymerization Kinetics Through Near-Infrared Spectroscopy

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ABSTRACT: This article describes a method for the determination of kinetic constants in aniline polymerizations performed in the presence of dodecylbenzene sulfonic acid. The procedure was based on the measurement of light absorbances at 668 and 1026 nm. The absorption at 668 nm is related to pernigraniline formation and is ordinarily used for ultraviolet–visible kinetic studies. The absorption at 1026 nm is related to the second overtone of the N—H bonds, which may be used to monitor the aniline consumption along the reaction time. Tzou and Gregory's empirical reaction model was used as a reference for kinetic studies. The best fits were obtained when the kinetic constants were evaluated at 1026 nm because of the lower noise/signal ratio in this spectral region and the smaller sensitivity to the pernigraniline/emeraldine transition during the last stages of the polymerization. The remarkable innovation supplied by this study is the possibility to study aniline polymerizations *in situ* in realistic reaction conditions, which will allow the use of concentrated monomer solutions, large reaction volumes, efficient cooling conditions, and agitation. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 112: 157–162, 2009

Key words: conducting polymers; infrared spectroscopy; kinetics (polym.)

INTRODUCTION

Polyaniline (Pani) has attracted much attention in the last 2 decades because of its potential for different electro/electronic applications.[1–7] In addition, Pani, when compared to other conducting polymers, shows remarkable advantages, including easy chemical synthesis, high stability toward environmental exposition, and special electronic properties, which can be reversibly controlled through charge-transfer doping and protonation.[8]

Among the several methods available for the preparation of Pani, the one-step *in situ* polymerization is perhaps the most attractive.[9,10] Until now, several techniques have been used to study the kinetic parameters of aniline polymerizations. Among them, cyclic voltametry,[11] H-NMR,[12] calorimetry,[13] ultraviolet–visible spectroscopy,[14,15] and gas chromatography[16] have ordinarily been used to perform kinetic analyses. Some of these techniques require that unreal reaction conditions, such as ambient temperature and very low aniline concentrations, be used to carry out the polymerizations. Other techniques depend on the sampling of the reaction medium along the experimental time to monitor the polymerization progress. These invasive techniques are usually expensive, time-consuming, and/or relatively imprecise. Therefore, it may be said that the kinetics of aniline polymerization has not yet been studied under real conditions.

The experimental difficulties described in the previous paragraph are not exclusive of the aniline polymerization problem. As a matter of fact, the kinetic analysis of other polymerization reactions leads to similar challenges because of the complex nature of the reacting polymer systems (and, particularly, of heterogeneous polymer systems). Modern monitoring techniques have greatly improved the kinetic analysis of polymerization reactions by the combination of spectroscopic methods and fiber-optic technology, which allows for reliable *in situ* and inline acquisition of process data. Among them, techniques based on near-infrared spectroscopy (NIRS) certainly are the most important for a large number of reasons.[17] First, absorption in the near-infrared (NIR)

region (800–2500 nm) is much less intense than in the mid-infrared region (2500–25,000 nm), as absorption decreases by a factor of 10–100 when overtones are considered (compared to the fundamental transitions). Second, combinations and overtones of the —OH, —NH, and —CH absorption bands present appreciable intensities in the NIR region, which means that NIR spectra may contain significant amounts of information about the organization of most organic solvents, polymer compounds, and their respective solutions. Third, the smaller absorptivities and larger scattering coefficients at the shorter NIR wavelengths lead to larger scattering/ absorption ratios, which allows for the development of effective diffuse-reflection analytical techniques and provides information about particle sizes and morphology.

The literature about aniline polymerizations and Pani shows that NIRS has been ordinarily used to study the effects of delocalized and localized charge carriers,[18] the evolution of spectroelectrochemical properties during growth and dedoping/redoping of Pani,[19] and the impact of hydrogen bonds on Pani chain conformations.[20] To the best of our knowledge, NIRS has never been used to provide inline and in situ data for the kinetic analysis of aniline polymerizations. For this reason, the main objective of this study was to develop a NIRS-based monitoring technique to provide kinetic parameters for aniline polymerizations in realistic operation conditions for reactions performed in agitated vessels at low temperatures. To reach this objective, we synthesized Pani doped with dodecylbenzene sulfonic acid (DBSA), Pani·DBSA, through a one-step route described elsewhere.[21] The reaction medium was monitored inline and in situ with the help of a fiber-optic probe, which was coupled with an NIR spectrometer. Homemade software was developed to monitor and perform the kinetic analysis in accordance with the empirical model developed by Tzou and Gregory.[16]

