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Structure and Properties of Segmented Block Copolyetheresters Based on PBT and PTMGT. 1. Thermal Properties of Dynamically Crystallized Samples

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1. INTRODUCTION

Segmented block copolyetheresters defined as copolymers having sequences of alternating polyester hard blocks and polyether soft blocks create labile physical cross-links upon crystallization of hard polyester blocks[1-3]. Since the nature of the physical interlocking is a crystallite formed exclusively from the crystallizable hard segment, the basic understanding of interrelationship between crystallization condition and phase morphology is very important for the property control of the segmented block copolyetheresters. Though many researchers have studied the structure-property relationship of these polymer, the contradictory results of their experimental studies have led to a variety of models of the supermolecular structure for these materials[4-9].

In the present study segmented block copolyetheresters based on poly(butylene terephthalate) and poly(tetramethylene ether glycol) (molecular weights: 650, 100, 2000) with various hard segment contents were synthesized and characterized in order to investigate the effect of hard segment content and hard segment length on the thermal properties of the block copolyetheresters.

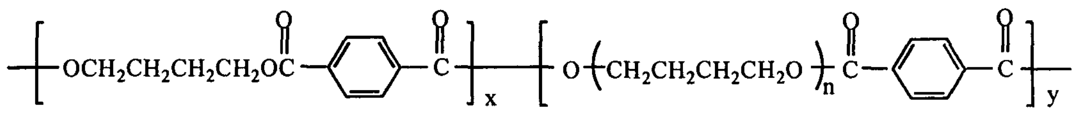
2. EXPERIMENTAL

The copolymers were prepared using commercial grade starting materials: dimethyl terephthalate, 1,4-butanediol, and poly(tetramethylene ether glycol) (PTMG) with number average molecular weight 650, 1000, and 2000. The two-stage polymerization was performed on a lab scale polymerization reactor in the melt[4,5]. The intrinsic viscosity of the polymer dilute solutions in a phenol/1,1,2,2-tetrachloroethane (volume ratio 1:1) mixture at 30℃ was measured using an Ubbelohde viscometer. ^{1}H-NMR spectroscopy (Varian Unity 300 Nuclear Magnetic Resonance Spectrometer) was used for determining hard segment content (HSC) in the copolyetheresters synthesized[10]. The copolymer samples melted on a DSC (Perkin-Elmer DSC-4) were dynamically crystallized with a cooling rate of 3, 7, 20, and 50℃/min. The crystallization temperatures and heats of crystallization were measured on the cooling thermograms obtained at the various cooling rates. The melting temperatures and the heats of fusion were determined on the heating DSC thermograms of the dynamically crystallized samples.

3. RESULTS AND DISCUSSION

3.1 Synthesis and characterization

The segmented block copolyetheresters synthesized contain different amounts of hard and soft segments in the chains. The structure of these copolyetheresters is as follows:



The overall stoichiometry is chosen so that the resulting copolymers have 20, 35, 50, 65, and 80 wt% of hard segment for each of the three kinds of PTMG molecular weight.

The average segment lengths of hard segment (HSL) and soft segment (SSL) were calculated based on the assumptions that the polymerization reaction was carried out to a high extent and that the segment length distribution followed a most probable distribution[11]. Table 1 shows the compositions and segment lengths of the samples. Fig. 1 shows the schematic model of the copolyetheresters with different lengths of soft segment, which implies that we can separate the effect of HSC and HSL on the properties of 15 copolyetherester samples.

Table 1. Compositions and segment lengths of copolyetheresters

Sample	HSC (wt%)	HSC (mol%)	HSL	SSL	[η] (dl/g)
2000-H80	79.7	97.4	39.1	1.03	0.90
2000-H65	65.9	94.9	19.7	1.05	1.00
2000-H50	49.4	94.9	10.4	1.10	0.83
2000-H35	35.2	84.0	6.3	1.19	0.95
2000-H20	21.0	70.4	3.6	1.42	0.88
1000-H80	80.5	95.5	22.2	1.05	0.97
1000-H65	65.4	90.7	10.7	1.10	0.98
1000-H50	50.1	83.8	6.2	1.19	0.92
1000-H35	34.2	72.8	3.8	1.37	0.77
1000-H20	19.6	55.5	2.3	1.80	0.57
650-H80	0.803	0.935	15.2	1.07	0.69
650-H65	1.655	0.871	7.6	1.15	0.88
650-H50	0.489	0.772	4.5	1.30	0.83
650-H35	0.354	0.660	2.9	1.52	0.55
650-H20	0.206	0.479	1.9	2.09	0.66

3.2 Thermal properties

Fig. 2 shows the variation of melting temperatures (T_m) of the melt-crystallized samples (20℃/min cooling rate) with HSL. As shown in Fig. 2, the melting temperature of a copolyetherester depends strongly on the HSL. Fig. 3 shows the variation of melt crystallization temperatures (T_{cm}) obtained at 20℃/min cooling rate with HSL. As shown in Fig. 3, the melt crystallization temperature of a copolyetherester depends on the HSL, although the dependency is not good as in the melting temperature.

