

향상된 열 특성 및 차단 특성을 가진 1,4-Cyclohexanedimethanol, Terephthalic Acid, 그리고 2,6-Naphthalenedicarboxylic Acid로부터 합성된 Copolyester

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Synthesis and Properties of Copolyesters Derived from 1,4-Cyclohexanedimethanol, Terephthalic Acid, and 2,6-Naphthalenedicarboxylic Acid with Enhanced Thermal and Barrier Properties

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초록: Terephthalic acid(TPA), 2,6-naphthalenedicarboxylic acid(NDA), 1,4-cyclohexanedimethanol(CHDM)을 사용하여 poly(1,4-cyclohexylenedimethylene terephthalate-co-1,4-cyclohexylene dimethylene 2,6-naphthalenedicarboxylate) (PCTN)를 용융중합하였다. DSC를 통해 열특성을 분석하였고, NDA와 CHDM이 첨가된 PCTN 공중합체의 유리전이온도는 poly(ethylene terephthalate)(PET) 대비 크게 향상됨을 확인하였다. 열분해 거동은 TGA를 사용하여 확인하고 ¹H NMR을 통해 화학구조를 규명하였다. PCTN 공중합 폴리에스터는 TPA와 NDA의 함량에 따라 변화되는 광학특성을 보여주었고, 또한 PCTN 필름이 기존의 PET와 poly(ethylene naphthalate)(PEN) 필름과 비교하여 뛰어난 열특성 및 차단 특성을 보여주었다.

Abstract: In this work, a series of poly(1,4-cyclohexylenedimethylene terephthalate-co-1,4-cyclohexylene dimethylene 2,6-naphthalenedicarboxylate) (PCTN) copolymers with different compositions of two diacids: terephthalic acid (TPA) and 2,6-naphthalenedicarboxylic acid (NDA), and stoichiometry matched 1,4-cyclohexanedimethanol (CHDM) were synthesized directly by a melt polymerization technique. Thermal properties of synthesized copolymers were measured by a differential scanning calorimetry (DSC). The incorporation of either NDA or CHDM improved the glass transition temperature (T_g) of PCTN compared to poly(ethylene terephthalate) (PET). Thermal degradation behaviors were analyzed using a thermogravimetric analysis (TGA). Chemical structures of the obtained copolyesters were investigated by a nuclear magnetic resonance spectroscopy (¹H NMR). Our results showed that the thermal and optical properties (determined by UV-Vis spectrophotometer) of the PCTN copolyesters were directly dependent on the ratio of TPA and NDA. It was also found that PCTN films have superior optical, thermal, and barrier (reduced water absorption) properties than PET and poly(ethylene naphthalate) (PEN) films.

Keywords: copolyester, 1,4-cyclohexanedimethanol, 2,6-naphthalenedicarboxylic acid, melt polymerization, optical and barrier properties.

Introduction

Polymers have gained the attention of scientists and researchers because of their many desirable properties. Among

numerous polymers, poly(ethylene terephthalate) (PET) is one of the most well-known polymer because of its wide range of applications. It is used worldwide to produce textiles, electronics substrates, food packagings, beverage bottles, and molded plastic parts.¹⁻⁵ Because of the intensive industrial applications of polyester, researchers have keen interest to synthesize newly developed polyesters having enhanced thermal stability and barrier properties compared to original PET.

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Owing to the growing demand of the advanced polyester, many efforts have been attempted to improve the thermal and barrier properties of PET. Recently, there have been many studies for using PET as flexible film substrate for electronic devices,³ textile fibers,⁶ thermoplastic resin,⁷ transparent and shrinkable films, and elastomers.^{8,9} However, the tendency of PET to crystallize at a relatively low glass transition temperature (T_g) exerts as an obstacle to use this polymer at an elevated temperature. The moisture barrier property of PET drops rapidly above its T_g . Because of this limitation, PET is unsuitable to be used for the products that require moisture barrier at a temperature above 100 °C.