EXPERIMENTAL

Synthesis of Pani·DBSA

Pani·DBSA was synthesized through a one-step route in water according to a procedure reported elsewhere.[8,21] The reactions were performed under a normal air atmosphere, as we never observed significant differences among the results obtained from different runs (probably because of the relatively large concentrations of free radicals in the system). In a typical procedure, 7.63 g (0.082 mol) of aniline and 36.13 g (0.110 mol) of DBSA were dissolved in 560 mL of water/isopropilic alcohol (7 : 3) under constant stirring. The medium was kept at −10°C, and

an aqueous solution containing 3.68 g (0.017 mol) of ammonium peroxydisulfate (APS) in 40 mL of water was quickly added to the reaction flask. After 2.5 h, the reaction medium was poured into ethanol, filtered, washed several times with ethanol, and dried.

NIR characterization

The reaction medium was monitored inline and in situ with a transflectance fiber-optic probe, which was coupled with an NIR spectrometer (FOSS 6500 online, Laurel, MD). The width of the probe gap used for sampling was equal to 1 cm. NIR probe scans were performed in full-range mode between 400 and 2500 nm (resolution = 2 nm) at intervals of 1 min. Sample scans were saved as averages of 30 consecutive scans. The NIR spectra were used as obtained, without any sort of preliminary filtering.

Experimental procedures and results

Data acquisition

The reaction medium was kept at low temperatures with the help of a cooling jacket [with a water/ethylene glycol mixture (1 : 1 vol) as cooling fluid] placed around a 1-L glass reactor. Aniline and DBSA were added to the reactor only when the solvent temperature reached −10°C. After stabilization of the reactor temperature, the fiber-optic probe was inserted into the reaction flask. After restabilization of the reactor temperature, the APS solution was quickly added, and collection of the NIR spectra was started. After 2.5 h of reaction, acquisition was stopped, the fiber-optic probe was removed from the vessel, and the reaction data were saved for posterior kinetic analysis.

Kinetic analysis

The kinetic analysis performed here was based on the empirical model developed by Tzou and Gregory.[16] Despite that, one must observe that more involving kinetic models can certainly be used for kinetic interpretation of reaction data. In accordance with the model proposed by Tzou and Gregory, the proposed kinetic analysis used spectral data obtained before the formation of esmeraldine, through the assumption that the NIR absorbance was proportional to the pernigraniline concentration.[22] According to González,[23] the maximum pernigraniline concentration (PE_{max}) can be calculated as follows:

$$PE_{max} = \frac{[APS]}{[Ani]} \Big/ 1.5 \qquad (1)$$

where [APS] and [Ani] represent the initial concentrations of APS and aniline, respectively, in the

TABLE I
Aniline Conversions Under Different Reaction Conditions

Experiment	[Aniline]	[APS]	[DBSA]	Gravimetric conversion (%)	NIR conversion (%)
1	0.045	0.028	0.183	31.19	41.82
2	0.137	0.028	0.183	8.22	13.70
3	0.137	0.137	0.183	57.37	64.70
4	0.092	0.057	0.183	35.62	39.54
5	0.092	0.057	0.183	41.80	42.00

reaction medium and 1.5 is a characteristic stoichiometric coefficient of the reaction. On the basis of the NIR spectra, it is possible to characterize the moment when the formation of pernigraniline is interrupted, as absorptions at 668 and 1026 nm stabilize. Therefore, it is possible to characterize the values of t_{max} and A_{max}, which represent the time and absorbance, respectively, when the concentration of pernigraniline reaches the maximum value. Therefore, the aniline conversion can be obtained at any time as[23]

$$PE = \frac{A(t) - A_0}{A_{max} - A_0} \times PE_{max} \qquad (2)$$

where PE is the aniline conversion at time t, $A(t)$ is the measured absorbance at time t, and A_0 is the initial absorbance at $t = 0$.

