

Preparation and Properties of Highly Functional Copolyetheresters

Yun Heum Park,^{1,2} Ki Young Kim,¹ Myong Hee Han³

¹School of Applied Chemistry and Chemical Engineering, Sungkyunkwan University, Suwon 440-746, South Korea

²Hyperstructured Organic Materials Research Center, Seoul 151-744, South Korea

³Department of Fashion & Textile, Hyejeon College, Chungnam 350-702, South Korea

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ABSTRACT: Block copolyetheresters with hard segments of poly(trimethylene 2,6-naphthalene dicarboxylate) and soft segments of poly(tetramethylene ether)glycol 2,6-naphthalene dicarboxylate were prepared by the melt polycondensation of dimethyl 2,6-naphthalene dicarboxylate (NDC), 1,3-propanediol (PD), and poly(tetramethylene ether)glycol (PTMEG) with molecular weights of 1000. The block copolyetheresters were characterized by ¹H-NMR spectroscopy, differential scanning calorimetry, thermogravimetric analysis, and dynamic mechanical analysis. The block copoly-

etheresters synthesized with NDC/PD/PTMEG were more heat resistant than those synthesized with dimethyl terephthalate/PD/PTMEG. The block copolyetheresters synthesized with NDC/PD/PTMEG showed stronger elastoplastic behavior than those synthesized with NDC/1,4-butanediol/PTMEG. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 139–145, 2003

Key words: elastomers; polyesters; polyethers; thermal properties

INTRODUCTION

Thermoplastic polyester elastomers are multiblock copolyetheresters with alternating, random-length sequences of either long-chain or short-chain oxyalkylene glycols connected by ester linkages. They contain high melting blocks (hard segments) capable of crystallization and amorphous blocks (soft segments) with relatively low glass-transition temperatures (T_g 's).¹ The hard polyester blocks create a labile physical network on crystallization. The hard segments are dispersed in the amorphous matrix, consisting of soft polyether segments and the noncrystalline part of the hard segments.² A variety of starting materials can be used for the preparation of block copolyetheresters. The majority of studies have been done on block copolyetheresters based on poly(tetramethylene terephthalate) or poly(tetramethylene isophthalate) hard segments.^{3–9} There have been few studies on the synthesis of block copolyetheresters with 1,3-propanediol (PD) and their properties.

Poly(trimethylene terephthalate) (PTT) fiber has a high elasticity compared to poly(butylene terephthalate) fiber because of different crystalline structures. Thus, block copolyetheresters with trimethylene groups in their hard segments are also expected to

have a higher elasticity than block copolyetheresters with tetramethylene groups in their hard segments.

In this work, PD was used as a component of hard segments of the block copolyetheresters. The lower melting temperatures (T_m 's) of poly(tetramethylene terephthalate) and poly(tetramethylene isophthalate) limit the ultimate heat resistance for these block copolyetheresters. The use of a more rigid aromatic dicarboxylate monomer may improve the heat resistance. Thus, we chose dimethyl 2,6-naphthalene dicarboxylate (NDC) to design a more heat-resistant block copolyetherester. In this article, we present the synthesis and characterization of the block copolyetheresters with good elastoplastic and thermal properties.

EXPERIMENTAL

Chemicals

NDC was supplied by Amoco Co. (Naperville, IL). Poly(tetramethylene ether)glycol (PTMEG) with a number-average molecular weight of 1000 (M_n) and tetrabutyl orthotitanate were supplied by BASF (Ludwigshafen, Germany). PD, 1,4-butanediol (BD), dimethyl terephthalate (DMT), trifluoroacetic acid, and chloroform were reagent grade and supplied by Aldrich (Milwaukee, WI).

Synthesis

The block copolyetheresters with poly(trimethylene 2,6-naphthalene dicarboxylate) (PTN) hard segments and

Correspondence to: Y. H. Park (yhpark@speed.skku.ac.kr).

