EFFECT OF BLOCK LENGTH ON THE CRYSTALLIZATION BEHAVIOUR OF POLY (ETHYLENE TEREPHTHALATE) POLY (BUTYLENE TEREPHTHALATE) BLOCK COPOLYMERS

by

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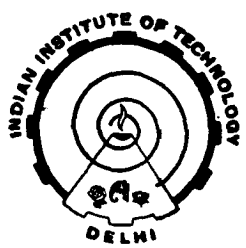
CENTRE FOR MATERIALS SCIENCE AND TECHNOLOGY

A thesis submitted

In fulfilment of the requirements of the degree of

DOCTOR OF PHILOSOPHY



to the

INDIAN INSTITUTE OF TECHNOLOGY, DELHI

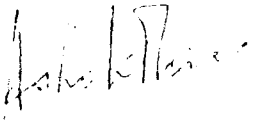
FEBRUARY, 1986

Dedicated to
my Guruji
and to my parents

CERTIFICATE

This is to certify that the thesis entitled, "Effect of Block Length on the Crystallization Behaviour of Poly(ethylene terephthalate), Poly(butylene terephthalate) Block Copolymers" being submitted by Mr. Ashok Tendolkar to the Indian Institute of Technology, New Delhi, for the award of the degree of Doctor of Philosophy in the Centre for Materials Science and Technology, is a record of bonafide research work carried out by him. Mr. Ashok Tendolkar has worked under my guidance and supervision and has fulfilled the requirements for the submission of the thesis.

The results contained in this thesis have not been submitted, in part or in full, to any other University or Institute for the award of any degree or diploma.



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A C K N O W L E D G E M E N T

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Abstract

The block copolymers of polyethylene terephthalate (PET) and polybutylene terephthalate (PBT) were synthesized by end coupling the oligomers of PET and PBT. PBT being in very small amount (3.5 wt.%) acts as a nucleating agent to enhance the crystallization rate of PET. Thus an attempt was made to improve the crystallization rate of PET for its use in moulding applications. The molecular weight of PBT in the block copolymers was varied from 10,000 to 1,000 with an aim to study the effect of block length on the crystallization rate of block length on the crystallization rate of these copolymers. The molecular weight of PET was kept constant at 10,000. The crystallization kinetics were compared at appropriate places with the homopolymer PET and the random copolymer with equivalent composition as that of the block copolymers. These copolymers were characterized by viscosity, DSC, FT-IR and NMR. The glass transition temperatures and the melting temperatures remained constant inspite of variable block lengths of PBT. FT-IR and NMR spectra show an incorporation of PBT blocks into the PET backbone.

The rates of crystallization of these polymers were measured by observing changes in mass density as a function of time. The crystallization rate increased as the block length of PBT in the block copolymers decreased. The block copolymers proved to be faster crystallizing than the homopolymer PET and the random copolymer. The crystallization behaviour was analysed by Avrami equation. Avrami plots of the homopolymer PET as well as those

of the random copolymers were different from the Avrami plots of the block copolymers. This was attributed to the difference in the crystallization rates. The crystallization rate was also investigated by FT-IR spectroscopy. The absorption intensity of the crystalline bands of PET had a remarkable effect when PBT was incorporated into the PET backbone. The half-times of crystallization of the copolymers as well as the homopolymers determined by FT-IR studies were compared with those obtained by density measurements and were found comparable.

Light scattering studies were carried out to investigate the role of PET in the crystallization of the block copolymers. In the initial stages of crystallization of the block copolymers, a four-lobed unusual type scattering pattern with lobes along the polarizer directions were observed, which is typical of PBT under similar crystallization conditions. This indicates that PBT component crystallizes first. The unusual patterns change to usual patterns with lobes at 45° to the polarizer directions during the later stages of crystallization, which is typical of PET. Thus, it has been proposed that in a block copolymer of PBT and PET, PBT crystallizes first, and then acts as nuclei to form the nucleation sites for PET to crystallize. The nucleation density depends upon the block length of PBT. For an equivalent level of PBT in the block copolymer, lower the block length, higher the number of blocks and thus higher the nucleation density. The ultimate spherulite size decreased with an increase in the nucleation density.

The effect of polycondensation time on the structure of the block copolymer was studied by varying the polycondensation time. The crystallization temperature increased upto a polycondensation time of 4 hours and then decreased. SALS studies did not show any unusual pattern during the initial stages of crystallization for the samples with a polycondensation time of more than 4 hours. The NMR signals for the carbonyl group show a broadening after a period of 4 hours.

All these results pointed towards the randomization of the block copolymers at later timings of polycondensation.

In another short study, PET was crystallized from melt state at lower crystallization temperatures, and it was found that PET shows unusual spherulites as the crystallization temperature was lowered.

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