

Polyesterification Kinetics Between Adipic Acid and Hexamethylene Glycol Using Diphenylammonium Triflate as Catalyst

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ABSTRACT

The kinetics of melt polyesterification of adipic acid with hexamethylene glycol in an equimolar ratio has been studied over a temperature range of 120°C to 150°C in the absence and presence of *p*-toluene sulphonic acid (PTSA) or diphenylammonium triflate (DPAT) as catalyst. The rate equations for polymerizations fit the rate equations proposed by Tang-Yao for 80-480 min. For acid-catalyzed and non-catalyzed polyesterifications at various temperatures, plots of $1/(1-p)$ and $1/(1-p)^{3/2}$ have been made against time, respectively. The fits test accuracy was also ensured by the least squares method. The experimental results show that reaction orders are 2.5 and 2 for uncatalyzed and acid-catalyzed reactions, respectively, with up to 97% conversion. The rate constants and activation energies for uncatalyzed and acid-catalyzed reactions were calculated. The activation energies are 45.01 kJ/mol for the self-catalyzed system, 35.32 kJ/mol for DPAT catalyzed system and 31.55 kJ/mol for PTSA catalyzed system. Activation energies are compared to literature data for polyesterification reactions of adipic acid with hexamethylene glycol in equimolar quantities. We found that the catalytic activity of DPAT in polycondensation is similar to that of PTSA.

Key Words:

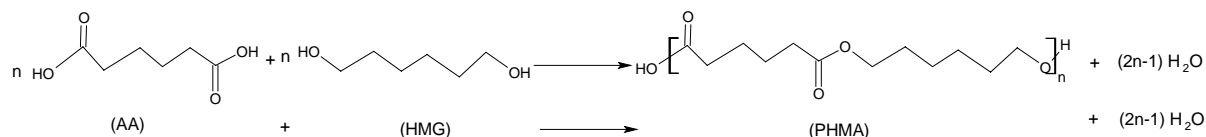
polycondensation;
kinetics;
diphenylammonium triflate;
catalyst;
polyesters.

INTRODUCTION

Polyesters are one of the most versatile synthetic polymers. They are widely used commercially as fibres, plastics, and coatings. Melt polyesterification is a major route to the synthesis of polyesters. This solventless route involves high temperatures with relatively long

reaction times that involves reduced pressures in the final step. Catalysts are required to decrease reaction times. Well-known catalysts for esterification are *p*-toluene sulphonic acid (PTSA) and the salts of Ti(IV) and Sn(IV). Recently Ishihara et al. [1] have

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reported that a related catalyst, the $\text{HfCl}_4(\text{THF})_2$ complex catalyzed the direct polycondensation of diols and dicarboxylic acid compounds, more efficiently than conventional catalysts. Furthermore, recent esterification processes took advantage of the use of mild catalysts, 4-(nitro)-diphenylammonium triflate (NDPAT) [2] and diphenylammonium triflate (DPAT) [3]. Therefore, it is important to clarify the kinetics of polyesterification.

The kinetics of polyesterification reactions of adipic acid and hexamethylene glycol have been studied extensively (Scheme I), but quite varied results have been obtained. The original studies on the kinetics and mechanisms of polyesterification reactions were carried out by Flory [4-5]. He concluded that self-catalyzed polyesterifications follow third-order kinetics with a second-order dependence on the carboxyl group concentration and a first-order dependence on the hydroxyl group concentration, whereas the acid-catalyzed polyesterification reactions are second-order overall with a first-order dependence on the carboxyl group concentration and on the hydroxyl group concentration. Tang and Yao [6] considered that hydrogen ions dissociated from the diacid molecules continue to coordinate weakly to the diacid molecules, suggesting that the reaction is 2.5th order for self-catalyzed polyesterification reactions. Hamann et al. [7] have studied a later-stage reaction by adding the polyester to a mixture of diacid and diol equivalent to obtain 80% conversion. Szmercsanyi and Makay-Böli [8] indicated that in the condensed phase no free hydrogen ions are present; a hydrogen ion that leaves one molecule becomes bonded to another. Collisions of two acid molecules and of one acid molecule and one alcohol molecule can both lead to proton transfer. Lin and Hsieh [9] proposed that the reaction is third-order with a second-order dependence on hydroxyl group concentration and first-order dependence on carboxyl group concentration for the ratio of diacid.