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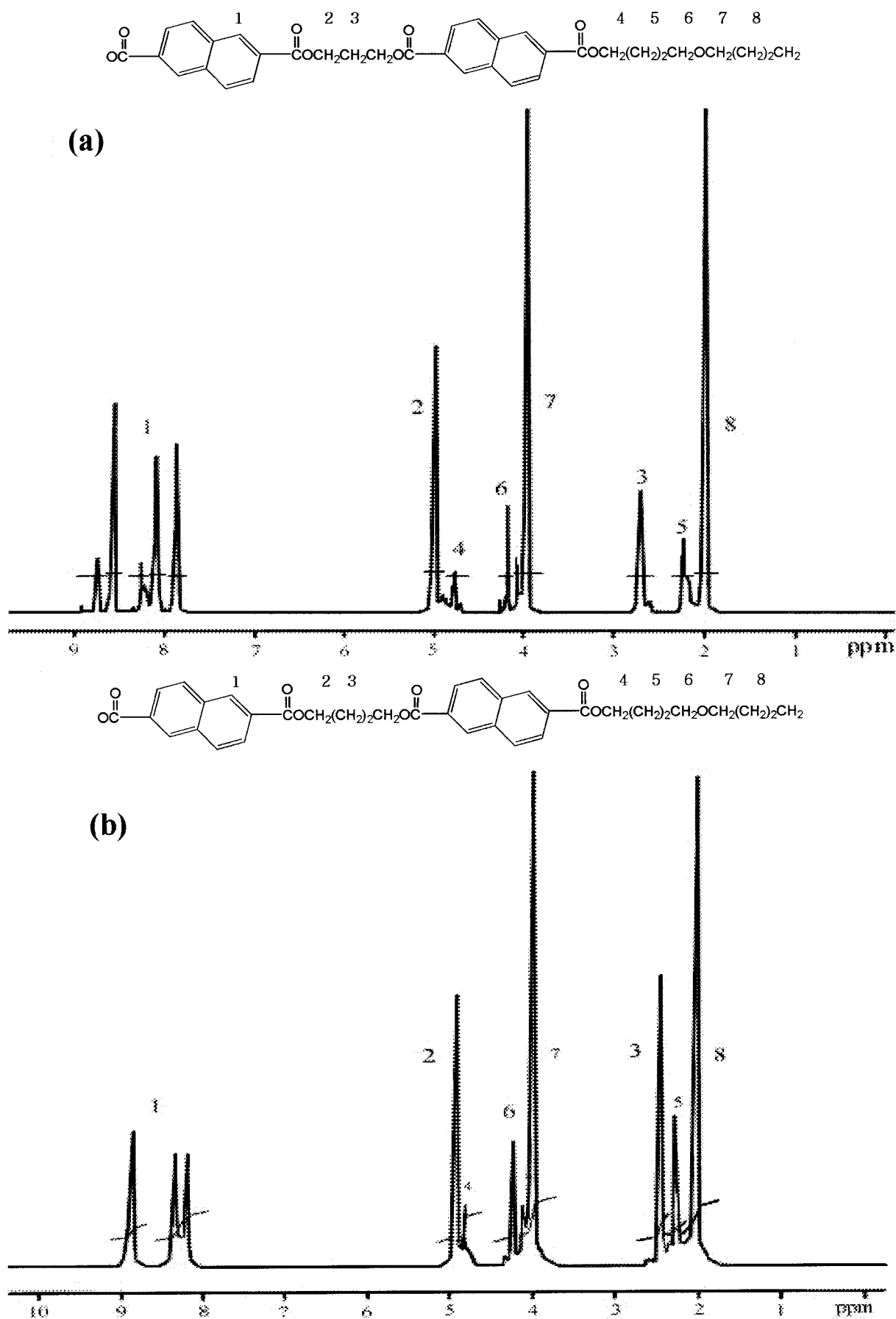


Figure 1 ¹H-NMR spectra of block copolyetheresters of samples (a) A-1, (b) B-1, and (c) C-1.

