The Growth, Dissolution and Aging of Terephthalic Acid Crystals

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Terephthalic acid (TPA) is a major commodity chemical manufactured by the air oxidation of *p*-xylene. TPA is a crystal which contains two carboxylic groups in the para position on a benzene ring. It is reacted with ethylene glycol via a condensation reaction in the manufacture of polyethylene terephthalate (PET), a polyester, which is used as a fiber and for plastic containers.

Commercially, the majority of terephthalic acid is produced by the air oxidation of *p*-xylene in acetic acid, promoted by cobalt and bromine catalysts. The impurities present in terephthalic acid are generally intermediates, oxidation byproducts, and catalyst. The intermediate 4-carboxybenzaldehyde (4-CBA) is one of the most difficult contaminants to remove, and unfortunately, probably one of the most deleterious. 4-CBA contains an aldehyde group and a carboxylic group in the para position on a benzene ring. The aldehyde group is unable to undergo the condensation reaction with ethylene glycol during PET polymerization. The removal of 4-CBA from TPA is, therefore, of great commercial importance.

The aging of TPA crystals at a variety of conditions has been studied for a number of years by Myerson and coworkers (Gaines and Myerson, 1982, 1983; Myerson and Saska, 1984; Saska and Myerson, 1985, 1987). These studies demonstrated that TPA particles of initial globular appearance will transform into larger needle crystals when suspended in their own saturated solution at temperatures ranging from 353–490 K. Purity levels of TPA which were aged in this process were found to improve substantially, with levels of the impurities, 4-CBA and cobalt, declining as much as 80 and 90%, respectively. Saska (1984) and Saska and Myerson (1987) examined the aging process by enclosing a small amount of a TPA-water mixture in a glass capillary, capable of withstanding high pressures. The capillary was sealed at both ends and placed on the hot stage of a microscope. These experiments revealed rod-shaped, faceted, particles which had nucleated and grown on the original globular TPA particles (see Figure 1). The nucleation and growth of these new crystals indicates that a finite supersaturation must exist in the solution. The rapid change of TPA solubility with temperature (in the temperature range of interest) indicates that small temperature fluctuations could result in periods of crystal dissolution followed by periods of crystal nucleation and growth. A transformation of habit from globular to faceted needles would result from a series of dissolution and growth cycles since at low supersaturations all nucleation and growth is in the faceted needle form. It is the purpose of this work to directly measure the aging rate of TPA in aqueous solution and relate this to a mechanism based on temperature fluctuations, crystal dissolution, and crystal growth.

Crystal Aging Experiments

Experimental apparatus and procedure

The apparatus employed to determine the rate of crystal aging appears in Figure 2. The vessel was constructed from titanium to resist corrosion and was designed for temperatures up to 525 K and pressures up to 22 atm. A magnetic stirrer is used for agitation. Heating, temperature control and temperature measurement are supplied by an Omega PID temperature controller. Control of temperature was ±1 K in the 373–473 K range. The apparatus was constructed to allow the injection of TPA particles into the vessel after the saturated solution was prepared and heated to the desired temperature.

The purpose of these experiments was to directly measure the crystal aging rate. This was accomplished by employing deuterated TPA (supplied by Sigma Chemical) as a tracer compound. The deuterated TPA has four deuterium atoms in place of hydrogen atoms on the benzene ring. A saturated solution of deuterated TPA was prepared and TPA crystals aged (or the reverse) and the exchange between the two measured. Prior to crystal injection, the solution was heated above the saturation temperature and held for several hours to insure complete dissolution. After the solution was brought to the desired tempera-

