

Structure-Property Relations of Segmented Block Copolyetheresters.

I. Synthesis and Thermal Properties

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Segmented copolyetheresters based on poly(butylene terephthalate) and poly(tetramethylene ether glycol) with various hard segment contents were synthesized by the equilibrium melt transesterification of dimethyl terephthalate with 1,4-butanediol and poly(tetramethylene ether glycol) (M.W.=1000). Intrinsic viscosity data revealed that the copolyetheresters synthesized had fairly high molecular weight. The hard segment content in copolyetheresters were determined by ^1H nuclear magnetic resonance spectroscopy and the copolyetheresters showed any sign of degradation of poly(tetramethylene ether glycol) used. 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 a most probable distribution. The melting temperatures and the heats of crystallization were determined by differential scanning calorimetry for samples with various thermal history, i.e., for isothermally crystallized, dynamically crystallized, and annealed samples. By annealing copolyetheresters whose hard segment contents were greater than 50 wt% showed considerable decrease of the hard segment content in the amorphous phase. On the other hand the sample containing 20 wt% of hard segment did not show any considerable change of the hard segment content in the amorphous phase after annealing, which suggested that the copolyetherester of high soft segment content must have very short hard segments and hence they preferred the fringed micelle type crystals rather than the folded chain crystals. The degree of phase separation, defined as the soft segment weight fraction in the amorphous phase, increased with decreasing hard segment contents. The range of hard segment length which would participate in the crystals were calculated with the assumption that only the sequences whose length was located in the vicinity of the average value were able to crystallize.