

Preparation and Characterization of Poly(ether ester) Thermoplastic Elastomers Containing the 2,6-Naphthalenedicarboxyl Group

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ABSTRACT: Poly(ether ester) elastomers (PEEs) were synthesized in which dimethyl terephthalate (DMT) was the primary diester compound in the hard segment (H/S) and dimethyl 2,6-naphthalene dicarboxylate (NDC), which has a more rigid aromatic chemical structure than DMT, was the secondary diester in the H/S. The block PEEs with poly(tetramethylene terephthalate) (PTMT) and/or poly(tetramethylene 2,6-naphthalate) (PTMN) as the H/S and poly(tetramethylene ether glycol terephthalate) (PTMEGT) as the soft segment (S/S) were synthesized through transesterification and polycondensation of DMT, NDC, 1,4-butanediol (BD), and poly(tetramethylene ether) glycol (PTMEG) of molecular weight 1000. The melting temperature and heat of fusion of the PEEs decreased with increasing NDC content up to an NDC content of 44.4% in the H/S, but increased on further

increase of the NDC content. In addition, the higher the fraction of NDC in the H/S, the higher the glass transition temperature of the copolymer. X-ray diffraction analysis revealed that the crystallinity of the sample decreases as the NDC content in the H/S is increased relative to that of DMT. Increasing the PTMN content in the H/S reduced the effect of UV photodegradation on the elongation at break. The results show that the introduction of the NDC component into the H/S as a secondary diester compound improves the UV resistance of the resulting PEE. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 3473–3480, 2003

Key words: thermoplastic elastomers; poly(ether ester) elastomers; dimethyl 2,6-naphthalene dicarboxylate; UV stability

INTRODUCTION

Thermoplastic elastomers (TPE) are used in various engineering applications due to their advantageous mechanical properties such as elasticity, toughness, strength, and low-temperature flexibility.^{1,2} They are composed of soft and hard segments and their elastomeric properties are influenced by physical cross-linking and their heterophase microstructures. The soft segment (S/S) is derived from flexible oligomers with low glass transition temperatures; thus, this segment is viscous at the TPE service temperature and imparts flexibility to the TPE. The hard segment (H/S) serves as a thermally reversible physical cross-linking between molecular domains, contributing elasticity, mechanical strength, and dimensional stability to the TPE.^{3–7}

The mechanical properties of a block copoly(ether ester) elastomer, a thermoplastic polyester elastomer,

are influenced by the type, content, and sequence length of the H/S and S/S, the miscibility between the S/S and H/S, as well as the polymer morphology, crystallization behavior, and thermal history.^{8–10}

The block copoly(ether ester) elastomers (PEEs), based on poly(tetramethylene ether glycol terephthalate) (PTMEGT) as the S/S and poly(tetramethylene terephthalate) (PTMT) and poly(tetramethylene isophthalate) (PTMI) as the H/S, which exhibit lower melting temperatures and lower crystallization rates than those based on PTMEGT and PTMT, can be extruded and injection-molded without losing their thermoplastic elasticity.^{1,11,12}

To improve the heat resistance of PEEs, a more rigid aromatic diester monomer is needed for the H/S. Block PEEs with the H/S of poly(alkylene 2,6-naphthalenedicarboxylate) and poly(alkylene 4,4'-bibenzoate) have been investigated in numerous studies,^{13–15} which show that these PEEs have higher melting temperatures.

Wolfe et al.¹³ studied a series of block PEEs in which the H/S was poly(tetramethylene 2,6-naphthalate) (PTMN) and the S/S was poly(tetramethylene ether glycol 2,6-naphthalate) (PTMEGN). Tsai et al.¹⁶ re-

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TABLE I
Composition and Intrinsic Viscosity of the Synthesized Copoly(ether esters)

| Sample code | ^a Feed ratio of DMT:NDC | Calculated NDC content in H/S (mol %) | ^b Measured NDC content in H/S (mol %) | Intrinsic viscosity (dl/g) |
|-------------|------------------------------------|---------------------------------------|--|----------------------------|
| PTMTN-1 | 9:0 | 0 | 0 | 1.227 |
| PTMTN-2 | 8:1 | 11.1 | 10.0 | 1.319 |
| PTMTN-3 | 7:2 | 22.2 | 20.2 | 1.373 |
| PTMTN-4 | 5:4 | 44.4 | 41.3 | 1.436 |
| PTMTN-5 | 2:7 | 77.8 | 75.2 | 1.495 |
| PTMTN-6 | 0:9 | 100.0 | 100.0 | 1.524 |

^a The feed ratio of DMT and NDC to PTMEG is 9:1 for all the samples.

^b Measured by ¹H-NMR spectroscopy.

ported on the synthesis and properties of PEEs based on PTMN and PTMEGN with various sequence lengths.

The object of the present study was to develop PEEs with improved UV stability and thermal properties. To achieve this aim, this research focused on synthesizing PEEs in which the H/S was constructed from dimethyl terephthalate (DMT) as the primary diester monomer and dimethyl 2,6-naphthalene dicarboxylate (NDC) as a secondary diester monomer. The synthesis and properties of a series of block PEEs with hard segments of PTMT and/or PTMN and soft segments of PTMEGT and/or PTMEGN are described.