Inferior moisture barrier property of PET above its T_g can be improved by introducing some fillers like graphene,⁸ silica nanoparticles, or nano tubes.^{10,11} Another, most widely used approach is by controlling the chemical structures of polyester themselves. Some new polyester-based materials have been synthesized with proper molecular design. 1,4-cyclohexanedimethanol (CHDM) is a commercially available cycloaliphatic diol with a reasonable price and is used for the synthesis of commercial polyester, poly(cyclohexane 1,4-dimethylene terephthalate) (PCT). CHDM strongly influences the physical and thermal properties of resulting polyester. Compared to PET, the cyclic repeating unit present in this polyester imparts better thermal (T_g and T_m), hydrolysis resistance, and barrier properties. Due to enhanced thermal properties of PCT, it is principally used as injection molded polymer for electronic and automotive parts.¹² However, PCT has a high T_m (about 295 °C) so the final esterification reaction during synthesis must be carried out at a temperature higher than 300 °C which is very close to its decomposition temperature, making the processing difficult. Due to the high crystallinity and limited processing window, PCT homopolymer is not suitable to be fabricated into film. For the film application PCT should be modified with different level of comonomer to decrease the melting temperature (T_m).

Another type of polyester having enhanced thermal property is poly(ethylene naphthalene 2,6-dicarboxylate) (PEN). Terephthalic acid (TPA) of PET is replaced by a naphthalenedicarboxylic acid and the resulting polymer has much higher T_g (about 120 °C). This polymer rapidly finds applications in the industries as performance materials for printing and embossing films, electrical devices, and packaging materials. Due to thermal stability along with its good barrier, electrical, and chemical characteristics, PEN has earned a strong position in the high temperature applications.¹³ But, PEN exhibits high bire-

fringence phenomenon which limits its applications as optical films. In addition, the high cost of a monomer, 2,6-naphthalenedicarboxylic acid (NDA) used for the synthesis of PEN renders an obstacle for the applications of this polymer in versatile areas.

It would be highly appreciable to introduce a synthesis of new polyester having enhanced thermal and barrier properties by combining three polyesters mentioned so far, that is, PET, PCT, and PEN. In this study, the synthesis of poly(1,4-cyclohexylenedimethylene terephthalate-*co*-1,4-cyclohexylenedimethylene 2,6-naphthalenedicarboxylate) (PCTN) copolymers was attempted. To the best of our knowledge, it is the first time that thermal and optical properties of PCTN films are reported. The main objective of this work was to synthesize a series of PCTN copolymers and investigate the thermal and barrier (especially barrier to water absorption) properties of films fabricated from them. We focused on 1,4-cyclohexanedimethanol (CHDM) as a single component for diol and various compositions of TPA and NDA as a diacid component for the constituents of resulting copolyester. The copolymers were synthesized directly by a melt polymerization technique. The thermal stability and barrier properties of obtained copolyester were compared to those of PET and PEN.

Experimental

Materials. Ethylene glycol (EG) and terephthalic acid (TPA) were purchased from Daejung Chemicals and Metals Co. Ltd. 1,4-cyclohexanedimethanol (CHDM) (99.8% purity) with 70 mol% trans-isomer was supplied by SK Chemicals (Korea). 2,6-naphthalenedicarboxylic acid (NDA) was supplied by BASF (Germany). Titanium-*n*-butoxide (TNBT), antimony oxide (99% purity), and phosphorous acid (99% purity) were purchased from Sigma-Aldrich. All chemical reagents were stored in the desiccator before use. PET and PEN films for references were supplied from SKC (Korea) and Dupont Teijin Films U.S. Limited Partnership, respectively.

Synthesis of Polyester by Melt Polymerization Followed by Solid-state Polymerization. Each polyester is synthesized in two step reactions; 1) esterification (either transesterification or direct esterification, and 2) polycondensation. The first step is the forming of prepolymer and second step is the forming of high molecular weight polymer. After melt polymerization, solid-state polymerization (SSP) was carried out for 10 h at a temperature between T_g and T_m to increase the molecular weight furthermore.¹⁴ PET and PCT homopolymers were also

synthesized and compared with PCTN copolymers.

Typical polymerization of PET was carried out as follows. As an example, PET was synthesized via melt polymerization in a 5-L batch reactor equipped with an agitator, distillation column, condenser, and trap. In an esterification step, 559 g (9.0 mol) EG, 997 g (6.0 mol) TPA (mol ratio of diol/diacid=1.5), 0.635 g (460 ppm) antimony oxide, and 1.095 g (210 ppm) phosphorous acid were charged into an esterification reactor.

Figure 1 describes the reactor employed for the synthesis. The temperature of reactor was gradually increased to 260 °C. The reaction proceeded under nitrogen atmosphere and by-product (water) from esterification reaction was collected in Receiver 1. Water level indicated the progress of reaction. After the completion of esterification, bis-(2-hydroxyethyl) terephthalate (BHET) was obtained and transferred to the condensation reactor. Condensation reaction was carried out at very low pressure (under 1 Torr) at 90 rpm. The temperature was gradually heated to 280 °C. The by-product (EG) from condensation reaction was collected in Receiver 2. As the molecular weight of the polymer was increased, viscosity was also increased. Polycondensation proceeded isothermally until the torque value reached to the optimum value. Torque meter value was used to determine the end point of reaction. After the completion of the reaction, the pressure of reactor was returned to atmospheric pressure. The product was pulled out from the condensation reactor to produce pellets. The continuous strand of a product was quenched in water bath and pelletized.