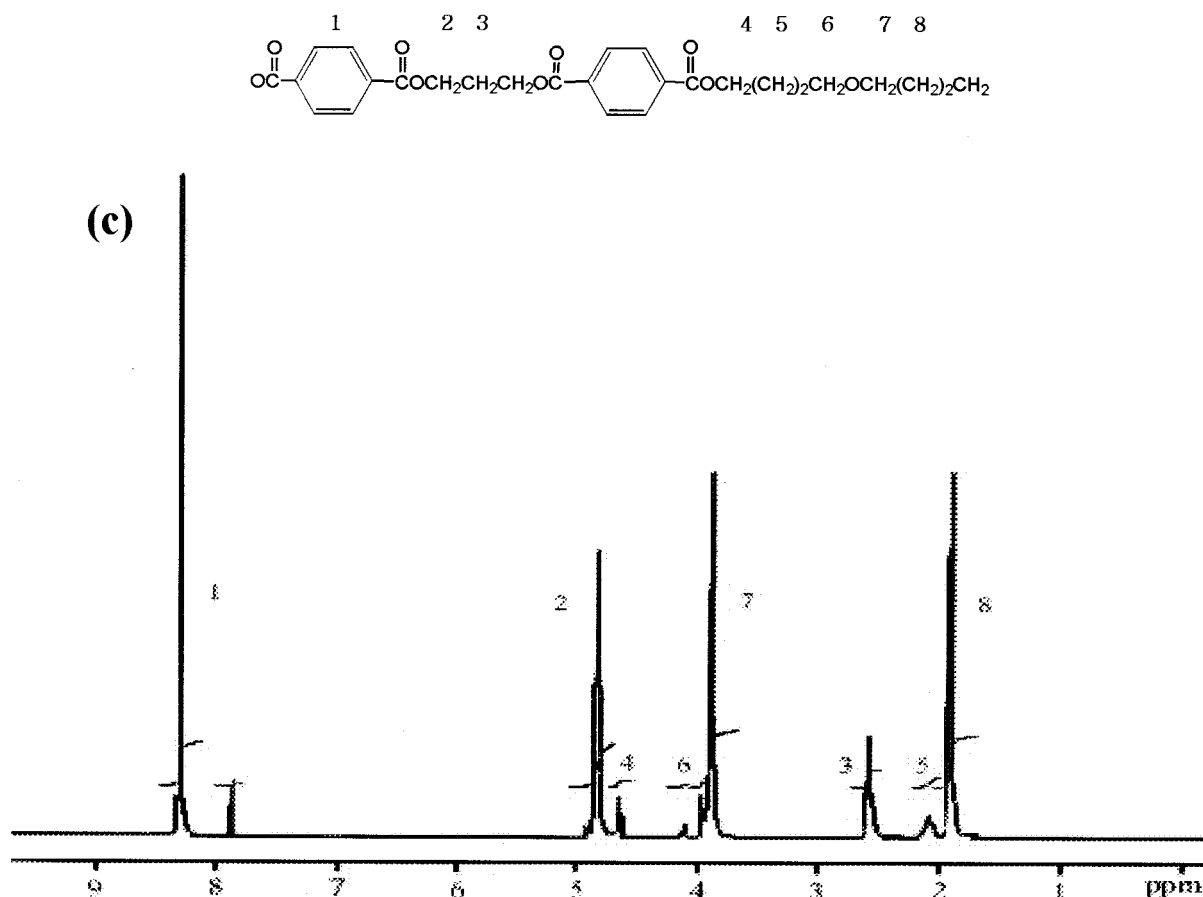


Figure 1 (Continued from the previous page)

-60°C , and a second scanning was carried out for the measurement of T_m . The thermogravimetric curves were determined by thermogravimetric analysis (TGA) on a TA Instruments 2950 TGA analyzer at a heating rate of $10^{\circ}\text{C}/\text{min}$ under nitrogen. The dynamic mechanical analysis data, $\tan \delta$, and complex modulus were obtained with a TA Instruments 983 DMA analyzer at a heating rate of $2^{\circ}\text{C}/\text{min}$. Samples were prepared by compression molding.

RESULTS AND DISCUSSION

The reaction synthesis of the block copolyetheresters is presented in Scheme 1. The feed compositions and η_{inh} values of the prepared block copolyetheresters are listed in Table I. Because PD is volatile, excess PD was used in synthesis. In Table I, the theoretical composition is given. Block copolyetheresters with η_{inh} 's of 0.6–0.9 were obtained.