EXPERIMENTAL

Materials and synthesis

NDC was supplied by Amoco Chemical (Naperville, IL), and 1,4-butanediol (BD) and poly(tetramethylene ether glycol) of molecular weight 1000 (PTMEG 1000) were obtained from BASF (Ludwigshafen, Germany). Reagent-grade DMT, BD, and tetrabutyl orthotitanate were purchased from Aldrich Chemical (Milwaukee, WI) and used as received. The block copoly(ether esters) were prepared in a 2-L stainless steel autoclave equipped with a mechanical stirrer, a nitrogen inlet tube, and a distillation head connected to a condenser. The following reagents were combined in the reactor: 620.0 g of DMT (3.19 mol), 197.3 g of NDC (0.91 mol), 526.4 g of BD (3.65 mol), 456.3 g of PTMEG 1000 (0.46 mol), 2.7 g of thermostabilizer (Irganox B 1171, Ciba-Geigy (Basel, Switzerland)), and 1.8 g of tetrabutyl orthotitanate.

The transesterification reaction was carried out at 210°C for 1 hour. After all of the methanol in the reactor was distilled off, the reaction mixture was heated to 250°C and maintained at that temperature for 2 hours under vacuum (approximately 0.1 mmHg) during the polycondensation reaction. At the end of the polymerization, the resulting polymer was pushed out of the autoclave by a nitrogen flow and then transferred to a cooling bath.

Characterization

The intrinsic viscosity of the copoly(ether esters) in phenol/1,1,2,2-tetrachloroethane (60/40 wt/wt) at 30°C was determined using an Ubbelohde viscometer (Cannon Instrument Co. (State College, PA)). FT-IR spectra were measured using a Digilab division FTS-40 (Digilab (Randolph, MA)). ¹H-NMR spectra of the copoly(ether esters) in *d*-chloroform were obtained on a Varian 300 Nuclear Magnetic Resonance Spectrometer (Varian Medical Systems (Palo Alto, CA)). The optical anisotropy of a copoly(ether ester) film was investigated using a cross-polarized microscope (Carl Zeiss Co. (Oberkochen, Germany)). Film specimens were prepared by dissolving 1 wt% of the copoly(ether ester) in 1,1,2,2-tetrachloroethane, casting the copoly(ether ester) solution on a glass plate, and evaporating the solvent. The microstructure of the copoly(ether ester) was investigated using scanning electron microscopy (JSM-T330, Jeol Ltd. (Tokyo, Japan)), differential interference contrast microscopy (PHOTOMI-3, Carl Zeiss Co., Oberkochen, Germany), and transmission electron microscopy (TEM) (FX-2000, Jeol Ltd. (Tokyo, Japan)). The specimen for TEM investigation was stained in an aqueous solution of 0.2 wt% phosphotungstic acid. X-ray diffraction patterns were recorded on a Ru-200B diffractometer (12 kw) (Rigaku Denki (Tokyo, Japan)) using Cu-K α radiation. Thermal properties were determined using a Perkin-Elmer DSC-7 (Perkin-Elmer, Norwalk, CT) at a heating rate of 20°C/min under nitrogen atmosphere from -70 to 260°C.

RESULTS AND DISCUSSION

In the preparation of the PEEs, the feed molar ratio of all the ester compounds to PTMEG was 9:1 which correspond to the hard segment weight fraction from 0.633 to 0.670. The NDC content in the H/S was calculated from the ratio of the integrated intensities of the ¹H-NMR peaks. The PEEs are denoted as PTMTN-*n*, where PTMTN implies that the H/S is composed of PTMT and PTMN except PTMTN-1 and PT-

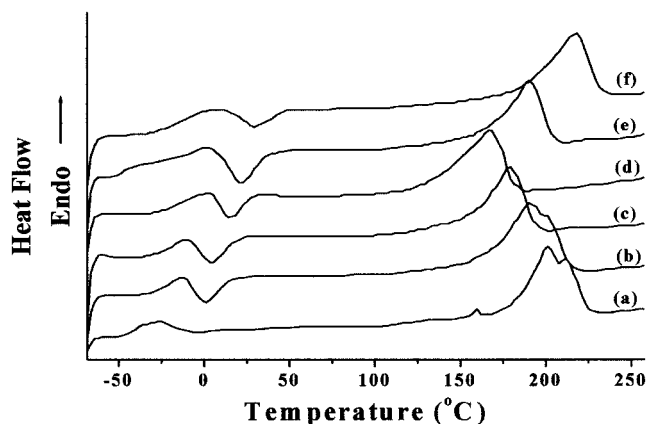


Figure 1 DSC thermograms of the PTMTN series: (a) PTMTN-1, (b) PTMTN-2, (c) PTMTN-3, (d) PTMTN-4, (e) PTMTN-5, and (f) PTMTN-6.