We have reported in the previous paper [10] the effect of diphenylammonium triflate catalyst on poly-

esterification reactions. We continue to be interested in the kinetics of polyesterification using DPAT as catalyst for the following reasons: (1) We believe that it is still a challenging subject to study kinetically because it is important to bring out into the open all details from a technology viewpoint: (2) Despite the large number of triflate based on esterification catalysts known, [2-3] our knowledge, there are no detailed records of polyesterification kinetics using them: (3) As it is evident from the literatures, the DPAT catalyst does not require water removal from the reaction medium, but esterification reactions are equilibrium processes. As a result, we believe that we will obtain interesting results using DPAT as catalyst. In this connection, the degree of polymerization, the rate of reaction, the order of reaction and the rate constant for polycondensations have been determined. Non-catalyzed, PTSA catalyzed and DPAT catalyzed polycondensations between adipic acid and hexamethylene glycol were carried out at 120-150°C.

EXPERIMENTAL

Materials

DPAT was synthesized and purified according to a procedure previously described [3]. Adipic acid (Merck) 99%, KOH Pancreac 85%, hexamethylene glycol (Merck) 97%, methanol (Reidel de Haen) 99.9%, acetone (Symras) 99.5% and *p*-toluene sulphonic acid (Across) 97.5% were used as received.

Melt Polymerization

Adipic acid (AA) and hexamethylene glycol (HMG) (at equal molar ratios, 0.1 mol/kg) were preheated to the reaction temperature separately, and then poured into a 50 mL glass reaction vessel equipped with an agitator operated at 130 rpm and a condenser. The reaction vessel was immersed in an agitated thermostatic oil bath and was purged with deoxygenated dry nitrogen (40 mL/min) by bubbling in order to remove the water produced during the reaction. The tempera-

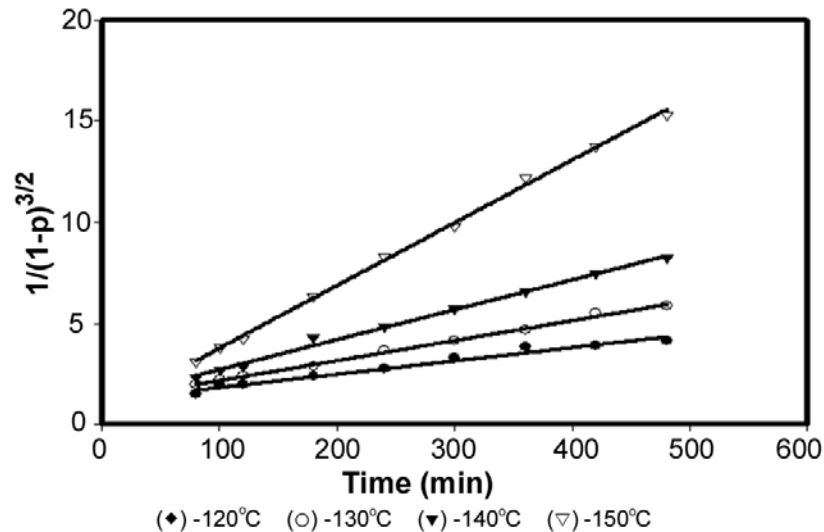


Figure 1. Plots of $1/(1-p)^{3/2}$ vs. reaction time t for equimolar self-catalyzed polyesterification reactions of adipic acid with hexamethylene glycol at different temperatures.

