

## Depolymerization of terephthalic acid using hot compressed water

Zhiyan Pan, Junliang Wang, and Ke Bei

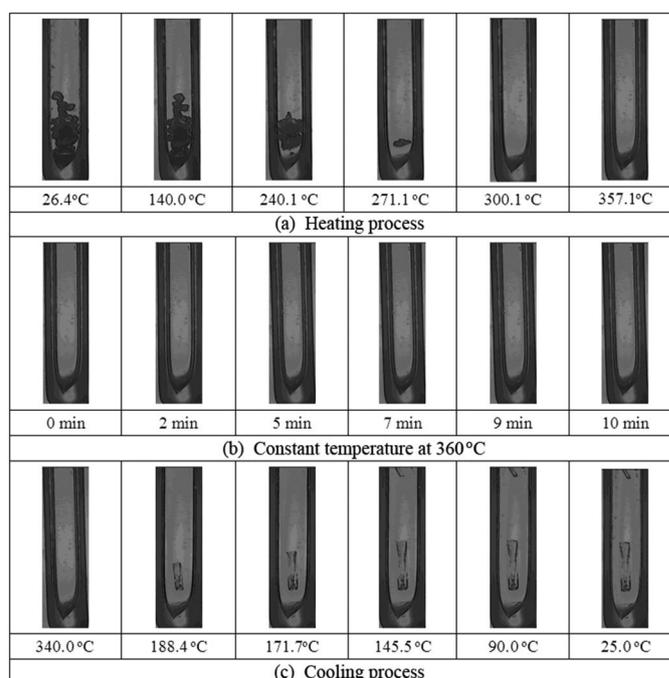
*Investigations into the phase behavior, stability, and the mechanism for stability of terephthalic acid in hot compressed water may enable more effective recycling of polybutylene terephthalate.*

Hot compressed water (HCW)—i.e., water at temperatures of above 200°C and under sufficiently high pressure (saturated vapor pressure)—has been proposed as a reaction medium for the liquefaction, gasification, combustion, depolymerization, and oxidation of hydrophobic organic compounds.<sup>1–3</sup> Among such compounds, polybutylene terephthalate (PBT) is a popular engineering thermoplastic for automotive and electrical applications. The widespread use of PBT has, however, led to an increase in solid waste.<sup>4</sup> An effective method for PBT recycling is therefore highly desired.

Terephthalic acid (TPA), an important chemical raw material, is the main monomer of PBT degradation. A number of techniques have been suggested for the depolymerization of PBT, but these approaches do not yield TPA<sup>5</sup> or require the use of harsh solvents.<sup>6</sup> Depolymerizing PBT into TPA monomers using HCW is an effective, economical, and environmentally friendly method for recycling waste polymers and obtaining TPA.<sup>7</sup> Studying the change of TPA in HCW may therefore lead to more efficient recovery of TPA from PBT.

In our work,<sup>8</sup> we investigated the phase behavior, stability, and the stability mechanism of TPA under HCW conditions. For this purpose, we used two types of reactor (i.e., a fused-silica capillary reactor, FSCR,<sup>2,8</sup> and a stainless steel autoclave reactor) and compared the results from each.

Our first experiment focused on the use of an FSCR. We used a microscope (Leica DM2500 P) to observe the phase changes undergone by TPA under HCW conditions in an FSCR during the heating, reaction, and cooling processes. We recorded images of the TPA at different temperatures (see Figure 1) using a digital camera (JVC TK-C9501). At low temperatures, we found that TPA begins to melt in the HCW and, as the temperature increases, the TPA gradually dissolves. The TPA completely dissolves at 300°C, and we observed no obvious phase change