MTN-6, which contain only PTMT and PTMN, respectively. The feed compositions used in the synthesis of the copoly(ether esters) are shown in Table I, along with the intrinsic viscosities of the final copolyetheresters. The NDC contents in the H/S calculated from the $^1\text{H-NMR}$ results are in good agreement with the feed NDC content. The intrinsic viscosities of the copoly(ether esters) increase with increasing NDC content in the H/S. Thus, the inclusion of a greater amount of the rigid component, NDC, in the H/S increases the flow resistance of the resulting copoly(ether ester).

To investigate the thermal properties of the copoly(ether esters), DSC thermograms were collected during the second heating scan. The resulting thermograms are illustrated in Figure 1. The melting behaviors of the PEEs are mainly determined by the nature of the H/S. Thus, the differences in the melting thermograms observed in Figure 1 can be attributed to differences in the sequence length and composition of the H/S. PTMTN-1 shows two endothermic melting peaks, which are thought to be due to the melting–recrystallization–remelting process of the PTMT. As the amount of PTMN in the H/S composition is increased, the intensity of the remelting peak gradually weakens until finally only one endothermic melting peak is observed. The loss of the remelting peak is attributed to the decrease in the crystallization rate of the H/S as the content of the more rigid secondary diester, NDC, is increased.

Figure 2 shows the dependence of the glass transition temperature (T_g) and the cold crystallization temperature (T_{cc}) on the amount of PTMN (designated by NDC content in H/S) in the PEE. Both T_g and T_{cc} increase with increasing PTMN content. Since the chain will become stiff with increasing NDC units, T_g of PEE will increase with NDC content. Generally, the rate of crystallization of a copolymer decreases with

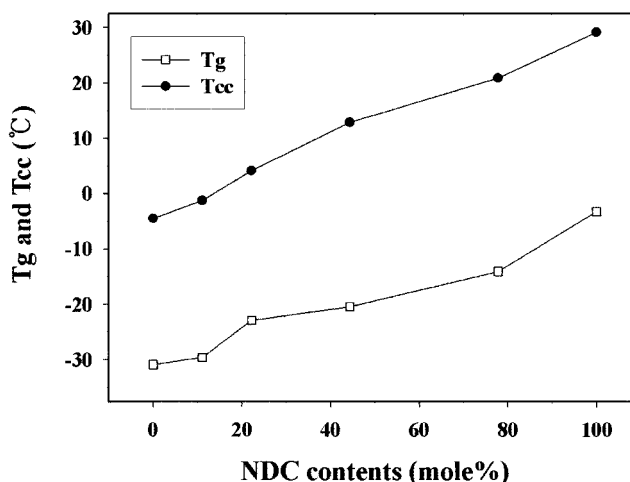


Figure 2 The glass transition temperature (T_g) and cold crystallization temperature (T_{cc}) of PTMTN vs NDC content in the H/S.

increasing comonomer content. So, the gap, $T_{cc} - T_g$, which has a close relationship with the driving force of cold crystallization, will increase with the comonomer content. As can be seen in Figure 2, the gap ($T_{cc} - T_g$) increases with comonomer (NDC when DMT is a major component or DMT when NDC is a major component) content.

The behavior of the melting temperature (T_m) and the heat of fusion (ΔH_f) of the copoly(ether esters) with changing PTMN content was also measured, as shown in Figure 3. In contrast to the monotonic behavior of T_g and T_{cc} , the values of T_m and ΔH_f initially decrease with increasing PTMN content, but reach a minimum at 44.4% NDC content in the H/S and then increase. PTMTN-6, which contains only PTMN in the H/S, melted at $T_m = 222$ °C, a temperature approximately 20° higher than the T_m of PTMTN-1, which contains only PTMT in the H/S, the usual result in a crystal-

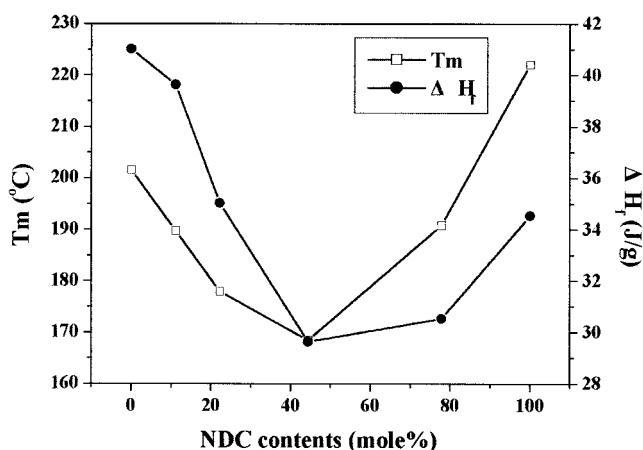


Figure 3 The melting temperature (T_m) and heat of fusion (ΔH_f) of PTMTN vs NDC content in the H/S.