Table I and Figure 1 compare the aniline conversion values obtained with the proposed NIR technique, in accordance with eq. (2), and gravimetrically, in accordance with eq. (3):

$$PE_g = \frac{M_{PANI}}{M_{ANI}\left(1 + 0.5\frac{PM_{DBSA}}{PM_{ANI}}\right)} \qquad (3)$$

where PE_g is the aniline conversion, M_{PANI} is the total mass of Pani collected at the end of the batch, M_{ANI} is the initial amount of aniline in the batch, and PM_{ANI} and PM_{DBSA} are the molecular weights of aniline and DBSA, respectively. NIR conversions were calculated with absorbance data obtained at 1026 nm. The gravimetric conversion of aniline was calculated with the assumptions that 50% of the nitrogen atoms of the Pani chains were in the imine form and that all imine groups were protonated by DBSA.[8]

Table I and Figure 1 show that there was a strong linear correlation ($R > 0.97$) between the conversion values obtained gravimetrically and those obtained with NIRS, which indicated that the proposed procedures were consistent and could be used with confidence for kinetic analysis. As a matter of fact, we believe that conversions obtained with the NIR spectrometer are more exact and precise that ones obtained gravimetrically, as they depend neither on sampling nor on purification of the polymer prod-

uct. Also, it was very difficult to guarantee that 50% of the nitrogen atoms of the final Pani chains were indeed in the imine form and protonated by DBSA.

The autocatalytic character of the aniline polymerization mechanism is well documented in the literature.[22,23] As termination steps are unimportant, the continuous generation of polymer chains leads to increasing rates of reaction. If volume effects are neglected, the mass balance equation for aniline polymerizations performed in batch can be written as[12,16,22–25]

$$\frac{-d[\text{Ani}]}{dt} = k_1[\text{APS}][\text{Ani}] + k_2[\text{Ani}][\text{Pani}] \qquad (4)$$

where k_1 and k_2 are rate constants for chain initiation and chain growth. Depending on the relative values of k_1 and k_2 (k_2 is much larger than k_1), one can observe the development of long induction periods before the acceleration of the reaction rates. Equation (4) can be integrated analytically as follows:[12,16,22,25]

$$\frac{[\text{Ani}]}{[\text{Ani}]_0} = 1 - PE = \frac{\beta_2}{\beta_1[\text{Ani}]_0(e^{\beta_2 t} - 1) + \beta_2 e^{\beta_2 t}} \qquad (5)$$

where $[\text{Ani}]_0$ represents the initial aniline concentration and β_1 and β_2 are effective kinetic constants, defined as[23]
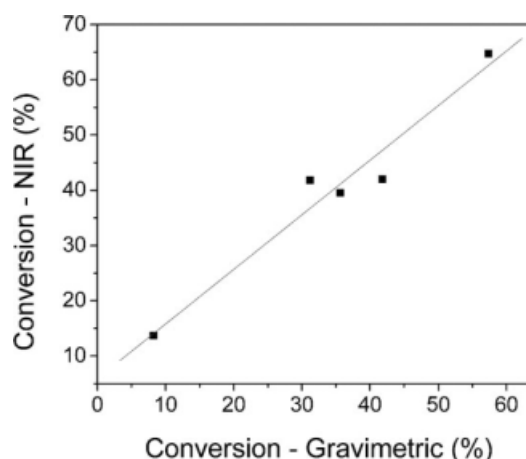

Figure 1 Comparison of NIR and gravimetric conversions.

TABLE II
Organization of Spectral Data

Wavelength	Time				
	t_1	t_2	t_3	$\ldots$	t_m
λ_1	$A_1(\lambda_1)$	$A_2(\lambda_1)$	$A_3(\lambda_1)$	$\ldots$	$A_m(\lambda_1)$
λ_2	$A_1(\lambda_2)$	$A_2(\lambda_2)$	$A_3(\lambda_2)$	$\ldots$	$A_m(\lambda_2)$
λ_3	$A_1(\lambda_3)$	$A_2(\lambda_3)$	$A_3(\lambda_3)$	$\ldots$	$A_m(\lambda_3)$
$\ldots$	$\ldots$	$\ldots$	$\ldots$	$\ldots$	$\ldots$
λ_n	$A_1(\lambda_n)$	$A_2(\lambda_n)$	$A_3(\lambda_n)$	$\ldots$	$A_m(\lambda_n)$
PE	PE_1	PE_2	PE_3	$\ldots$	PE_m