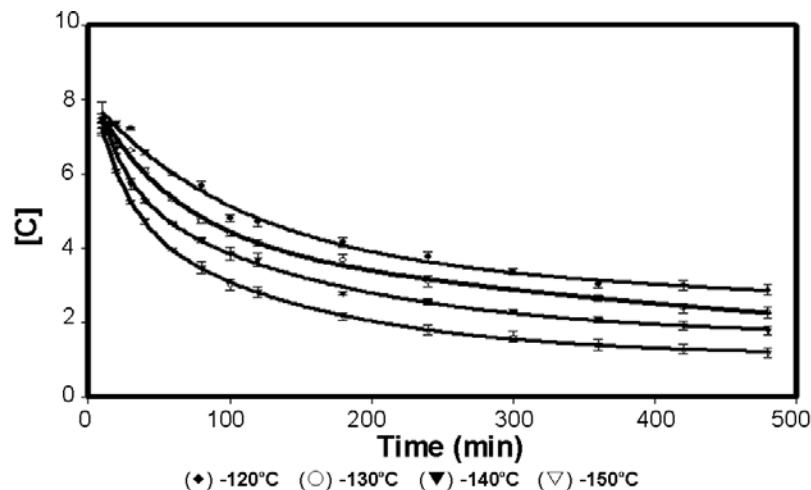


Figure 2. Plots of acid concentration vs. reaction time t for equimolar self-catalyzed polyesterification reactions of adipic acid with hexamethylene glycol at different temperatures.

ture inside the reactor was kept constant. The average temperature variation of the internal reactor was about $\pm 1^\circ\text{C}$. To examine reaction kinetics, a sample of about 0.1 g was withdrawn at different times into a flask and cooled immediately. The cooled sample was dissolved in acetone (5-10 mL) and was then titrated with methanolic KOH using phenolphthalein as an indicator. If the concentration change due to the removal of water is taken into consideration, the acid concentration may be calculated according to the following equation [7]:

$$C = \frac{C_e(W_0 - 18) \times 1000}{W_0(1000 - 18C_e)} \quad (1a)$$

$$C_e = \frac{N_{\text{KOH}} \times V_{\text{ml}}}{m} \quad (1b)$$

where C is the actual acid concentration in equivalent moles per kg sample, including water produced; C_e is the apparent acid concentration in equivalent moles per kg sample (N : normality of KOH, V_{mL} : consumption, m : sample quantity); and W_0 is the total mass of reaction mixture based on one equivalent mole of adipic acid.

In all the works reviewed above, except that of Hamann et al. [7], and Show-An et al. [11] the reactions were carried out under a constant oil-bath temperature. In this investigation, the recorded reaction

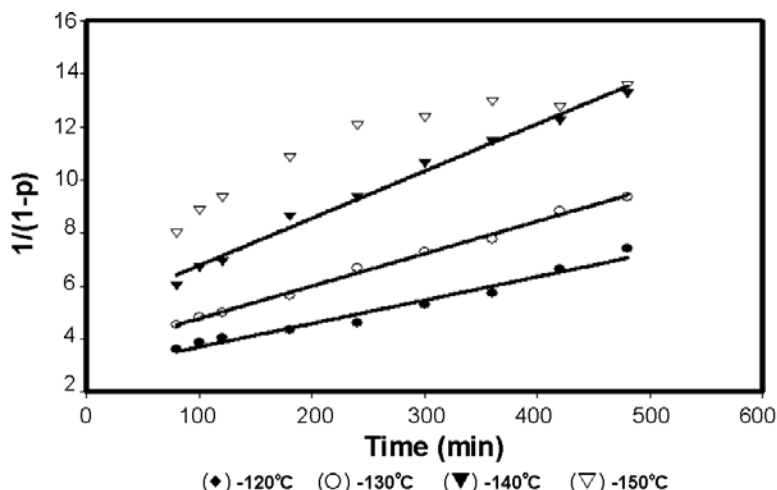


Figure 3. Plots of $1/(1-p)$ vs. reaction time t for equimolar polyesterification reactions of adipic acid with hexamethylene glycol catalyzed by DPAT at different temperatures.

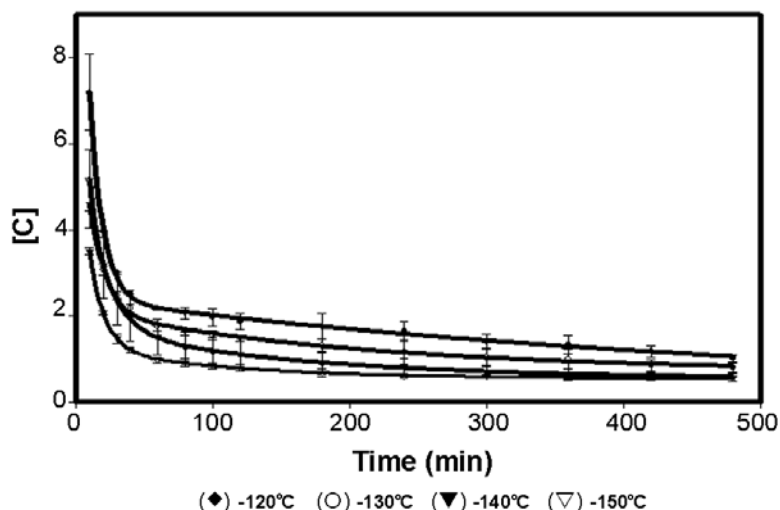


Figure 4. Plots of acid concentration vs. reaction time t for equimolar polyesterification reactions of adipic acid with hexamethylene glycol catalyzed by DPAT at different temperatures.