In Figure 1 the $^1\text{H-NMR}$ spectra of the typical block copolyetheresters are displayed. The calculation of polymer composition from $^1\text{H-NMR}$ spectra was based on the assumption that PTMEG would not be distilled off during the polycondensation. The calculated polymer composition and hard segment weight fraction were in good agreement with the fed polymer

composition and hard-segment weight fraction, respectively.

To investigate the effect of dicarboxylate components and the weight fraction of the hard segments in the block copolyetheresters on the thermal properties, T_m and heat of fusion (ΔH_f) data, obtained from the DSC thermograms, were tabulated and are shown in Table II. The thermal properties of the block copolyetheresters were dependent on their compositions. With increasing weight fraction of PTN hard segments in the A series, a marked shift of T_m toward higher temperatures was observed. As the weight fraction of PTT hard segments in the C series increased, T_m also increased. However, the block copolyetheresters pre-

TABLE II
DSC Results of Block Copolyetheresters Measured at a Heating Rate of $10^{\circ}\text{C}/\text{min}$ Under a Nitrogen Atmosphere

Sample code	T_m ($^{\circ}\text{C}$)	ΔH_f (J/g)
A-1	211.6	40.5
A-2	187.4	25.3
A-3	162.9	21.4
C-1	187.6	27.9
C-2	172.6	18.8
C-3	150.6	11.7

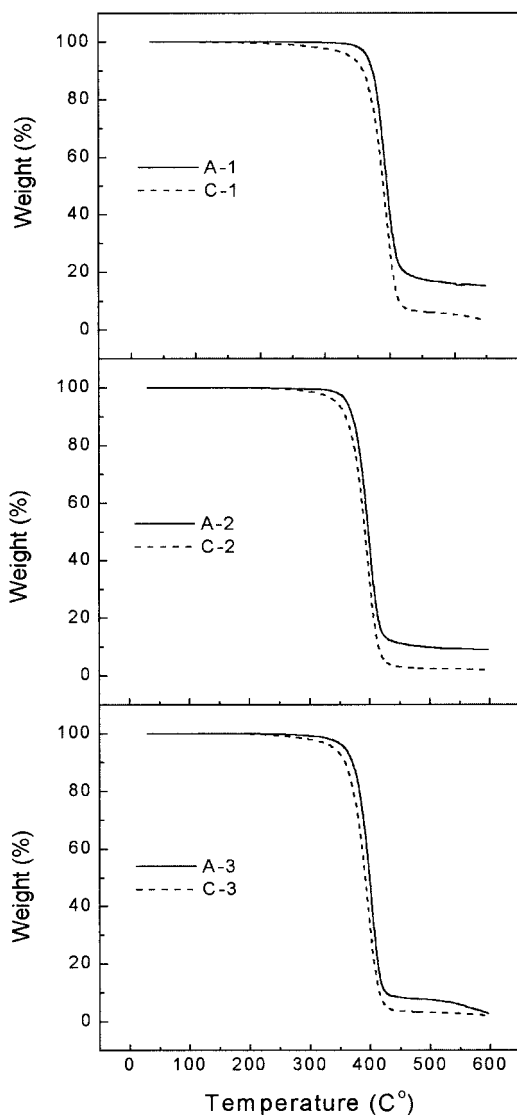


Figure 2 TGA thermograms of block copolyetheresters according to their compositions.

pared with NDC (A series) had a higher T_m and a higher ΔH_f than those prepared with DMT (C series), based on the same weight fractions of the hard segments (e.g., A-1 and C-1, A-2 and C-2, and A-3 and C-3, respectively).

Commercial block copolyetheresters such as Hytrel consist of polyester hard segments with a benzene ring within the repeat unit, and thus, the heat resistance of these are higher than those of other thermoplastic elastomers. In this work, we used a more rigid aromatic dicarboxylate monomer, NDC, in hopes of improving the heat resistance.

Figure 2 shows the thermogravimetric curve of the two different series of block copolyetheresters. The initial thermal degradation of the A series block copolyetheresters with PTN hard segments started at a higher temperature compared with that of the C series block copolyetheresters with PTT hard segments.

Also, the char residues of the A series were higher than those of the C series block copolyetheresters. These results suggest that the thermal resistance of the block copolyetheresters was improved with NDC as a dicarboxylate monomer.