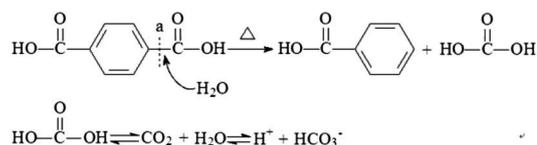
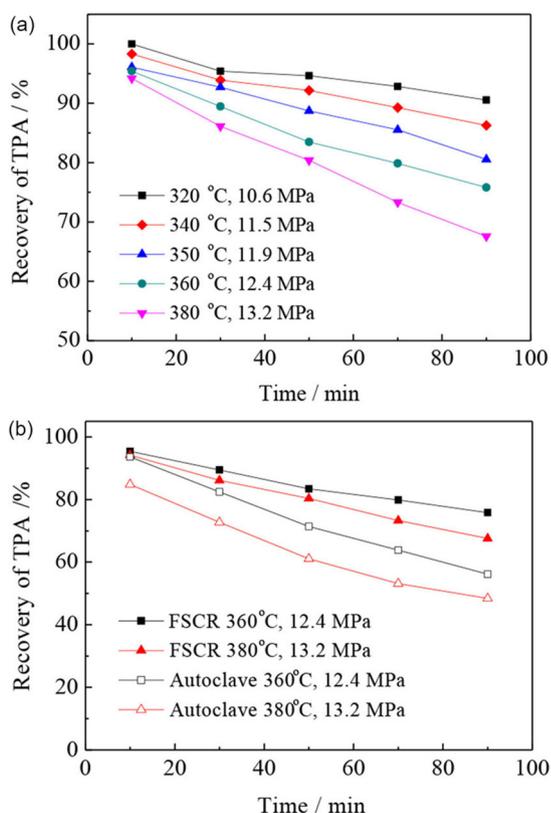


**Figure 1.** Photomicrographs of terephthalic acid (TPA) under hot compressed water (HCW) conditions in a fused-silica capillary reactor (FSCR) (a) during heating, (b) at constant temperature of 360°C, and (c) during cooling.

to the material as the reactor was heated from 300 to 360°C (even after 10 minutes). Figure 1(c) shows the appearance of crystals during the cooling process, which abruptly formed at around 188°C. The size of these crystals substantially increased during further cooling.

We then studied the effects of reaction temperature and reaction time on the stability of the TPA. The recovery percentages of the TPA in the FSCR under different temperatures and after varying lengths of time are shown in Figure 2(a). By carrying out experiments at temperatures and times varying from 320 to 380°C and from 0 to 100 minutes,

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**Scheme 1.** Chemical reaction mechanism for TPA stability in HCW.

Scheme 1. We hypothesize that high temperatures promote the decarboxylation reaction, and carbon dioxide is produced in the decomposition of TPA in HCW. An aqueous solution phase was also involved in the reaction. Knowledge about this mechanism will play an important role in determining the best conditions for the recovery of TPA from PBT.

In summary, we investigated the stability of TPA in an FSCR and an autoclave reactor by observing its phase behavior in HCW conditions during heating and cooling. We found that, in the FSCR, the stability of TPA is primarily influenced by the heating temperature and time. In the stainless steel autoclave, on the other hand, the wall effect promotes the decomposition of TPA, which leads to the production of solid-phase benzoic acid. In our future work, we intend to optimize the process conditions to enable the recovery of a higher percentage of TPA from PBT.

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**Figure 2.** (a) Effect of temperature and time on the recovery percentage of TPA in HCW. (b) Recovery of TPA under HCW conditions in the FSCR and the stainless steel autoclave reactor.

respectively, we found that the TPA recovery percentage decreases as reaction temperatures increase. Under a constant reaction temperature, however, the recovery percentage gradually decreases as reaction time increases. This suggests that longer reaction times and higher reaction temperatures lead to the degradation of TPA and are therefore not suitable for TPA recovery.

We also investigated the effects of the different reactors on TPA stability. TPA recovery percentages obtained when using the FSCR and the stainless steel autoclave reactor are shown in Figure 2(b). Our results show that the TPA recovery percentage is consistently higher in the FSCR than in the stainless steel autoclave under the same conditions. This suggests that TPA decomposition may have been promoted by the wall effect (i.e., the metal catalytic performance) in the stainless steel batch autoclave.

By using gas chromatography-mass spectrometry (GC-MS) to determine the structures of the autoclave-reactor products, we found benzoic acid to be the dominant stable product of TPA. A mechanism for the stability of TPA, obtained by combining this GC-MS information with the phase behavior that we observed in the FSCR, is shown in