temperature was the internal reactor temperature and calculations were carried out to account for this.

RESULTS AND DISCUSSION

For self-catalyzed polyesterification at various temperatures, plots of $1/(1-p)^{3/2}$ and $1/(1-p)^2$ versus time were made and the quality of fit was tested by a least squares method. The best linear plots were obtained by plotting $1/(1-p)^{3/2}$ vs. time (Figure 1) indicating that the reaction satisfies the following 2.5th order rate equation:

$$\frac{3}{2} C_0^{3/2} k_1 t = \frac{1}{(1-p)^{3/2}} - 1 \quad (2)$$

where C_0 is the initial concentration of acid. Concentration $[C]$ values have been plotted versus time (Figure 2).

Tang and Yao [6] proposed that polyesterification is promoted by catalysis due to the presence of hydrogen ions. When the dibasic acid and the glycol react in equimolar ratios in the presence of a foreign acid [12], the hydrogen ion is formed mainly from the added acid. Thus the polyesterification is a second-order reaction. On the other hand, in the absence of a for-

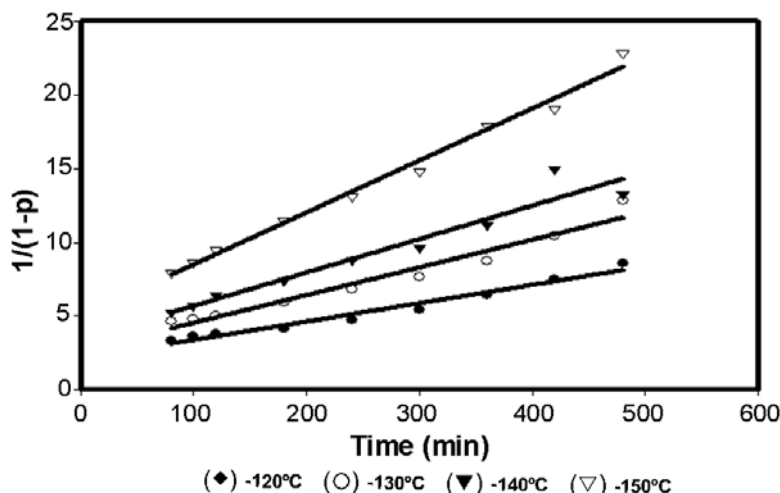


Figure 5. Plots of $1/(1-p)$ vs. reaction time t for equimolar polyesterification reactions of adipic acid with hexamethylene glycol catalyzed by PTSA at different temperatures.

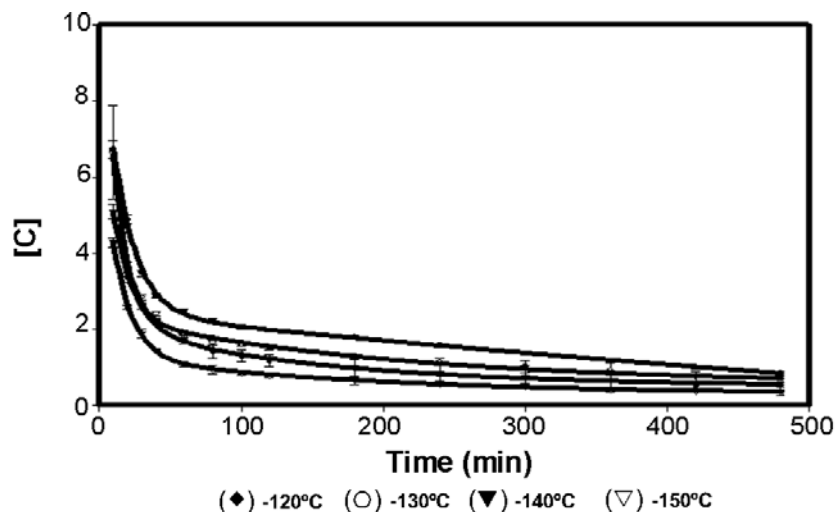


Figure 6. Plots of acid concentration vs. reaction time t for equimolar polyesterification reactions of adipic acid with hexamethylene glycol catalyzed by PTSA at different temperatures.

eign acid, the hydrogen ions are formed from ionization of the dibasic acid, and the order of the reaction is 2.5.