To investigate the effect of diol components and weight fractions of the hard segments on the dynamic mechanical properties of the block copolyetheresters, we show the $\tan \delta$'s and storage moduli (G'' 's) of the two different series of the block copolyetheresters (A and B series) in Figures 3 and 4, respectively. The $\tan \delta$ curves of the A and B series exhibited two relaxation processes, as shown in Figure 3. Particular attention should be given to the maximum relaxation associated with the glass transition in the $\tan \delta$ curve because its magnitude usually reflects the relative amount of amorphous material in block copolyetheresters. As the hard segment content in the A and B series increased, the maximum relaxation peak shifted to higher temperatures, its magnitude decreased, and its breadth increased considerably. These results are in agreement with those reported by other workers.^{3,10} As the frac-

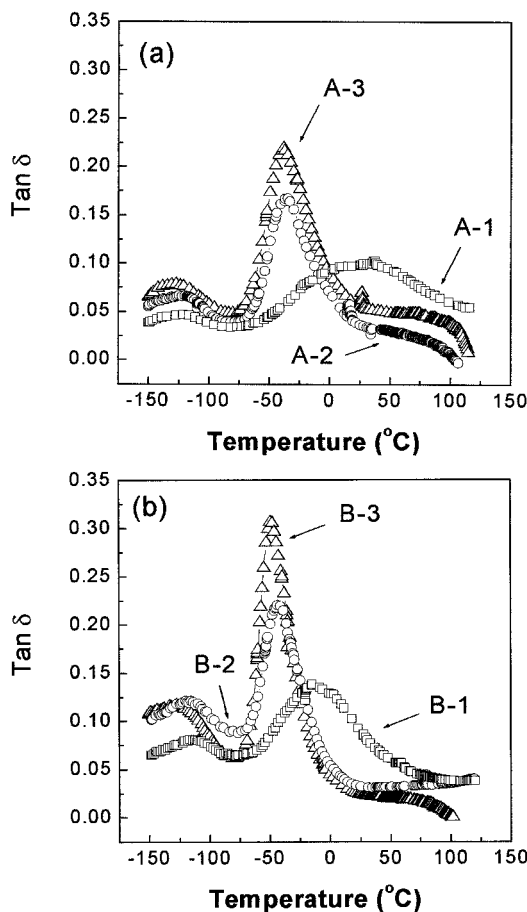


Figure 3 $\tan \delta$ behaviors of block copolyetheresters according to their weight fractions of hard segment: (a) A series (NDC/PD/PTMEG) and (b) B series (NDC/BD/PTMEG).

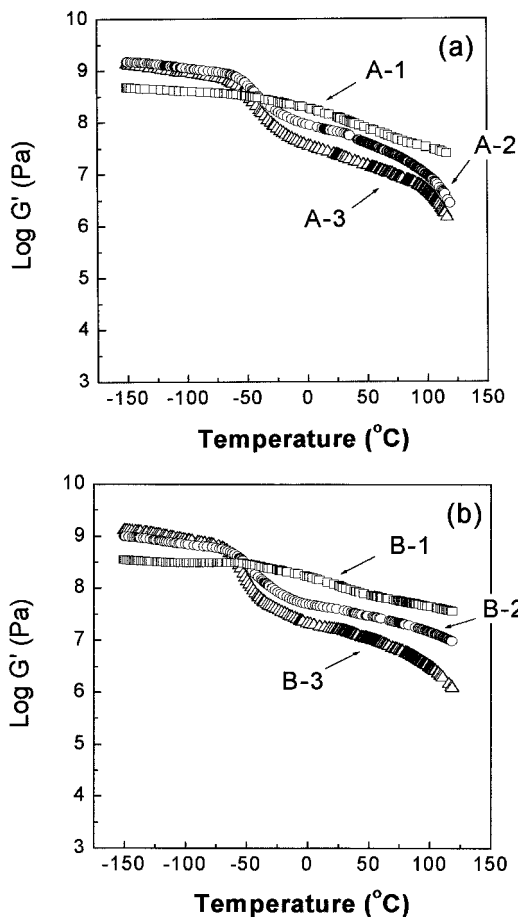


Figure 4 G' behaviors of block copolyetheresters according to their weight fractions of hard segment: (a) A series (NDC/PD/PTMEG) and (b) B series (NDC/BD/PTMEG).

tion of hard segments increased, G' (Fig. 4) decreased more slowly on increasing temperature.

