Effect of Segment Length on the Crystallization Behavior of Segmented Block Copolyetheresters Based on Poly(butylene terephthalate) and Poly(tetramethylene ether glycol)

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Segmented block copolyetheresters based on poly(butylene terephthalate) and poly(tetramethylene ether glycol) (4GT/PTMGT) with various hard segment contents were synthesized by the equilibrium melt transesterification of dimethyl poly(tetramethylene ether and 1.4-butanediol terephthalate with (M.W.=1000 and 2000). The copolyetheresters synthesized were found to be true segmented block copolymers from the results of 1H-NMR and melting temperature depression data. The average segment length of hard and soft segment were calculated with the assumptions that polymerization was carried out to high extent of reaction and that the segment length distribution followed temperatures, melt-crystallization Melting distribution. probable most temperatures, heats of fusion, and heats of crystallization were determined by differential scanning calorimetry for samples with various thermal history, i.e., annealed samples and dynamically crystallized samples in order to find out the effect of annealing and dynamic crystallization condition on the morphology and melting behavior of the copolyetheresters. The response of polymers to annealing was found to depend on the hard segment length. The overall crystallinity X_c increased with the hard segment length. Upon annealing, Xc also increased for all the samples examined and the hard segment length dependencies of Xc in 4GT/PTMG-1000 and 2000 resemble each other in shape. The effect of dynamic crystallization condition on the phase structure of copolymer was also examined at the cooling rates of 7, 20, and 50°C/min. For all the cooling rates examined both the overall and the hard segment crystallinity of the 4GT/PTMGT-2000 were larger than those of 4GT/PTMGT-1000 at the same hard segment length. The minimum hard segment length for crystallization, which was calculated on the assumption that all the sequences longer than this minimum length participate in crystallization, is nearly the same as the average hard segment length both for 4GT/PTMGT-1000 and 2000.