The experimental results obtained using equimolar quantities of AA and HMG are given in Figures 1 and 3 and 5 for the self-catalyzed and the acid-catalyzed reactions. Also concentration $[C]$ values have been plotted versus times (Figures 4-6).

For acid-catalyzed polyesterification at various temperatures plots of $1/(1-p)$ and $1/(1-p)^2$ have been made versus time. The accuracy of fits was also tested by the least squares method for PTSA catalyzed and DPAT catalyzed polyesterifications. The best linear plots were obtained by plotting $1/(1-p)$ vs. time

(Figures 3 and 5) for both catalysts, indicating that the reaction satisfies the second-order rate eqn (3) which applies in equimolar systems.

$$C_0kt = \frac{1}{(1-p)} - 1 \quad (3)$$

Plots of acid concentration versus time for non-catalyzed, PTSA catalyzed and DPAT catalyzed polycondensations between AA and HMG are shown in Figure 7, at 140°C. The same work was repeated at 120°C and 130°C. From the figure it is seen that the $[C]$ value obtained for the non-catalyzed reaction after 480 min is higher than those obtained for the DPAT catalyzed and the PTSA catalyzed condensation after

Table 1. Rate constants k_{1self} , k_{2DPAT} and k_{2PTSA} for self-catalyzed and acid-catalyzed (DPAT and PTSA) polyesterification reactions of equimolar quantities of adipic acid and hexamethylene glycol.

| Temperature (°C) (oil bath) | Temperature (°C) (reaction medium) | $k_{1self}^a \cdot 10^3$ kg ^{3/2} /mol ^{3/2} min | $k_{2DPAT}^b \cdot 10^3$ kg/mol.min | $k_{2PTSA}^b \cdot 10^3$ kg/mol.min |
|--------------------------------|---------------------------------------|---|--|--|
| 120± 1 | 109 ± 1 | 0.216±0.02 | 1.18±0.08 | 1.68±0.1 |
| 130± 1 | 118 ± 1* | 0.324±0.02 | 1.64±0.04 | 2.52±0.2 |
| 140± 1 | 133 ± 1 | 0.487±0.02 | 2.34±0.09 | 3.06±0.3 |

* measured at 120°C for PTSA catalyzed reaction: (a) calculated by eqn (2) and (b) calculated by eqn (3).

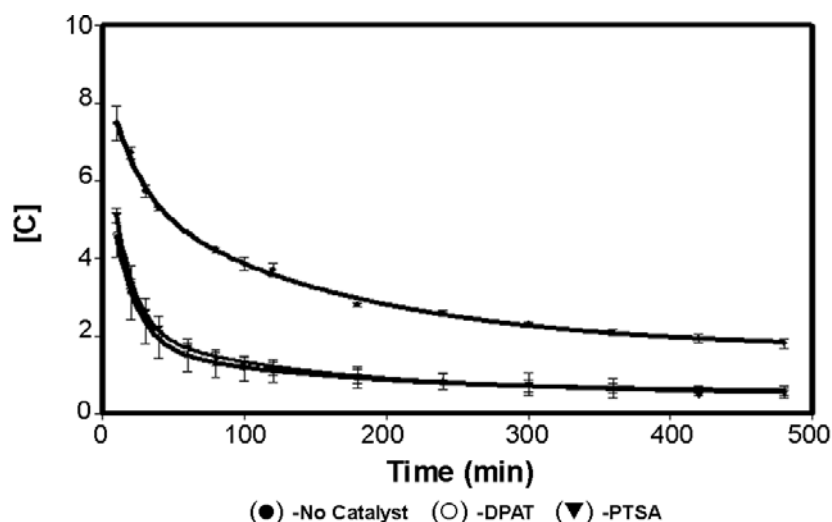


Figure 7. Plots of acid concentration vs. reaction time t for equimolar polyesterification reactions of adipic acid with hexamethylene glycol at 140°C.