PCT was synthesized by following the sample protocol. 907 g of CHDM, 696 g of TPA, 0.818 g of TNBT, and 0.073 g of phosphorous acid were used as chemical reagents. Esterification and polycondensation reactions were carried out at

270 and 290 °C, respectively.

PCTN was also synthesized by the same process as used for the synthesis of PET and PCT. It was prepared with different compositions of TPA and NDA as summarized in Table 1.

Excess CHDM as a diol component, various ratios of TPA and NDA as diacids component (molar ratio of diol to diacid=1.5), 300 ppm TNBT, and 100 ppm phosphorous acid were used. Esterification and condensation reactions were carried out at 260~280 and at 280~290 °C, respectively. The chemical structure of obtained PCTN copolymers is shown in Scheme 1.

Solid-state polymerization (SSP) was proceeded for the produced copolymer pellets at a temperature between T_g and T_m to increase the molecular weight furthermore. All possible reactions occurring at solid-state polymerization of PCTN copolymers are shown in Scheme 2. The reaction temperature of SSP may affect the mobilities of the end-groups of polymer and by-products.¹⁵ It was found that the optimal temperature for SSP is different from one another. SSP was carried out for 10 h at 250, 215, 215, 210, and 235 °C for PCT, PCTN73,

Table 1. Composition of Synthesized PCTN Copolymers

Sample code	Molar ratio of feed (TPA/NDA)	Molar ratio obtained (TPA/NDA) ^a
PCTN73	70/30	74.1/25.9
PCTN64	60/40	66.5/33.5
PCTN55	50/50	57.0/43.0
PCTN37	30/70	39.8/60.2

^aThe composition determined from ¹H NMR analysis.