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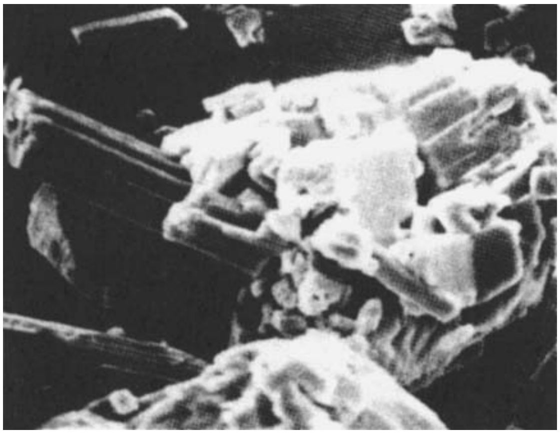

Figure 1. Aged TPA particle (×820) after 60 min at 480 K in a glass capillary.

ture, crystals were injected. After crystal addition, temperature vs. time was carefully monitored and recorded. The change in temperature vs. time was due to the on/off nature of the temperature controller.

Samples of crystal and solution were taken at periodic intervals and filtered hot, using a PALL porous metal filter. The crystals were dried and weighed. Solution obtained was cooled to room temperature (to precipate virtually all of the TPA) and filtered. The solids obtained were then ready for analysis.

Carbon 13 (^{13}C) NMR was used to determine the fraction of deuterated and nondeuterated TPA in the solid samples. The solvent used for the analysis was DMSO. ^{13}C-NMR spectroscopy allows observation of the carbon skeleton and carbon-containing functional groups through naturally occurring ^{13}C, which has a spin of $\frac{1}{2}$. With the use of wide-band heteronuclear (noise) decoupling, a single sharp peak results for each chemically nonequivalent ^{13}C atom. Deuterated and nondeuterated carbon atoms are chemically nonequivalent, and there is a slight upfield shift in deuterated ^{13}C atoms. The accuracy of the *d*-TPA determination was within 5% for 60% or more *d*-TPA, and 15% for less than 60% *d*-TPA. Details of the analysis procedure can be found in Brown (1989).

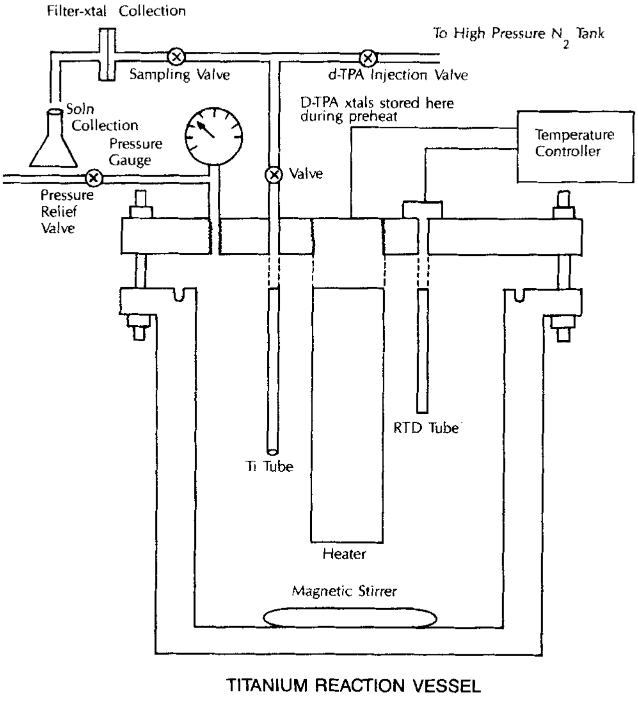

Figure 2. Crystal aging apparatus.

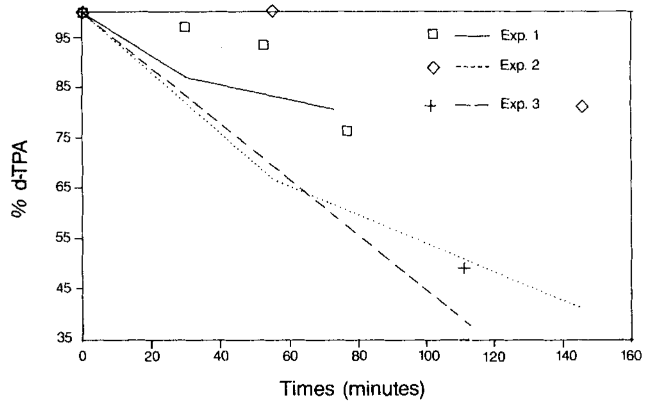

Figure 3. Crystal aging rate of TPA in water at 413 K as measured by deuterium exchange and estimated using the temperature fluctuation mechanism.