480 min. Therefore $[C]$ values obtained in these three cases are summarized as: $[C]$ values in DPAT catalyzed polycondensation \cong $[C]$ values in PTSA catalyzed condensation $<$ $[C]$ values in non-catalyzed polycondensation.

The rate constants k_{1self} , k_{2DPAT} and k_{2PTSA} for the self-catalyzed, DPAT catalyzed and PTSA catalyzed (reference catalyst) polyesterification reactions, respectively, have been calculated and presented in Table 1. We were not able to calculate a rate constant for the polyesterification reaction catalyzed by DPAT at 150°C because of the non-linearity between $1/(1-p)$ and time. We think that depolymerization occurs in polyesterification.

Table 2. Activation energies and frequency factors for polyesterification reactions of adipic acid with hexamethylene glycol in equimolar quantities.

| Catalyst | E_a (kJ/mol) | $\ln A$ |
|-------------|----------------|---------|
| No catalyst | 45.01 | 5.72 |
| DPAT | 35.32 | 4.43 |
| PTSA | 31.55 | 3.6 |

Reaction rates obtained by non-catalyzed, PTSA catalyzed and DPAT catalyzed polycondensations between AA and HMG demonstrate that the reaction catalyzed by PTSA is much faster than the non-catalyzed reaction. However, in the case of polycondensation catalyzed by DPAT, the reaction rates are almost the same as that of the PTSA catalyzed reaction.

The Arrhenius equation was found to be obeyed since good straight lines were obtained when $\ln k_{1self}$, $\ln k_{2DPAT}$ and $\ln k_{2PTSA}$ values were plotted vs. $1/T$ (temperature of reaction medium) according to Table

Table 3. Comparison of activation energies for polyesterification reactions of adipic acid with hexamethylene glycol in equimolar quantities.

| Sources | Self-catalyzed E _a (kJ/mol) | PTSA catalyzed E _a (kJ/mol) | DPAT catalyzed E _a (kJ/mol) |
|--------------------|---|---|---|
| Chen and Wu | 46.43 | 36.40 | - (*) |
| Vansco-Szmercsanyi | 47.23 | - (*) | -(*) |
| This work | 45.01 | 31.55 | 35.32 |

(*) not found in literature.

1. The activation energies and Arrhenius constants were calculated and given in Table 2.

The activation energies for polyesterification of AA-HMG are 45.01 kJ/mol for the self-catalyzed system, 35.32 kJ/mol for DPAT catalyzed system and 31.55 kJ/mol for PTSA catalyzed system.

Comparison of activation energies for polyesterification reactions of AA with HMG in equimolar quantities for different sources is shown in Table 3. It is understood from Table 3 that the catalytic activity of DPAT in polycondensation is similar to that of PTSA.

CONCLUSION

Polyhexamethylene adipate was synthesized under constant reaction temperature using self, DPAT and PTSA catalyses by melt polymerization methods. We saw that the rate equations of polymerizations fit the rate equations proposed by Tang-Yao for 80-480 min. In each case, the rate constant was evaluated from the slopes of straight lines. The rate constants for self-catalyzed, DPAT catalyzed and PTSA catalyzed polycondensations at 140°C were $0.487 \times 10^{-3} \text{ kg}^{3/2} / \text{mol}^{3/2} \cdot \text{min}$, $2.34 \times 10^{-3} \text{ kg/mol} \cdot \text{min}$, and $3.06 \times 10^{-3} \text{ kg/mol} \cdot \text{min}$, respectively. It was observed that the rate of DPAT catalyzed melt polycondensation is 4.8 fold higher than self-catalyzed melt polycondensation but 1.3 times lower than PTSA catalyzed melt polycondensation. Similar results were obtained at other temperatures. Therefore, the catalytic activity of DPAT in melt polycondensation is close to that of PTSA. This situation is reflected in the activation energies of adipic acid-hexamethylene glycol that were found to be 45.01 kJ/mol for the self-catalyzed system, 35.32

kJ/mol for the DPAT catalyzed system and 31.55 kJ/mol for the PTSA catalyzed system.

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