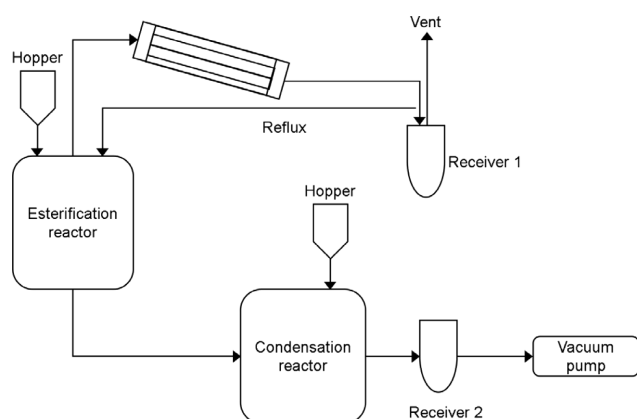
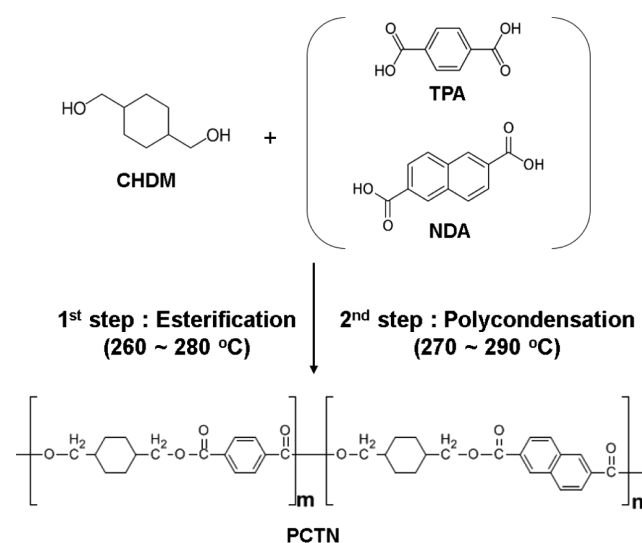
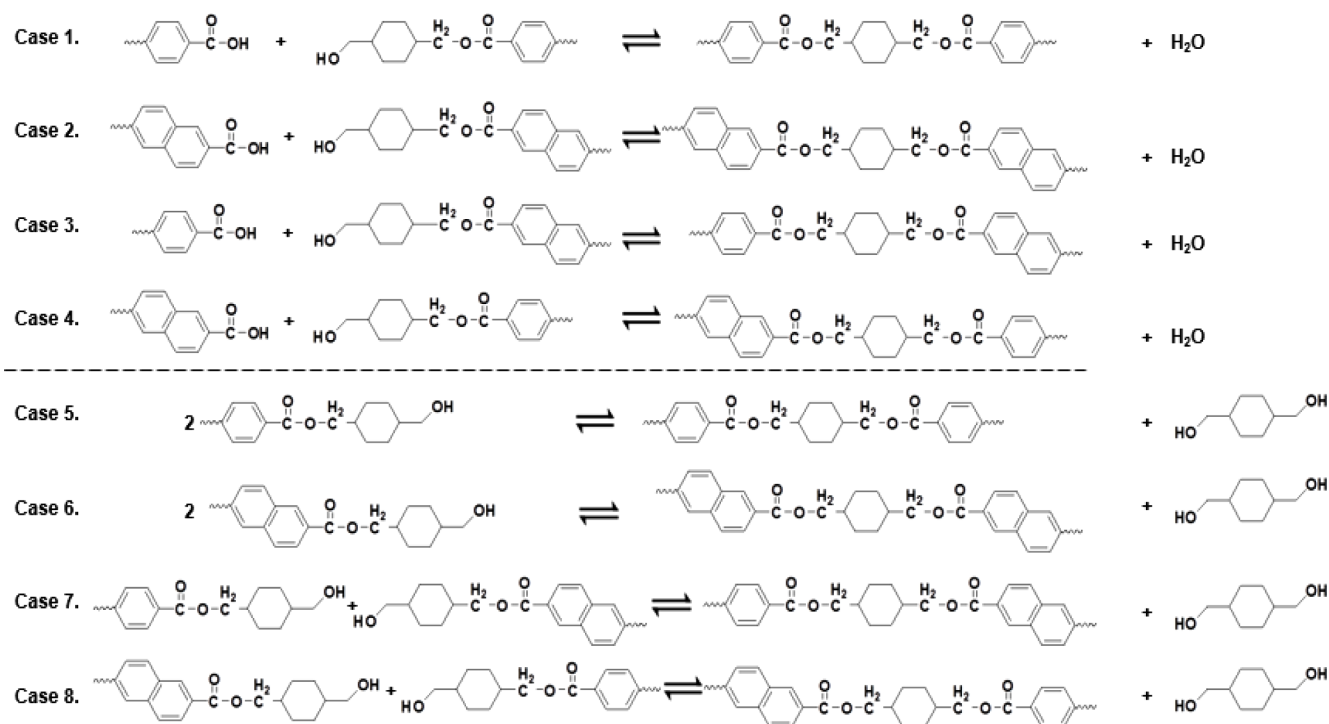


Figure 1. Simplified sketch of melt polymerization reactor.



Scheme 1. Polymerization of PCTN copolymers.



Scheme 2. Possible reactions during SSP of PCTN copolymers.

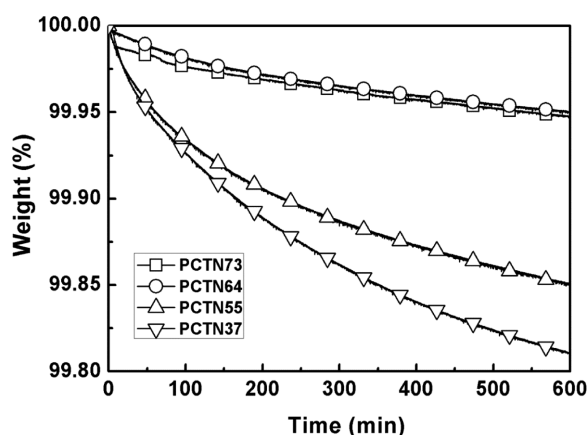


Figure 2. Changes in weight during SSP at designated isothermal temperatures determined by TGA.

PCTN64, PCTN55, and PCTN37, respectively. It was carried out under nitrogen atmosphere with a purge flow of 50 mL min⁻¹. The weight loss during isothermal SSP is recorded and the results are shown in Figure 2, indicating that the SSP actively takes place. SSP was more active for PCTN copolymers having NDA content greater than 50 mol%, implying that, in the transesterification reaction, the CHDM linked to the naphthalenic unit participates more easily than the CHDM linked to the TPA unit.