Exp. 1: period = 20 min, amplitude = 1 K, equilibrium *d*-TPA = 32%

Exp. 2: period = 20 min, amplitude = 2 K, equilibrium *d*-TPA = 15%

Exp. 3: period = 20 min, amplitude = 3 K, equilibrium *d*-TPA = 15%

Experimental Results

Crystal aging experiments employing deuterated TPA as a tracer material were conducted at temperatures of 413 K, 433 K, and 473 K. The temperature fluctuations, measured by recording the system temperature, ranged from ±0.5–3.0 K,

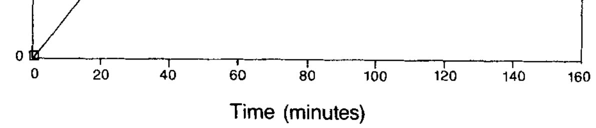

Figure 4. Crystal aging rate of TPA in water at 433 K as measured by deuterium exchange and estimated using the temperature fluctuation at mechanism.

Exp. 1: period = 20 min, amplitude = 0.5 K equilibrium *d*-TPA = 84%

Exp. 2: period = 10 min, amplitude = 0.5 K, equilibrium *d*-TPA = 12%

Exp. 3: period = 20 min, amplitude = 1.5 K, equilibrium *d*-TPA = 10%

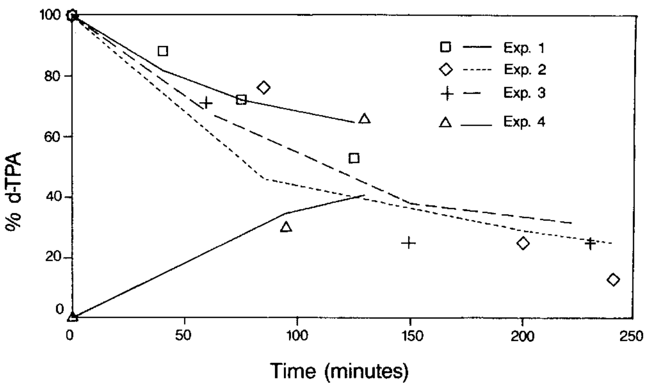

Figure 5. Crystal aging rate of TPA in water at 473 K as measured by deuterium exchange and estimated using the temperature fluctuation mechanism.

Exp. 1: period = 40 min, amplitude = 1 K, equilibrium *d*-TPA = 27%
Exp. 2: period = 40 min, amplitude = 1.5 K, equilibrium *d*-TPA = 19%
Exp. 3: period = 60 min, amplitude = 1 K equilibrium *d*-TPA = 18%
Exp. 4: period = 40 min, amplitude = 1.5 K, equilibrium *d*-TPA = 69%

with the period of the fluctuations ranging from 10–60 min. The percent *d*-TPA in the mixture ranged from 84–10%. Experiments were conducted with deuterated TPA initially in the solid phase and with deuterated TPA in solution. Results of these experiments appear as the points in Figures 3–5. The results show that significant exchange occurs in the time periods studied (40–240 min), that the rate of crystal aging increases with increasing temperature, and that the rate of exchange decreases as the aging process progresses. These results are in agreement with observation made of the aging of lead and barium sulfate (Kolthoff and Noponen, 1938 a, b; Kolthoff and Von Fisher, 1938). Examination of the aged crystals under a microscope revealed the habit transformation from amorphous "boulder-like" solid to faceted needles and plates, as has been previously reported (Saska, 1984).