The $\tan \delta$ behaviors of the A and B series copolyetheresters with equivalent weight fractions of H/S are compared in Figure 5. Significantly different behavior was found for A-1 and B-1, as shown in Figure 5(a); the A-1 sample, with a PD component and a high weight fraction of H/S, had a higher maximum relaxation temperature, a lower magnitude of maximum $\tan \delta$, and a wider breadth of maximum relaxation than the B-1 sample, with a BD component and an equivalent weight fraction of H/S as A-1. This implies that the A-1 sample had a distinct phase separation into crystalline and soft domains,¹¹ but the phase separation in sample A-1 was less than that in B-1. These results suggest that the polyetherester with PD exhibited a strong elastoplastic behavior, and these behaviors became weaker as the weight fraction of H/S decreased, as shown in Figure 5(b,c).

CONCLUSIONS

A block copolyetherester with hard segments of PTN and soft segments of PTMEGN was prepared with

NDC, PD, and PTMEG with molecular weights of 1000 by transesterification and melt polycondensation.

This block copolyetherester showed a higher initial degradation temperature, a higher percentage of char residue, a higher T_m , and a higher ΔH_f than that synthesized with DMT, PD, and PTMEG. This block copolyetherester also showed a higher T_g and a stronger elastoplastic behavior than that prepared with NDC, BD, and PTMEG.

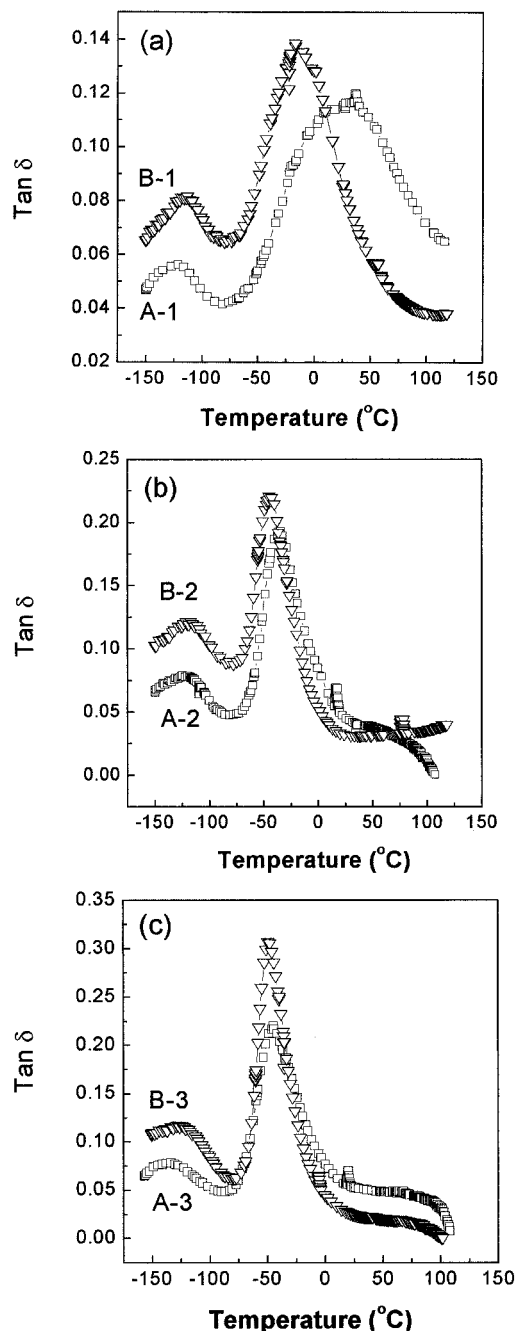


Figure 5 Comparison of $\tan \delta$ behaviors between A and B series copolyetheresters with (a) high, (b) medium, and (c) low weight fractions of H/S.

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