Molecular Weight and Chemical Composition. The molecular weight was measured by a gel permeation chromatography (GPC) using *m*-cresol as a mobile phase at the velocity of 0.7 mL min⁻¹. Separation was performed with two Shodex LF804 columns at 100 °C equipped with a refractive index detector as a detector. *M_n*, *M_w*, and polydispersity index (PDI) were determined from universal calibration with polystyrene standards. ¹H NMR was performed by a Unity Inova 500NB High Resolution 500 MHz NMR Console at 25 °C. Copolymers were dissolved in a mixture of deuterated chloroform (CDCl₃) and trifluoroacetic acid (TFA-*d*) (1/3), and tetramethylsilane (TMS) was used as an internal standard.

Measurement and Characterization. Thermal Properties: *T_g*, *T_m*, and the melting enthalpy of PCTN copolymer were measured by a differential scanning calorimeter (DSC) (Q20, TA instruments). About 4–7 mg of the sample was placed in an alumina hermetic pan and heated to 300 °C at a rate of 10 °C min⁻¹ under nitrogen with a purge flow of 50 mL min⁻¹. All the experimental values were determined from the second heating.

The crystallinity (*X_c*) of sample was calculated as follows:

$$X_c = \Delta H_m \div \Delta H_m^* \times 100\%$$

where ΔH_m is the melting enthalpy and ΔH_m^* is the melting

enthalpy of 100% crystalline PCT which is calculated by adopting a group contribution theory.

The thermal stability of the PCTN copolymer was investigated by a thermal gravimetry analysis (TGA) (Q50, TA instruments). About 10 mg of the sample was placed in alumina plate and heated to 600 °C at a rate of 10 °C min⁻¹ under nitrogen with a purge flow of 50 mL min⁻¹.

Film Characterization: Films of PCTN copolymers were prepared using the synthesized pellets by hot press at a temperature between T_g and T_m . Thickness of the obtained films was measured using a digital micrometer and found to be about 125 µm. For the comparison reasons, commercial PET and PEN films obtained by SKC and Dupont Teijin, respectively, were also employed. PET and PEN were melted above their T_m and were fabricated into films with the same method as used for PCTN film preparation.

The coefficient of linear thermal expansion (CTE) was measured by a thermo-mechanical analyzer (TMA) (TMA6100, Seiko Exstar 6000). TMA measurements were performed at a rate of 5 °C min⁻¹ over a temperature range from 30 to 180 °C under nitrogen atmosphere for the specimens having 60×5×0.1 mm³ dimensions.

The transmittance was measured by a UV-visible spectrophotometer (S-4100, Scinco). The percentage of transmittance (%) for wavelengths from 300 to 800 nm was recorded.

Water barrier properties of films were evaluated by following the ASTM D570 (Standard test method for water absorption of plastics). Specimens were placed in container of distilled water at 40 °C. The film was removed from the water after every 20 min and weighted after removing water with dry cloth. The experiments were performed for 24 h to confirm the point of saturation.

Results and Discussion

Molecular Weights and Polydispersity. The number- and weight-average molecular weights and polydispersity index of PCTN copolymers synthesized in this study were determined by GPC and the results are presented in Table 2. It is found that the molecular weights of PCTN copolymers are high enough to be fabricated into films for practical application purposes. It is worthy to note that the molecular weight decreases as the NDA content increases, indicating that it becomes more difficult to achieve high molecular weight polymer when more rigid naphthalenic unit is incorporated in the copolymer.

Chemical Compositions of Copolymers. The chemical

Table 2. Molecular Weight (M_n and M_w) and Polydispersity Index (PDI) for PCTN Copolymers Synthesized in This Study

Samples	M_n (g/mol)	M_w (g/mol)	PDI ^a
PCTN73	33618	60901	1.81
PCTN64	35825	61966	1.73
PCTN55	32096	53898	1.68
PCTN37	29821	50197	1.68

^aDefined as M_w/M_n .

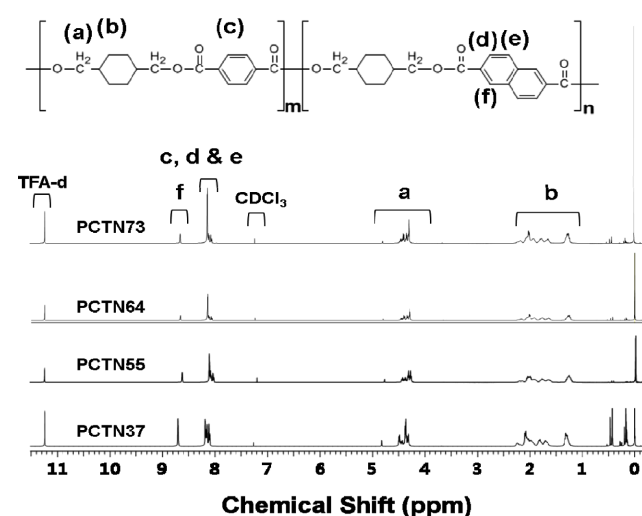


Figure 3. ¹H NMR spectra of PCTN copolymers with peak assignments.