Calculation of Crystal Aging Rate

A mechanism of crystal aging based on temperature fluctuations (hence, periodic crystal dissolution and growth) would allow calculations of the aging rate if accurate growth and dissolution kinetics were available as a function of temperature, along with the temperature history of the system, and solubility data. In order to test this aging mechanism, experiments were conducted to determine the crystal growth and dissolution kinetics of TPA as a function of temperature. Both growth and dissolution kinetics were measured, using the zero-time derivative method of Garside et al. (1982). Details of the experimental procedure and data analysis are given in Brown (1989). The crystal growth kinetics are expressed in terms of a mass flux given by the relation

$$\frac{dc}{dt} = k_g A (C - C_{sat})^g \tag{1}$$

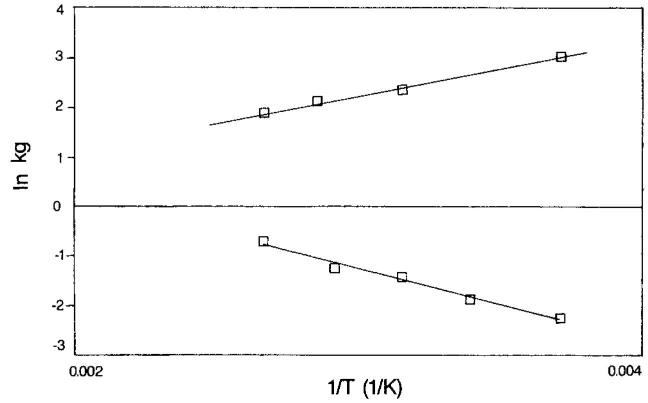

Figure 6. Arrhenius plots of crystal growth and crystal dissolution kinetic constants.

Experiments were conducted at temperatures ranging from 298–343 K. The power, *g*, was obtained for each experiment. Since *g* is assumed to be temperature invariant, an average *g* for all experiments (1.1 ± 0.18) was determined and used to calculate the constant k_g at each temperature. The constant obtained at each temperature was fit to the Arrhenius equation to allow extrapolation of the data to higher temperatures. The Arrhenius plot is shown in Figure 6, with the equation given below:

$$k_g = 2.58 \times 10^{-3} \exp(2.69 \times 10^{-3}/T) \tag{2}$$

Dissolution kinetics are expressed in terms of a mass flux,

$$\frac{dc}{dt} = k_d A (C_{sat} - C)^d \tag{3}$$

Dissolution is a diffusion-controlled process (Garside et al., 1982), so this *d* is assumed to be 1. Experiments were conducted at temperatures ranging from 298–353 K. An Arrhenius plot of the constant obtained at each temperature appears in Figure 6. The resulting equation for the dissolution constant, k_d, as a function of temperature is

$$k_d = 1.73 \times 10^3 \exp[-2.90 \times 10^3/T] \tag{4}$$

By employing this information, it is possible to estimate the crystal aging rate through a simple calculation. A monodisperse distribution of spherical particles is assumed to undergo a temperature time history identical to one used in the aging experiments. Using 1 min time intervals, the crystals either dissolve or grow (depending on the temperature), and surface area and the distribution of *d*-TPA in the crystal are calculated. This calculation assumes that the temperature fluctuations are the sole driving force for the aging process. Further details of the calculation can be found in Brown (1989).

A comparison of the experimental and calculated results appear in Figures 3–5. While the deviation between calculated and experimental results is large in some cases, the general trend shows that temperature fluctuations can account for the crystal aging observed in the TPA-water system. Temperature fluctuations, therefore, are likely to be a significant factor, influencing TPA crystal size, shape and purity in any process in which a high temperature TPA slurry occurs.

Acknowledgment

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Notation

A_T = total surface area, m^2/kg solvent
C = concentration driving force, kg/kg solvent
d = dissolution order
g = growth order
k_d = dissolution rate coef., kg/$m^2 \cdot s$
k_g = growth rate coef., kg/$m^2 \cdot s/(kg/kg\ solvent)^{g-1}$
R_g = growth rate, kg/$m^2 \cdot s$
t = time, s
T = temperature, K

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