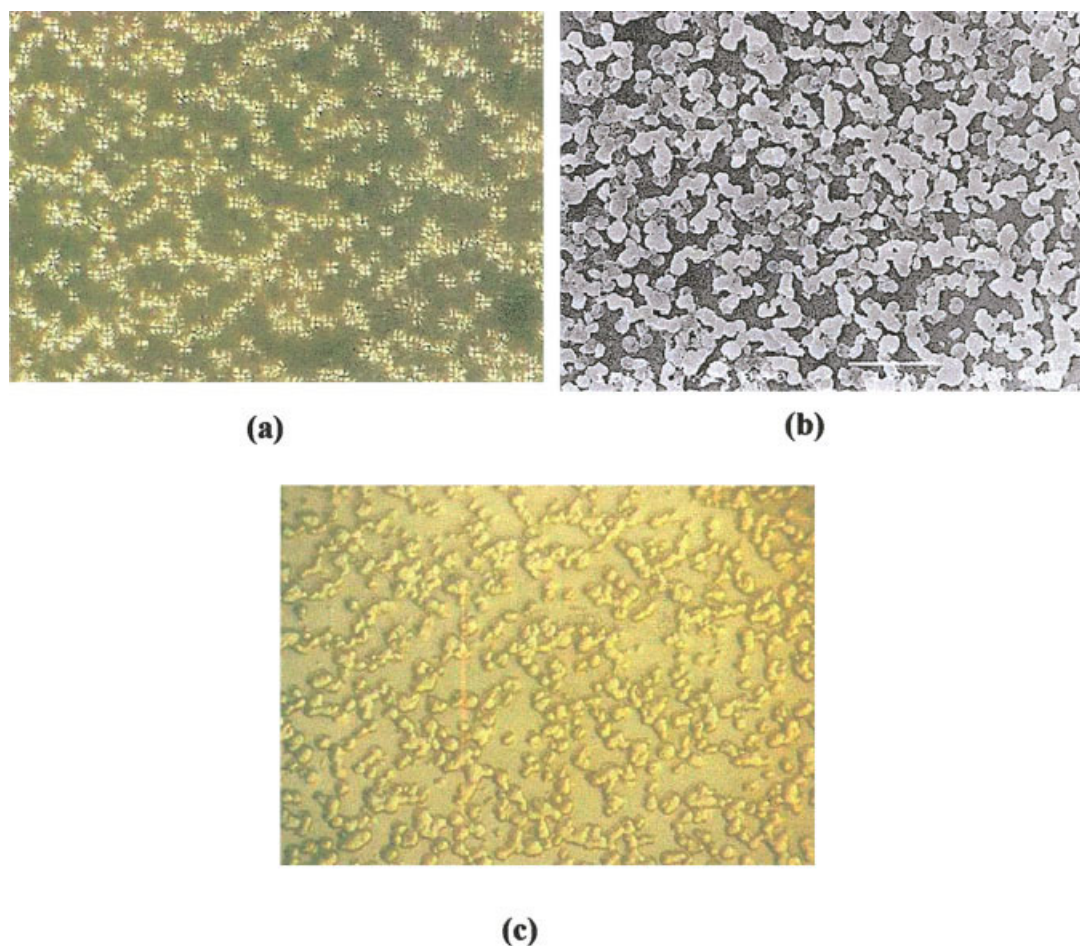


Figure 4 Photographs obtained using (a) polarized microscopy, (b) SEM, and (c) DICM for PTMTN-1.

lizable random copolymer. The melting temperature and crystallinity of a copolymer usually decrease with increasing comonomer content from the two extremes, i.e., the two crystallizable homopolymers.

The morphologies of PTMTN-1 through PTMTN-6 were characterized using polarized microscopy, SEM, and differential interference contrast microscopy (DICM). Representative images from these characterizations are shown in Figures 4, 5 and 6.

The diameter of spherulites was approximately 1.5–2.0 μm for the PTMTN-1 in Figure 4. A typical Maltese cross pattern was shown in the PTMTN-1. The morphology of PTMTN-6 as revealed by polarizing microscopy [Fig. 6(a)] differs considerably from the spherulite structure observed in the corresponding images of PTMTN-1 [Fig. 4(a)] and PTMTN-4 [Fig. 5(a)]. This result is consistent with the work of Lee et al.,¹⁷ who calculated the crystallization rate of PTMN using the Avrami equation. They obtained a value of approximately 2 for the Avrami exponent, which indicates that PTMN will tend to grow rodlike spherulites. The images of PTMTN-6 obtained by SEM and DICM [Fig. 6(b,c)] show the rod-shaped crystals being connected and forming a continuous phase like a

“bird’s footprint,” which agrees with the Avrami exponent value.

The X-ray diffraction patterns obtained from the PTMTN series are shown in Figure 7. PTMTN-1 shows diffraction peaks at $2\theta = 16.3, 17.3, 20.6, 23.4,$ and 25.1° (d-spacing = 0.544, 0.511, 0.430, 0.379, and 0.355 nm), which correspond to the lattice reflection planes (0 $\bar{1}1$), (010), ($\bar{1}01$), (100), and (1 $\bar{1}1$). Compared with PTMTN-1, PTMTN-6 (i.e., the PEE in which the H/S contains only PTMN) displayed similar diffraction peaks with different Bragg angles and the same reflection planes. The sharp diffraction peaks of PTMTN-6 appear at $2\theta = 14.6(0\bar{1}1), 15.4(010), 20.1(\bar{1}01), 24.1(100),$ and $28.3^\circ(1\bar{1}1)$ (d-spacing = 0.605, 0.576, 0.441, 0.369, and 0.315 nm).