λ_n is the wavelength, t_m is the reaction time, and $A_m(\lambda_n)$ is the absorbance at λ_n for time t_m.

$$\beta_1 = 0.8\,k_1 - k_2 \tag{6}$$

$$\beta_2 = k_1[\text{APS}]_0 - \beta_1[\text{Ani}]_0 \tag{7}$$

where $[\text{APS}]_0$ is the initial concentration of APS. (The parameters β_1 and β_2 are defined to minimize the parameter correlation and make parameter estimation easier, as usually performed in the field of kinetic modeling.[26]) Therefore, according to the model developed by Tzou and Gregory, the kinetic interpretation of aniline polymerizations requires the estimation of parameters β_1 and β_2 (or k_1 and k_2) of eqs. (5)–(7). This was performed here with the help of NIR spectra obtained *in situ* and in real time during the polymerization.

Software implementation

To carry out the estimation of the kinetic parameters, we assumed that NIR spectra were available and organized as presented in Table II. Then, eq. (2) was used to transform the absorption data into aniline conversion data. Finally, aniline conversion data were used to estimate the kinetic parameters with the help of standard least-squares procedures. The objective function (F_{obj}) minimized by the computer software is

$$F_{\text{obj}} = \sum_{i=1}^{m} \left(PE_i^e - PE_i^c\right)^2 \tag{8}$$

where the superscripts e and c represent experimental and calculated values, respectively. A standard Levenberg–Marquardt procedure, supplied by the ScientificPython module,[27] was used to perform the minimization of the objective function presented in eq. (8).

Figure 2 shows how the NIR spectra change with time for a typical polymerization run. It is very clear that the NIR spectra changed very significantly with time, which allowed kinetic analysis of aniline consumption. However, the absorption bands were not

clearly defined, as expected during typical infrared analysis. Additionally, the signal was noisy at shorter wavelengths, which may have been related to the lower transmission efficiency of the optical fibers around the visible region. Baseline spectral subtraction was performed, as shown in Figure 2(b), to compensate for unavoidable baseline shifts along the series of experiments. This also allowed easier observation of the pernigraniline ($\sim$ 668 nm)/emeraldine ($\sim$ 800 nm) transition during the last stages of the reaction, when APS was exhausted and the reaction halted.[14]

Figure 3(a,b) shows the evolution of the absorbances at 668 and 1026 nm for different polymerization runs. (As already discussed, the absorbances obtained at 668 nm were noisier than the ones obtained at 1026 nm.) The obtained dynamic absorbance profiles clearly indicated that the distinct polymerization runs experienced distinct dynamic trajectories. Therefore, the obtained NIR spectra indicated that the kinetic trajectories (and, possibly, the kinetic parameters) were different at different
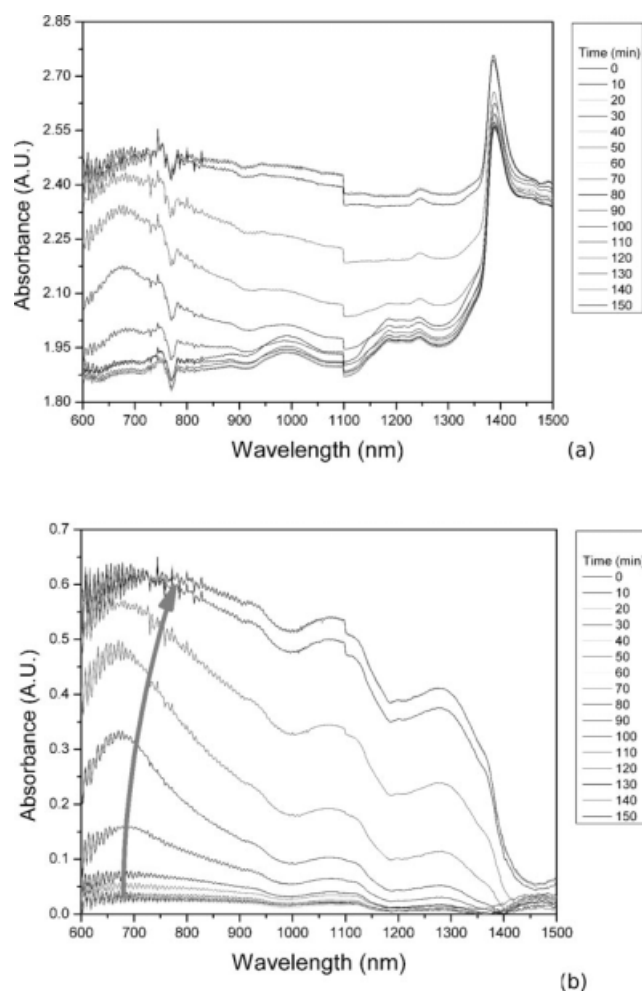