compositions of synthesized PCTN copolyesters were determined by ¹H NMR spectra whose results are given in Figure 3. Characteristic chemical shifts (δ) at 1.21–2.30, 4.28–4.49, and 4.82 ppm are assigned to hydrogen atoms of CHDM moiety. The δ peaks at 8.10–8.18 ppm are assigned to hydrogen atoms of TPA moiety represented as (c) in Figure 3. These peaks are overlapped at δ 8.10–8.18 ppm with hydrogen atoms (d and e) of NDA moiety. However, the δ peak at 8.71 ppm is assigned to hydrogen atom (f) of NDA only, enabling us to determine the chemical composition of copolymer. The analysis results are presented in Table 1. ¹H NMR results clearly show that higher amount of TPA and lower amount of NDA are incorporated in the synthesized copolymers when considering the compositions of feeding monomers, meaning that the reactivity of TPA is greater than that of NDA. For an example, the NDA content incorporated in produced PCTN37 is about 15% less than the amount of NDA initially fed into polymerization reactor.

Thermal Properties by DSC. Figure 4 shows the thermal

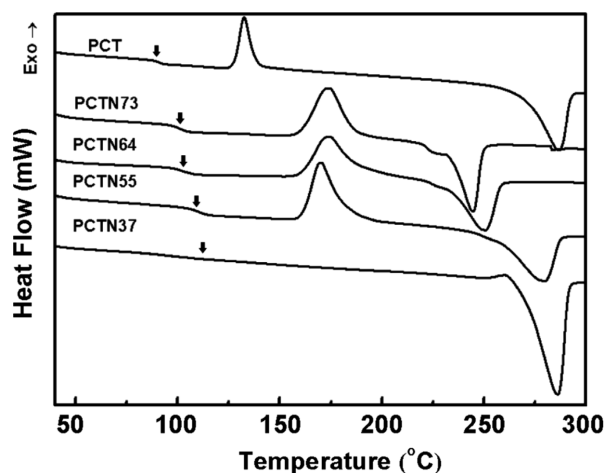


Figure 4. DSC thermograms of PCTN copolymers after SSP.

Table 3. Summary of Thermal Properties of PCTN Copolymers Obtained after SSP

Samples	T_g (°C)	T_m (°C)	ΔH_m (J·g ⁻¹)
PCT	90.89	286.29	51.14
PCTN73	97.91	244.88	29.05
PCTN64	100.93	251.14	25.39
PCTN55	102.09	270.98	26.06
PCTN37	110.28	279.76	29.06

properties of PCT and PCTN copolymers measured by DSC and the results for T_g , T_m , and melting enthalpy (ΔH_m) are summarized in Table 3. It is observed that T_g of PCTN copolymer is higher than that of PCT and increases gradually with increasing the NDA content. Higher T_g of PCTN copolymer can be attributed to the incorporation of more rigid naphthalenic unit in the PCTN copolymer.

It is well known that the Fox equation can be employed to predict the T_g of miscible two-component polymer mixture and statistical copolymer,¹⁶ which is expressed as follows:

$$1/T_g = x_1/T_{g,1} + (1 - x_1)/T_{g,2} \quad (1)$$

where x_1 and x_2 are the weight fractions of components 1 and 2, respectively, and $T_{g,1}$ and $T_{g,2}$ are the T_g of pure components. Since the composition of copolymer shown in Scheme 1 is determined by ¹H NMR experiments, T_g of all compositions can be calculated by adopting the Fox equation and the results are given in Figure 5.

It can be seen that the T_g values calculated by the Fox equation are in good accordance with the T_g values measured by

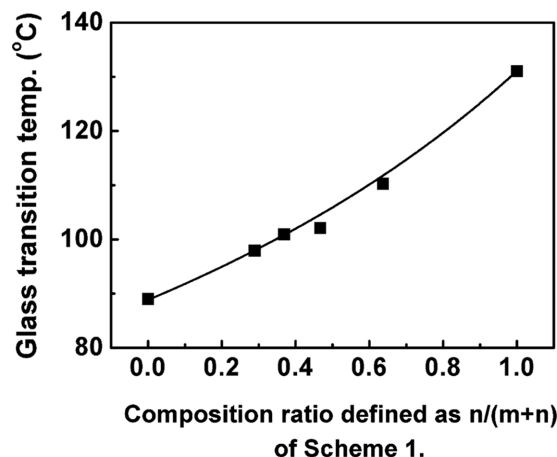


Figure 5. Plots of Fox equation and experimental data values.