The diffraction patterns of PTMTN-3 and PTMTN-4 show distinct differences in peak position. Analysis of these patterns reveals that the crystalline diffraction peaks of PTMTN-3 correspond to those of PTMT, and the crystalline diffraction peaks of PTMTN-4 correspond to those of PTMN. Thus, the shift in diffraction pattern upon going from PTMTN-3 to PTMTN-4 is possibly due to a change in the major crystallizing H/S from PTMT to PTMN. Similar results were ob-

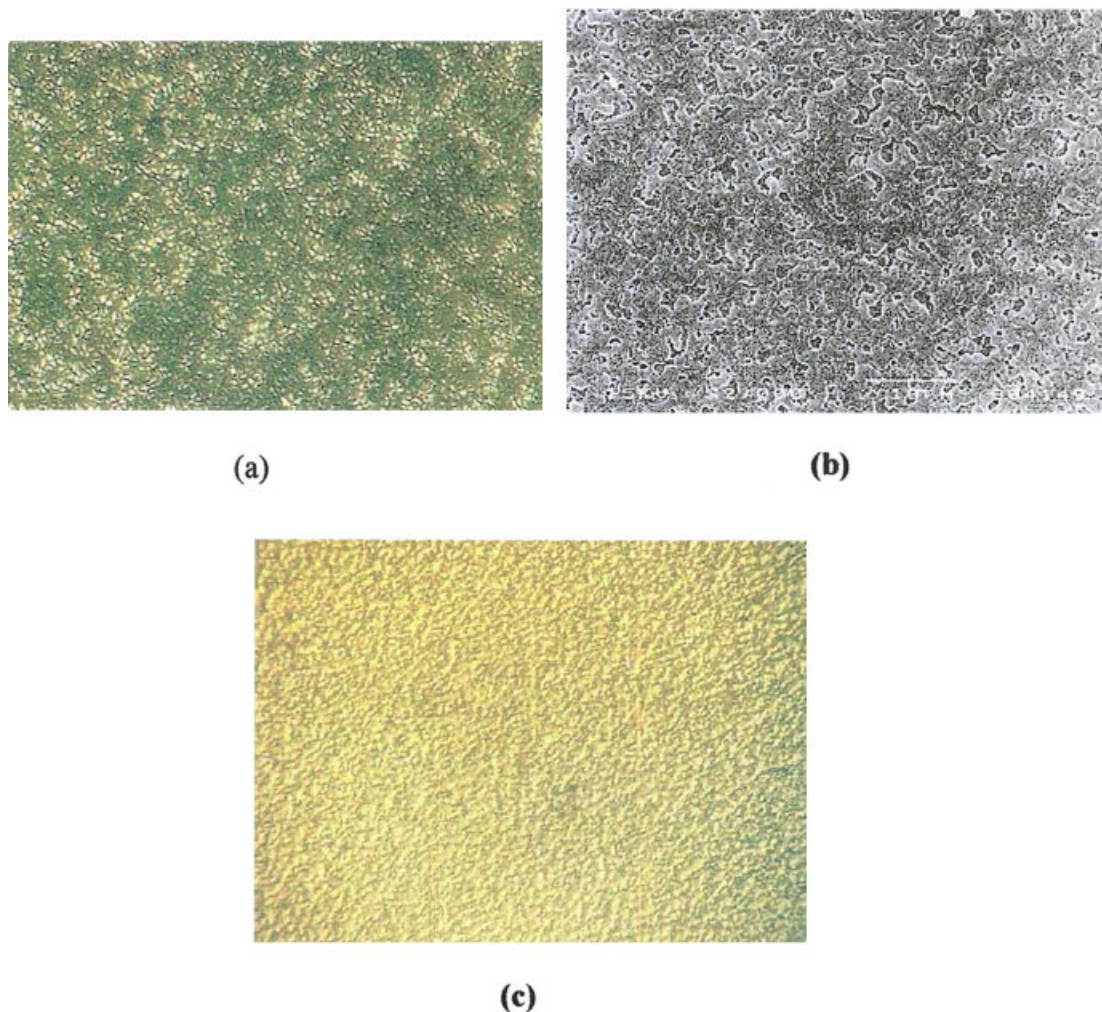


Figure 5 Photographs obtained using (a) polarized microscopy, (b) SEM, and (c) DICM for PTMTN-4.

tained previously by Castle et al.¹² in a study of poly(ether esters) containing PTMT and PTMI in the H/S.

The degree of crystallinity of PTMTN-1 through PTMTN-6 was calculated by Ruland's method¹⁸ to be 21.45, 21.53, 21.44, 19.69, 24.38, and 25.04%, respectively. Thus, the degree of crystallinity decreases with increasing NDC content in the H/S up to an NDC content of 44.4% and then increases upon further increase of the NDC content. This behavior is consistent with that observed in the DSC measurements of ΔH_f (Figure 3). These results imply that the comonomer, NDC or DMT, hinders the crystallization of the main crystallizable component, PTMT or PTMN, respectively. This is because the length of the main crystallizable component in the H/S decreases with increasing comonomer content.