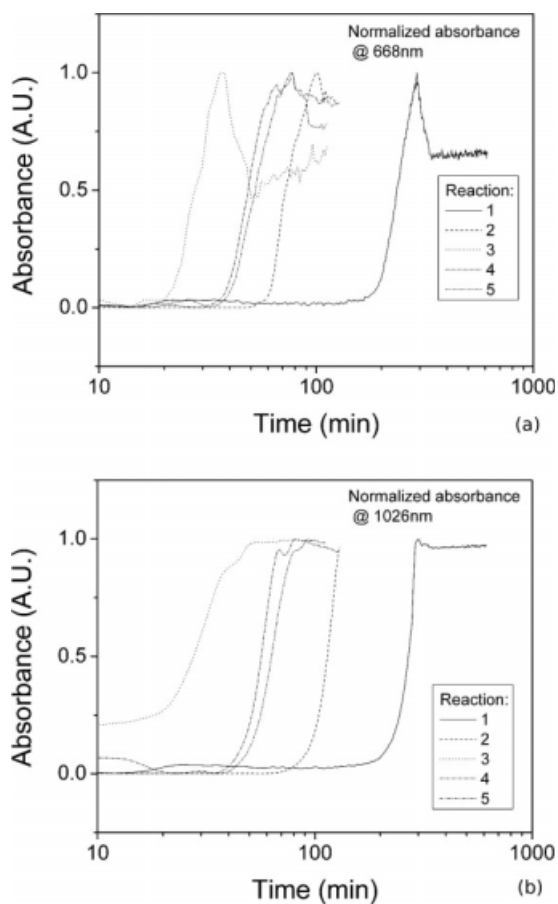**Figure 2** Evolution of NIR spectra for a typical polymerization (a) before and (b) after baseline subtraction.

Figure 3 Dynamic evolution of the absorbance at (a) 668 and (b) 1026 nm for different polymerization runs.

Figure 4 Dynamic evolution of the aniline conversion for polymerization run 2.

polymerization conditions. These results encouraged the use of the NIR spectral data for the kinetic analysis of aniline consumption.

Figure 3(a) shows the consistent reduction of the absorbances at 668 nm during the last stages of the reaction, which may have been related to the perni-graniline/emeraldine transition. This effect was not observed at 1026 nm (second overtone of N—H bonds), which made kinetic interpretation easier at this particular wavelength. Figure 4 compares the aniline conversion data for a polymerization run, as calculated from the absorbances obtained at 668 and 1026 nm. There were some persistent differences between the two curves, although the conversion trajectory obtained at 1026 nm was much more stable than the one obtained at 668 nm. Also, as shown in Figure 5, the obtained model fits were much better when the conversion data obtained at 1026 nm were used for parameter estimation. For all of these reasons, it seemed that the conversion data obtained at 1026 nm were more reliable than those obtained at 668 nm when the NIR spectral analysis was performed in real time and *in situ* with available commercial spectrometers. This may be regarded as a
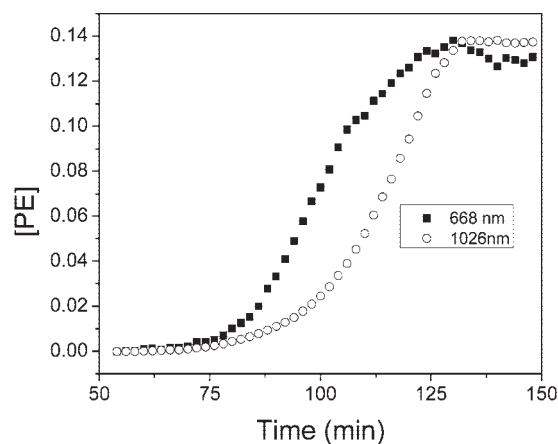
very interesting result, as spectral-based kinetic analysis has been usually performed at 668 nm in past studies.[14,15]