DSC experiments. This finding clearly indicates that synthesized PCTN copolyesters are random copolymers. On the other hand, T_m of PCTN copolymer drops significantly when TPA in PCT is replaced by NDA. High T_m (286.29 °C) is observed for PCT homopolymer. But, T_m of PCTN copolymers first decreases and then increases as the NDA contents increase. If TPA is completely replaced by NDA, that is, homopolymer is obtained, T_m is believed to be observed above 350 °C.¹² In conclusion, thermal property of PCTN is greatly influenced by the incorporation of NDA.

Thermal Stability. Figure 6 shows the thermal degradation behaviors of PCT and PCTN copolymers measured by TGA. Only single step degradation is observed for all the polymers investigated, indicating that the synthesized PCTN copolymers are random copolymers. It is clearly seen from the TGA results that the NDA content present in the PCTN copolymers greatly improves the thermal degradation temperature when compared

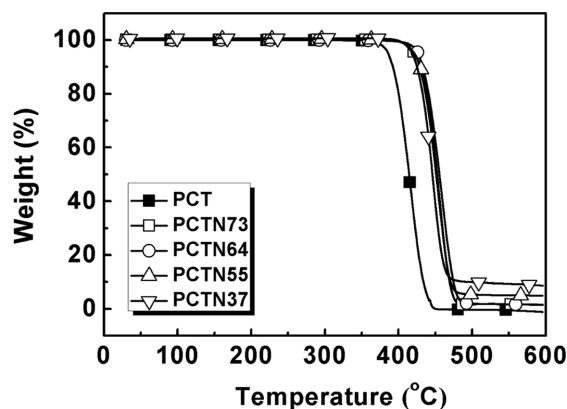


Figure 6. TGA thermograms of PCTN copolymers after SSP.

Table 4. Summary of TGA Results for PCTN Copolymers after SSP

Samples	T_{id} (°C)	T_d (°C)	Residues at 600 °C (%)
PCTN73	421.74	452.55	1.52
PCTN64	426.50	457.86	1.52
PCTN55	421.43	457.10	4.86
PCTN37	418.84	447.14	8.65

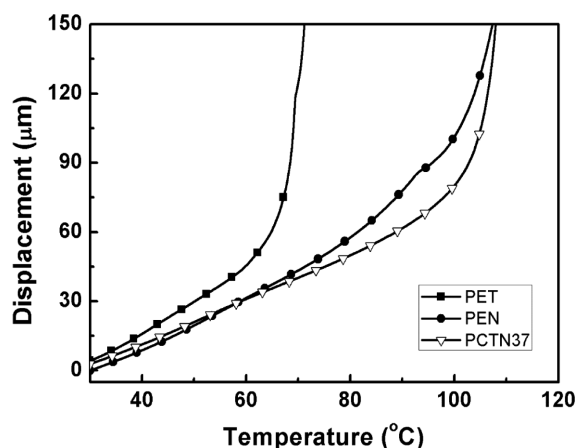
to PCT homopolymer.

The naphthalenic units of NDA incorporated in PCTN copolymer are thermally more stable compared to the benzene units of TPA. The specific data including the initial degradation temperature (T_{id}) at which 5 wt% loss of the initial weight is observed and the temperature (T_d) at which the main degradation on-set is observed are listed in Table 4. The residue amounts at 600 °C are also given in Table 4 and it is clearly seen that more residues remains with increasing the NDA content.

Thermo-mechanical Properties. Most common method to evaluate the thermo-mechanical property is the determination of linear thermal expansion by TMA.