The temperature dependence of $\tan \delta$ for each member of the PTMTN series is shown in Figure 8. All of the samples display two relaxations, one at lower temperature referred to as the γ relaxation, and one at higher temperature referred to as the β relaxation. The

γ relaxation peak appears between -140 and -95 °C, and the β relaxation peak appears between -70 and -90 °C. This single β relaxation indicates that the uncrystallized polyester sequence and the amorphous polyether sequence have some compatibility and are dispersed well. All the β relaxation peaks start from -70 °C. As the NDC content in the H/S increases from PTMTN-1 to PTMTN-6, the maximum peak temperature of β relaxation (β_{\max}), which is associated with $T_{g'}$, shifts to higher temperature. The $\tan \delta$ value at β_{\max} increases with the NDC content in the H/S, reaches a maximum at an NDC content of 44.4%, and then falls on further increase of the NDC content.

This behavior can be explained as follows. The poly(ether ester) with the highest $\tan \delta$ value at β_{\max} is PTMTN-4, which is the sample containing almost equal amounts of DMT and NDC in the H/S. Because the amounts of DMT and NDC are similar, the growth of PTMT crystal hinders that of PTMN and vice versa, and the packing of their chemical structures is difficult. As confirmed in the crystallinity measurement,

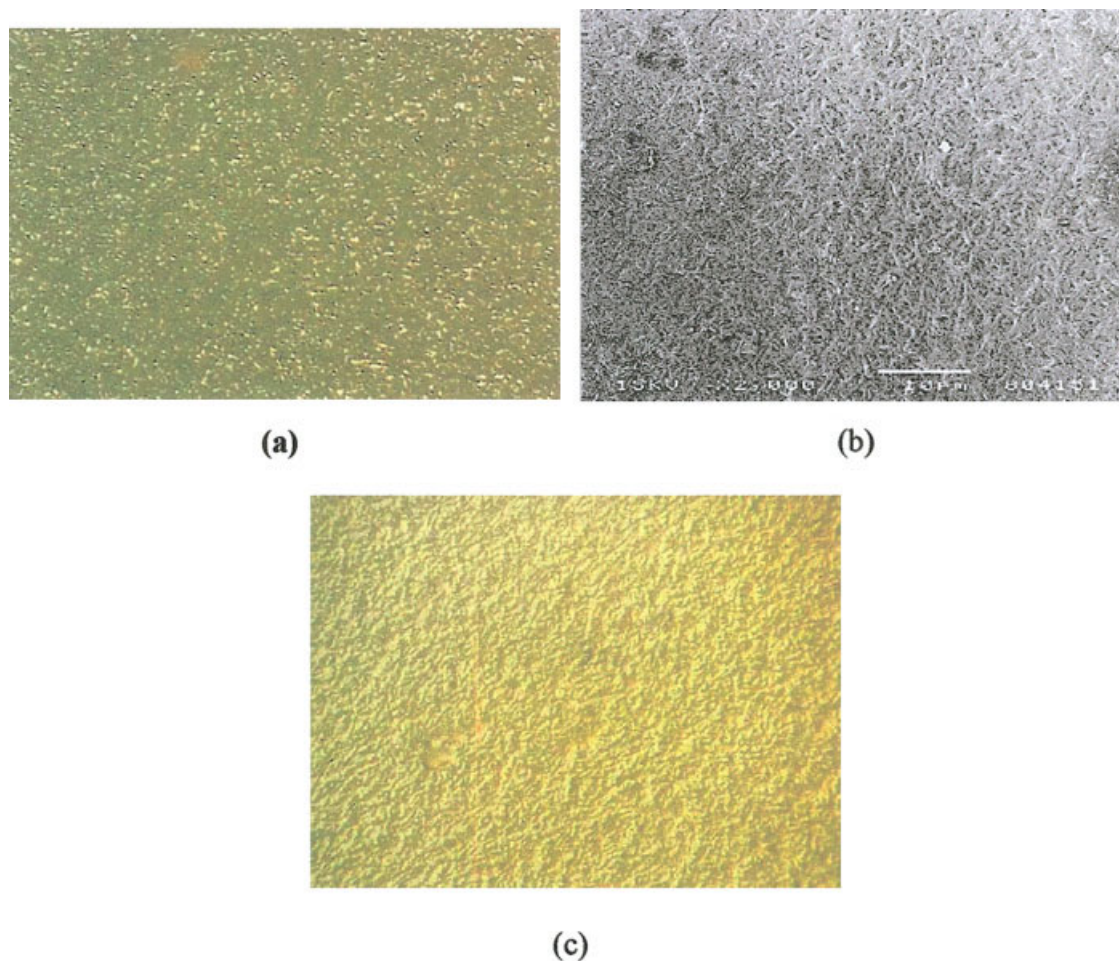


Figure 6 Photographs obtained using (a) polarized microscopy, (b) SEM, and (c) DICM for PTMTN-6.

PTMTN-4 has the lowest crystallinity and, consequently, it has the highest value of $\tan \delta$ at β_{\max} .