Fig. 4-6 show the three dimensional diagrams of the overall crystallinity (X_c), HSC, and the cooling rate. The overall crystallinity is defined as $\Delta H_f/\Delta H_f^o$, where ΔH_f^o=33.5 cal/g, the heat of fusion for pure crystallizable component. When PTMG 2000 was used, the samples crystallized at the cooling rate of 20℃/min always have the lowest crystallinity. On the contrary, for the PTMG 650 system, samples crystallized at the same cooling rate show the highest crystallinity. In the case of PTMG 1000, the samples containing 80 and 65 wt% of hard segment show similar behavior as the PTMG 2000 samples. On the other hand, for the samples whose hard segment contents are smaller than 50 wt%, the crystallinity shows similar behavior as the samples of PTMG 650 system. These results indicate that crystallization under dynamic crystallization process depends not only on the crystallizable hard block lengths but also on the non-crystallizable soft ones.

4. Conclusion

The effects of hard segment content and hard segment length on the thermal properties of segmented block copolyetheresters were examined. The melting temperature of a copolyetherester was found to be a function of HSL. The melt crystallization temperatures depended on the HSL, although the dependency was not good as in the melting temperature.

The PTMG 2000 samples crystallized at the cooling rate of 20℃/min always had the lowest crystallinity. On the contrary, the PTMG 650 samples crystallized at the same cooling rate showed the highest crystallinity. In the case of PTMG 1000, the samples containing 80 and 65 wt% of hard segment showed similar behavior as the PTMG 2000 samples, while the samples whose hard segment contents were smaller than 50 wt% the crystallinity showed similar behavior as the samples of PTMG 650 system. These results indicate that crystallization under dynamic crystallization process depends not only on the crystallizable hard block lengths but also on the non-crystallizable soft ones.

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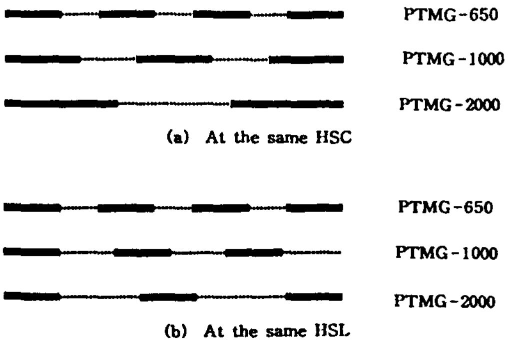

Fig. 1. Schematic model of the copolyetheresters with different lengths of soft segment (PTMG-650, 1000, 2000);
(a) at the same hard segment content (HSC), (b) at the same hard segment length (HSL).

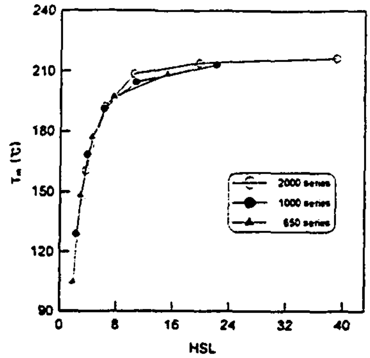

Fig. 2. Variation of Tm with hard segment length (HSL) for copolyetheresters at the cooling rate of 20℃/min.

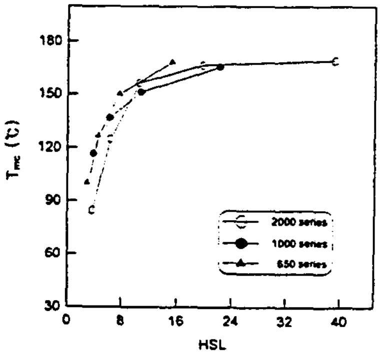

Fig. 3. Variation of T_{mc} with hard segment length (HSL) for copolyetheresters at the cooling rate of 20℃/min.

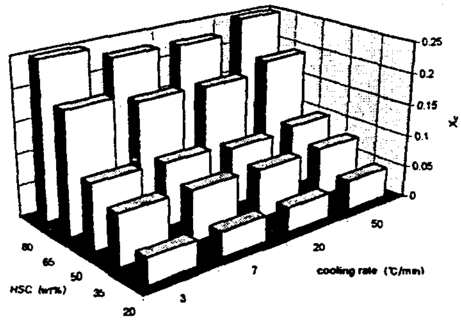

Fig. 4. Variation of X_c with hard segment content (HSC) for 2000 series at various cooling rates.

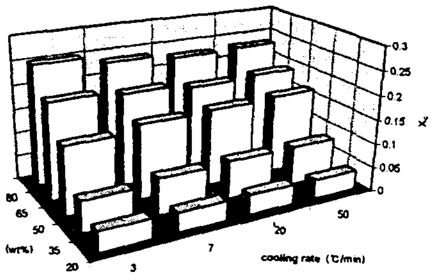

Fig. 5. Variation of X_c with hard segment content (HSC) for 1000 series at various cooling rates.

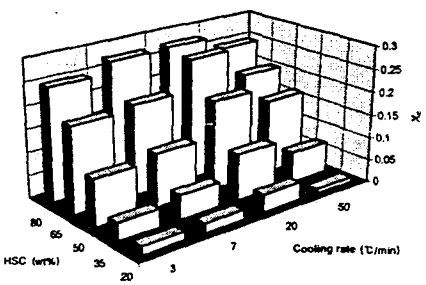

Fig. 6. Variation of X_c with hard segment content (HSC) for 650 series at various cooling rates.