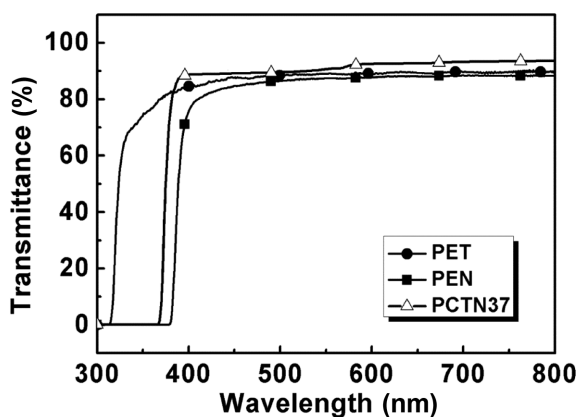
Biaxially stretched film would be the most suitable form of specimen for that purpose. In this study, the film specimens were prepared by compressing the produced pellets between its T_g and T_m . Biaxially stretched films are available for commercial PET and PEN. However, in order to remove the processing history, the obtained PET and PEN films were remelted, made into pellets, and compressed by a hot press to give newly fabricated films. Then, the thermo-mechanical properties of these films can be compared directly with films fabricated from PCTN copolymers since all the films have the same processing history and orientation. It is believed that all the films have random orientation when adopting this fabrication method. Figure 7. shows the results of coefficient of linear thermal expansion (CTE) measurements for PET, PEN, and PCTN37. It is found that PCTN37 has the lowest CTE value when compared to other films (PET>PEN>PCTN37). It is manifest that naphthalenic units present in PEN and PCTN copolymers are responsible for diminished thermal expansion. The CTE values evaluated from data shown in Figure 7 are summarized in Table 5. Superior thermo-mechanical property of PCTN37 films compared to PEN films is attributed to cycloaliphatic units of CHDM as well as naphthalenic unit.

Optical Property. The optical properties of PCTN films fabricated from synthesized copolymers were examined and

**Figure 7.** Thermal expansion between 30 and 110 °C measured by TMA.**Table 5. CTE Results for the Film Specimens Fabricated from PET, PEN, and PCTN Copolymers Synthesized in the Study**

Determined at	CTE (ppm)	
	30-60 °C	30-100 °C
PET	180	-
PEN	105	145
PCTN37	94	110

the results are given in Figure 8. For comparison reasons, PET and PEN films were also tested. Results indicate that the film made from synthesized PCT37 has a high transmittance over a wide range of wavelength. This noticeably good transmittance of PCTN37 film imply that it can be used for optical applications. No significant difference in transmittance was observed for the PCTN films whose NDA contents are different.

**Figure 8.** Comparison of transmittance among films fabricated from PET, PEN, and PCTN copolymer.

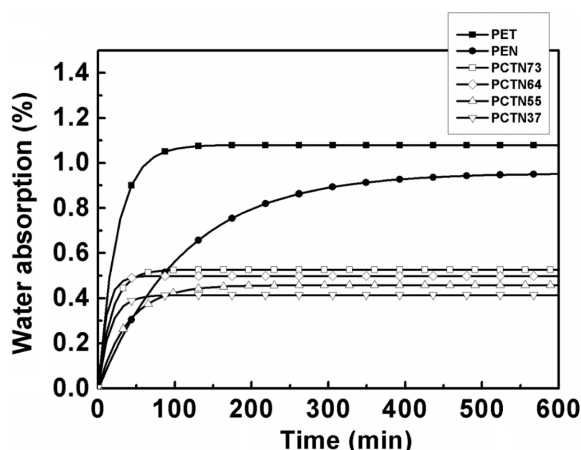


Figure 9. Comparison of water absorption for the film specimens fabricated from PET, PEN, and PCTN copolymers.

Water Barrier Property. Water absorption behaviours were tested for films fabricated from PET, PEN, and PCTN copolymers and the results are given in Figure 9. It is clearly seen from Figure 9 that PCTN films absorb lesser amount of water compared to PET and PEN and the amount of saturated water decreases with increasing the NDA content. It can be concluded that water barrier properties of PCTN film are superior to that of PET and PEN films. Cycloaliphatic units of CHDM in PCTN copolymers are responsible for diminished water absorption compared to PET and PEN.

Conclusions

A series of PCTN copolymers differing in chemical compositions were synthesized by melt polymerization. For that purpose, CHDM as a diol component and various amount of TPA and NDA as a diacid component were employed. The compositions of PCTN copolymers were determined by the ^1H NMR and it was found that NDA is less reactive than TPA. Thermal analysis results showed that all the copolymers were semi-crystalline in nature. DSC results revealed that the T_g of PCTN copolyesters increases with increasing the NDA content. Furthermore, thermal properties of PCTN copolymers are greater than that of PCT homopolymer. The films were fabricated from synthesized PCTN copolymers to evaluate optical and barrier properties. PCTN films show better optical and barrier properties than PET and PEN films. Rigid naphthalenic units of NDA and cycloaliphatic units of CHDM present in

PCTN is responsible for the enhanced properties. These findings clearly demonstrate that PCTN can be utilized in optical and barrier films at elevated temperature.

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