Synthesis and Characterization of Poly(trimethylene terephthalate) via TPA Process Using Titanium Catalyst

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Introduction

Poly(trimethylene terephthalate) (PTT) was synthesized via condensation polymerization using different molar ratios of 1,3-propane diol (PDO)/ terephthalic acid (TPA) in the presence of tetra-isopropyl titanate (TiPT) as a polyesterifi-cation catalyst. The effect of reaction conditions on the characteristics of as-polymerized PTT was investigated.

Experimental

Direct esterification (ES) was carried out under pressure for about 4 h at 275°C collecting water and then polycondensation (PC) was continued in vacuo at 265°C for another 3-7h with a removal of PDO. The PDO/TPA molar ratios were varied from 1.1 to 2.2 and the concentration of TiPT catalyst ranged from 25 to 150 ppm. Reaction profiles are seen in ***Figure 1***.

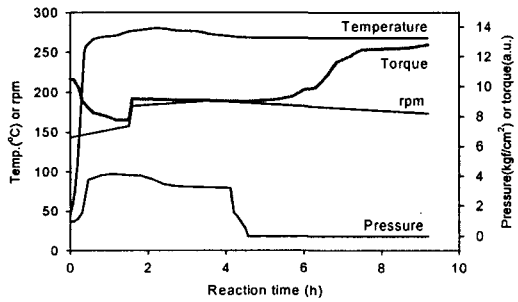

Figure 1. Changes in various reaction parameters in the course of PTT polymerization.

Intrinsic viscosity of PTT was measured using phenol/tetrachloroethane mixture solvent and a Ubbelohde viscometer at 25°C. The concentrations of allyl alcohol and acrolein produced during polymerization were measured using a HPLC. The concentration of dipropylene glycol (DPG) unit copolymerized in the PTT main chain was measured using an FT-proton NMR. Thermal transition curves of PTT samples were recorded using a Perkin-Elmer DSC-4. CIE L^*, a^*, b^* values of PTT chip were also measured.

Results and discussion

As the TiPT concentration is increased up to 50ppm, the rate of ES reaction is increased. Thereafter, however, no significant rate increase was observed with increasing catalyst content. As the molar ratio of PDO to TPA is increased, the rate of water removal is increased and the total amount of water removed at the end of ES reaction is also increased. The maximum intrinsic viscosity is obtained at 75 ppm of TiPT for all PDO/TPA molar ratios. The PDO/TPA molar ratio of 1.4 yields the maximum intrinsic viscosity (ca. 0.81 at 75 ppm of TiPT). As the polycondensation time is increased up to 5h, the intrinsic viscosity is increased. After that, however, the intrinsic viscosity is reduced due to the thermal degradation caused by TiPT. The intrinsic viscosity is increased by 30-40% after solid state polymerization at 190°C in vacuo for 15h.

The largest value of L^* (ca. 79.5) and the lowest value of b^* (ca. 3.2) are obtained at 75 ppm of TiPT and the PDO/TPA molar ratio of 1.4.

The concentration of allyl alcohol in water collected during ES reaction and in PDO collected during PC reaction is about 10 ppm regardless of the molar ratio of PDO/TPA and the TiPT concentration. The concentration of acrolein in water collect during ES reaction and PDO collected during PC reaction is increased with the PDO/TPA molar ratio at 75 ppm of TiPT and the amount of acrolein produced during PC reaction is about 5 times more than that produced during ES reaction.

The content of DPG unit in the PTT chain is increased nearly linearly with the PDO/TPA molar ratio. The molar ratio of 1.4 showed 3.3 mole% of DPG unit. As the DPG content is increased, the melt crystallization temperature and melting point are depressed significantly. However, DPG unit copolymerized in the PTT main chain was not observed in the PTT sample obtained via DMT process.

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