Structure and Characterization of Segmented Block Copolyetheresters Based on PTT and PTMGT

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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]. Most of the studies on these block copolyetheresters are concentrated on the poly(butylene terephthalate) (PBT)-based copolyetheresters, especially, the 4GT/PTMGT system. Though poly(trimethylene terephthalate) (PTT) is expected to be a good hard segment polymer, not many researches have been done on the segmented copolymers which have PTT blocks as hard segments.

In the present study segmented block copolyetheresters based on PTT and PTMGT with various hard segment contents were synthesized and characterized. The segment lengths were determined by NMR analysis and the effect of hard segment content and hard segment length on the thermal properties of the block copolyetheresters was investigated.

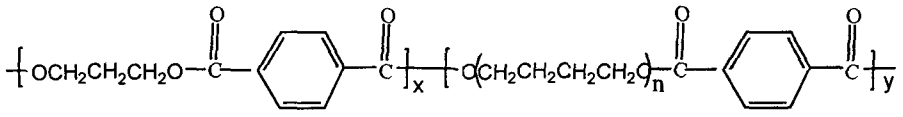
2. EXPERIMENTAL

The copolymers were prepared using commercial grade starting materials: dimethyl terephthalate, 1, 3-propanediol, and poly(tetramethylene ether glycol) (PTMG) with number average molecular weight 1000. The two-stage polymerization was performed on a lab scale polymerization reactor in the melt[4]. ^{1}H and ^{13}C-NMR spectroscopy (Bruker DRX-300 NMR Spectrometer) were used for determining hard segment content (HSC), hard segment length (HSL), and soft segment length (SSL) in the copolyetheresters synthesized[4,5]. The thermal properties of copolyetherester samples were measured by DSC (TA Instrument, DSC 2910) under nitrogen gas purging condition.

3. RESULTS AND DISCUSSION

3.1 Synthesis and characterization

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



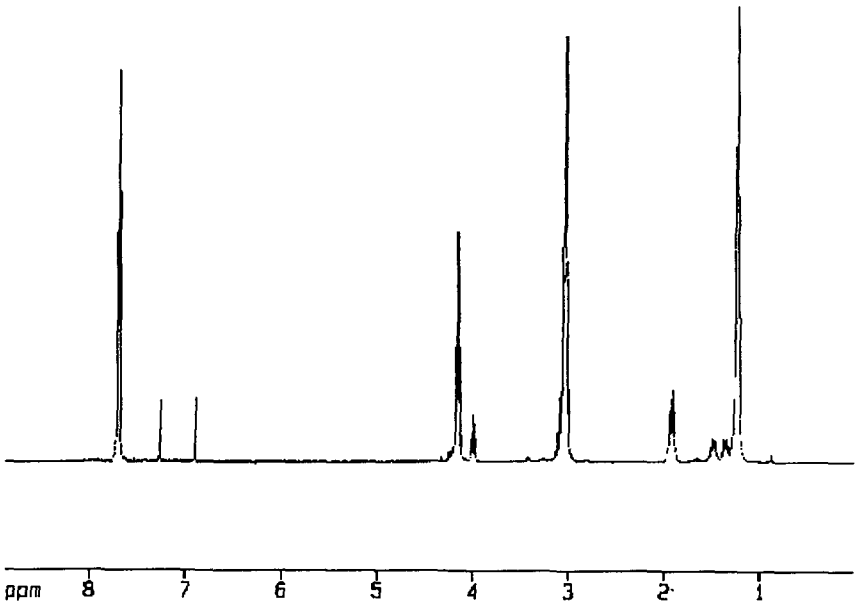


Fig. 1. A typical ^{1}H-NMR spectrum of 3GT\PTMGT.

Fig. 1 is the typical ^{1}H-NMR spectrum of the block copolyetheresters. The peak at 7.7 ppm is clearly due to the aromatic protons. Peak at 4.2 ppm is due to methylene protons of propanediol attached directly to the ester group and peak at 1.9 ppm is due to the central methylene protons of propanediol. Peak at 4.0 ppm is due to the methylene protons of PTMG attached directly to the ester group. The proton peaks of the second and the third methylene groups of PTMG from the ester group are shown at 1.5 and 1.3 ppm. Peaks at 3 ppm and 1.2 ppm are due to the methylene groups in the tetramethylene groups of PTMG which are not attached directly to the ester group.

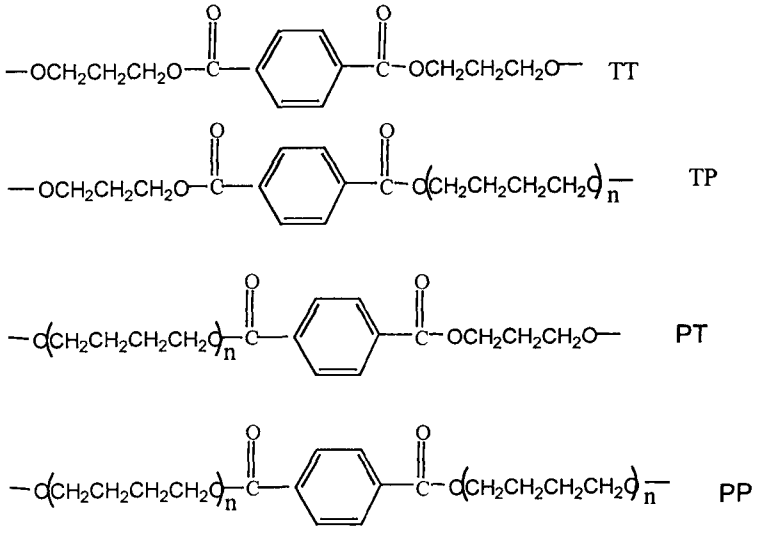
The hard segment content and the soft segment content in the copolymers can

be calculated from the ^{1}H-NMR spectra of the samples according to the peak assignment mentioned above. 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[6].

Table 1. Compositions and calculated segment lengths of copolyetheresters

sample	HSC(wt%)	HSC(mol%)	HSL	SSL
H80	79.3	95.6	22.94	1.05
H65	64.2	91.1	11.19	1.10
H50	50.2	84.6	6.49	1.18
H35	35	74.7	3.95	1.34
H20	19.7	57.8	2.37	1.73

Table 1 shows the compositions and the calculated segment lengths of the samples. Since the segment lengths in Table 1 are based not on the experiment but on the most probable distribution assumption, we still need experimentally calculatable segment lengths. In order to determine them experimentally we have used ^{13}C-NMR analysis[5]. There may be four possible triads in a 3GT/PTMGT sample:



TT and PP are characteristics of hard segment and soft segment, respectively. TP and PT are related with block joint. The probability of TT, TP, PT, and PP can be calculated from the ^{13}C-NMR data. We have calculated the probabilities and the segment lengths.

3.2 Thermal properties

The thermal properties of block copolyetheresters synthesized are listed in Table 2. The effect of hard segment content and hard segment length will be discussed later.

Table 2. Thermal properties of 3GT/PTMGT samples

sample	HSC (wt%)	T_m (℃)	T_{mc} (℃)	ΔH_f (cal/g)	ΔH_f^* (cal/g)	ΔH_c (cal/g)	ΔH_c^* (cal/g)
H80	79.3	223.39	164.31	12.53	15.80	12.37	15.59
H65	64.2	219.04	141.62	8.807	13.72	8.95	13.93
H50	50.2	207.59	118.5	7.55	15.04	10.93	21.77
H35	35	177.57	84.28	4.13	11.80	4.20	12.01
H20	19.7	130.98	-	2.37	12.03	-	-

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