Figure 9 shows the storage modulus, E' , as a function of temperature for the PTMTN series. The temperature dependence of E' shows regions characteristic of the glass state, glass–rubber transition state, rubbery plateau, and rubbery flow state. However, the rubbery plateau region for the poly(ether esters) considered here is smaller than that observed for conventional rubber. In this region, the storage modulus is the highest in PTMTN-1, decreases from PTMTN-1 to PTMTN-4, and then increases for PTMTN-5 and PTMTN-6. This result implies that PTMTN-1 is the most rigid member of the series¹⁹ and is consistent with the result of the initial modulus obtained from the stress–strain curves (data not shown). The modulus also depends upon the crystallinity of the sample.

In comparison with typical vulcanized elastomers, PEEs have relatively poor resistance to UV radiation in the external environment. Some studies have reported an improvement in the weather stability of PEEs on addition of a UV stabilizer such as hydroxybenzophenone or hydroxyphenyl benzotriazole.²⁰

However, it was found that the extent to which the weather resistance could be improved was limited because the elasticity and mechanical strength of the PEEs diminished when the loading of UV stabilizer exceeded 1 wt%.

Figure 10 shows the change in the yellowness of the PTMTN samples as a function of UV exposure time, where the degree of yellowing is indicated by the b^* value. The b^* value decreases with increasing PTMN content in the H/S. Therefore, PTMTN-6, which contains only PTMN in the H/S, shows the lowest b^* value. It is supposed that the conjugated double bond in the naphthalene ring of NDC absorbs the UV. Figure 11 shows the elongation at break as a function of UV exposure time for the PTMTN series. The elongation at break of PTMTN-1 containing 1 wt% of UV stabilizer Irganox 1098 (Ciba-Geigy (Basel, Switzerland)), as the reference sample, was compared with those of six other PTMTN copolymer samples. Increasing the PTMN content in the H/S reduced the lowering of the elongation at break caused by UV photodegradation. These results confirm that the introduction of the NDC component into the H/S as a

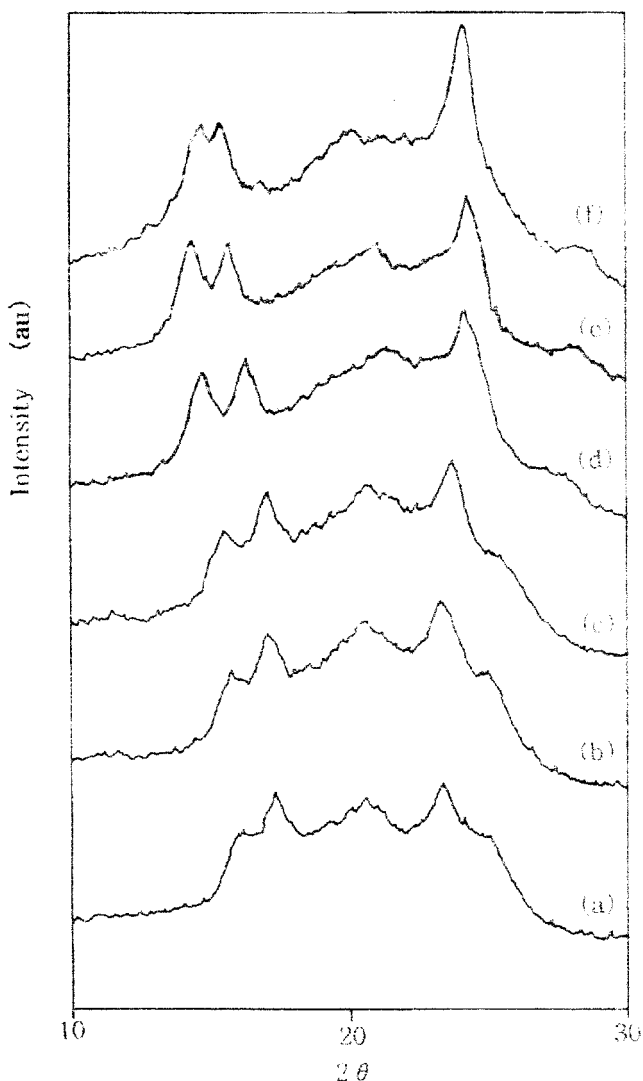


Figure 7 WAXD spectra of the PTMTN copolymers: (a) PTMTN-1, (b) PTMTN-2, (c) PTMTN-3, (d) PTMTN-4, (e) PTMTN-5, (f) PTMTN-6.

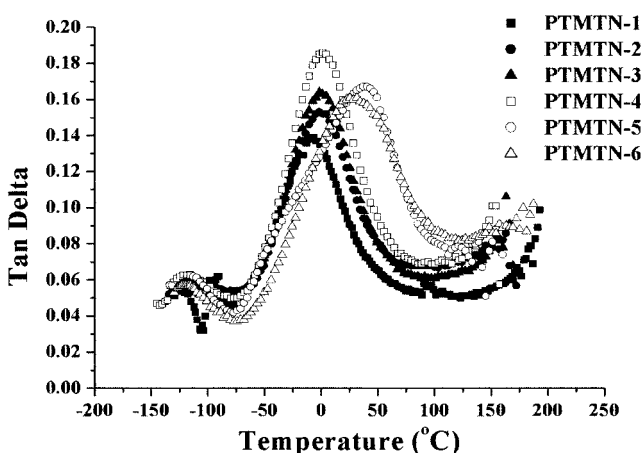


Figure 8 Tan δ as a function of temperature for the PTMTN copolymers.