Figure 5 illustrates the quality of the model fits when aniline conversions were calculated with the absorbance data obtained at 668 and 1026 nm for a typical polymerization run. The obtained results were much better when the conversions were calculated at 1026 nm, which led to a model correlation of 0.994. The model parameters are presented in Table III for both fits. It is important to emphasize that very good model fits could be obtained without the help of more complex chemometric procedures, such as partial least squares and principal component analysis. This is certainly an advantage of the proposed analytical method. The long induction times reported in Table III were due to the low APS concentration (<0.028 mol/L) and very low temperature ($-10°C$) used to perform the experiment.
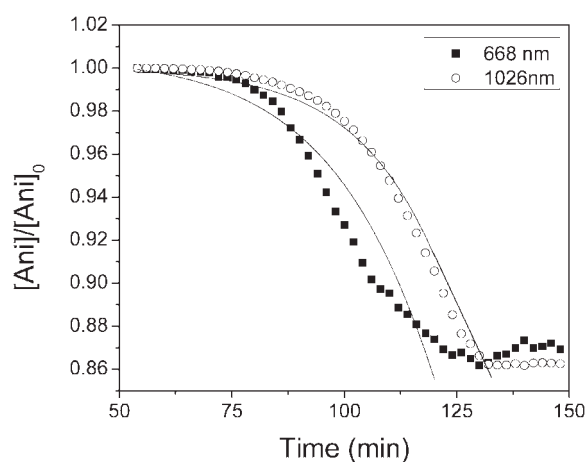

Figure 5 Model fits for aniline conversion trajectories in polymerization run 2.

Parameter	Wavelength (nm)	
	668	1026
β_1 (M^{-1} min^{-1})	$(5.3 \pm 0.6) \times 10^{-2}$	$(6.1 \pm 0.3) \times 10^{-2}$
β_2 (M^{-1} min^{-1})	$-(3.2 \pm 0.3) \times 10^{-1}$	$-(3.7 \pm 0.2) \times 10^{-1}$
k_1 (M^{-1} min^{-1})	$(5 \pm 1) \times 10^{-4}$	$(1.2 \pm 0.1) \times 10^{-4}$
k_2 (M^{-1} min^{-1})	$(3 \pm 1) \times 10^{-1}$	$(3.7 \pm 0.6) \times 10^{-1}$
R^2	0.974	0.994
Induction period (min)	54	58

When the values of k_1 and k_2 presented in Table III were compared to values reported by other workers,[12,16,23] we concluded that the obtained values presented the same order of magnitude of published data, which gives additional support to the proposed kinetic analysis. As discussed by Tzou and Gregory[16] and Fu and Elsenbaumer,[25] the value of k_2 depended on the type of acid and the acid concentration, whereas k_1 was affected by the acid catalyst and the initial reactant concentration. Also, previous kinetic analyses have been performed mostly under unreal reaction conditions (e.g., high temperatures, very small reactors, absence of agitation). Finally, despite the observed differences between the conversion trajectories calculated from the absorbances obtained at 668 and 1026 nm, as shown in Table III, the final parameter estimates were comparable and similar to each other. For these reasons, the obtained results can be regarded as very reliable and comparable to those already reported in the literature. Therefore, the use of the proposed analytical method for the kinetic analysis of aniline polymerizations should be encouraged.

CONCLUSIONS

A method for the determination of kinetic constants in aniline polymerizations performed in the presence of DBSA has been presented. The procedure was based on the measurement of light absorbances at 668 and 1026 nm. Tzou and Gregory's empirical reaction model was used as a reference for kinetic studies. The best fits were obtained when the kinetic constants were evaluated at 1026 nm because of the lower noise/signal ratio in this spectral region and the smaller sensitivity to the pernigraniline/emeraldine transition during the last stages of the polymerization. Parameter estimates obtained with the proposed analysis were similar to the ones published in the literature, which encourages the use of the proposed technique for kinetic analysis of aniline polymerizations performed under real reaction conditions (e.g., concentrated monomer solutions, large

reaction volumes, efficient cooling conditions, presence of agitation).

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