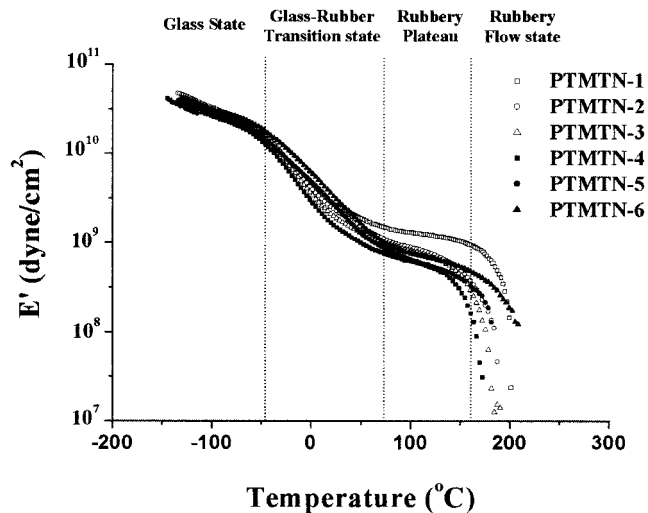


Figure 9 Storage moduli E' as a function of temperature for the PTMTN copolymers.

secondary diester compound improves the UV resistance of the resulting PEE.

CONCLUSIONS

Novel PEEs were synthesized from DMT, BD, and PTMEG 1000, along with NDC as a secondary diester monomer. The synthesized polymers were found to have improved UV and thermal stabilities. The NDC content in the in the copoly(ether esters) was confirmed by ^1H NMR, and the copolymer composition ratio was consistent with the monomer feed ratio. The intrinsic viscosities of the copoly(ether esters) increased with the NDC content in the H/S.

The glass transition and cold crystallization temperatures increased with increasing NDC content. How-

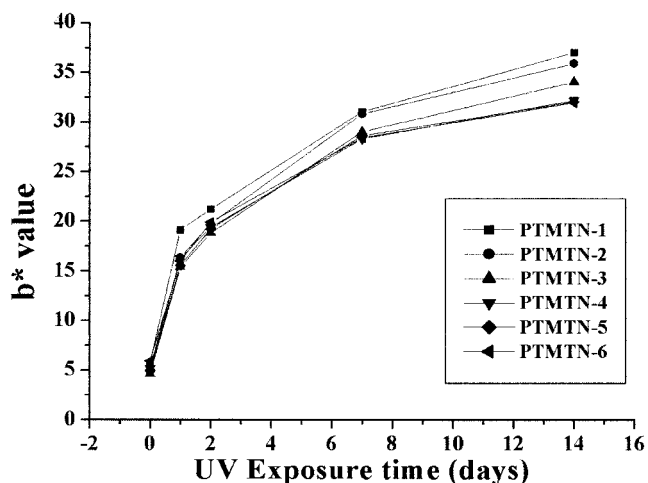


Figure 10 Color difference (b^*) of PTMTN copolymers as a function of aging time.

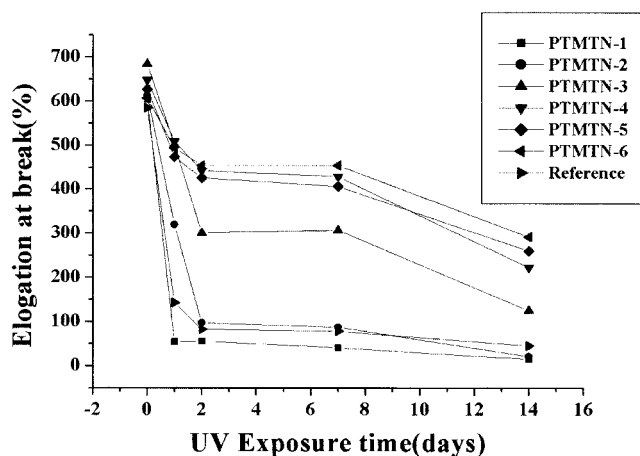


Figure 11 Elongation at break of PTMTN copolymers as a function of aging time.

ever, the melting temperature and the heat of fusion initially decreased with increasing NDC content, reached a minimum at 44.4% NDC content in the H/S, and then increased upon further increase of the NDC content.

The degree of crystallinity of the PTMTN series decreased for NDC contents below 44.4%, but increased as the NDC content was increased above 44.4%. The comonomer in the H/S, NDC or DMT, hinders the crystallization of the main crystallizable component, PTMT or PTMN, respectively, because the length of the main crystallizable component in the H/S decreases with increasing comonomer content.

The elongation at break and the ultraviolet-induced yellowing of the synthesized PEEs were greatly improved by the addition of the NDC component to the H/S.

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