

Synthesis and Characterization of a New Polyester Having Photo-crosslinkable Cinnamoyl Group

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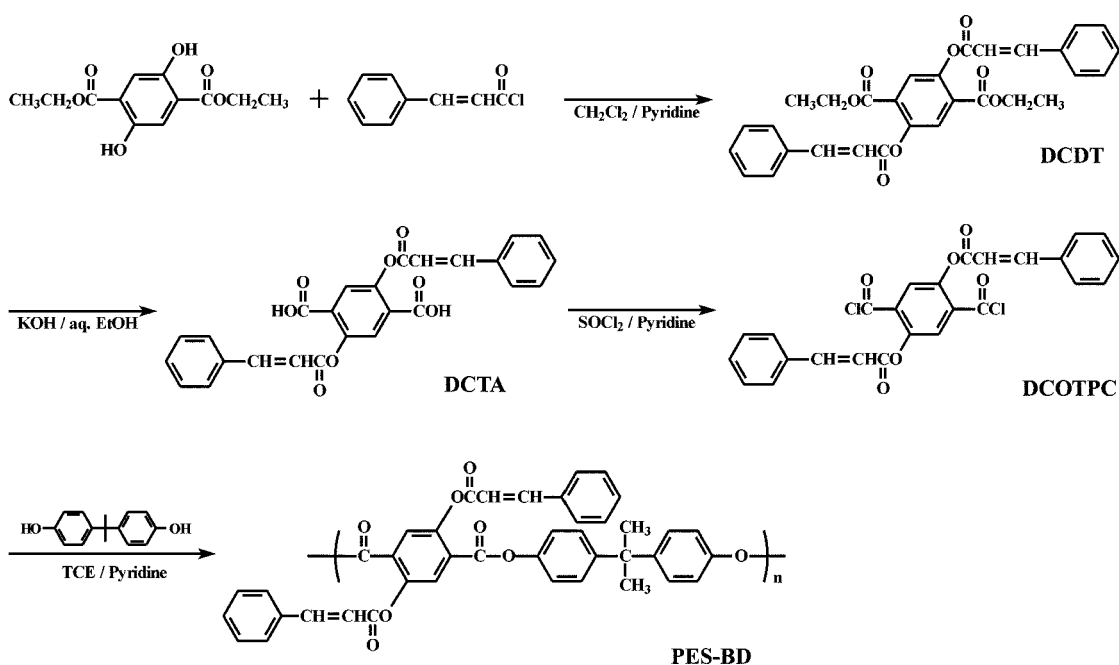
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Photosensitive polymers with photo-crosslinkable groups have gained a considerable interest in recent years owing to a wide variety of applications in the field of photoresists, photocurable coatings, microlithography, nonlinear optics, energy exchange materials, photosensitizers, etc.¹⁻⁶ Among various photo-crosslinkable groups, α,β -unsaturated carbonyl unit known as cinnamoyl group have attracted particular attention due to its excellent photoreactivity at UV absorption wavelength.⁷⁻¹¹ Here, cinnamoyl group either in the backbone or side chain of the polymer can easily be produced by crosslinking reaction through $[2\pi+2\pi]$ cycloaddition of the carbon-carbon double bond upon irradiation with UV light.¹²⁻¹⁴ In this paper, we report the synthesis and characterization of a new photo-crosslinkable aromatic polyester with cinnamoyl group onto polymer backbone.

The synthetic route for the monomer and the final polyester is presented in Scheme 1. To introduce a cinnamoyl moiety on an aromatic polyester, we first synthesized 1,4-

(2,5-dicinnamoyloxy)diethylterephthalate (DCDT) by the reaction of 1,4-(2,5-dihydroxy)terephthalate and cinnamoyl chloride. Then, using thionyl chloride, 1,4-(2,5-dicinnamoyloxy)terephthaloyl chloride (DCOTPC) was quantitatively obtained from 1,4-(2,5-dicinnamoyloxy)terephthalic acid (DCTA) which was prepared by the acid catalyzed hydrolysis reaction of DCDT. The aromatic polyester with a cinnamoyl moiety (PES-BD) was produced by using Schotten-Baumann reaction between bisphenol-A and the resulting monomer DCOTPC at 100 °C in pyridine solvent. The intermediates, monomer and polymer were confirmed by FT-IR, ¹H-NMR spectroscopy and elemental analysis. Their results were in good agreement with the structures presented in the synthetic scheme (see Experimental Section).

The polyester PES-BD was readily soluble in chlorinated solvents such as chloroform, dichloromethane, chlorobenzene and in polar aprotic solvents such as dimethylformamide, dimethylsulphoxide, dioxane and tetrahydrofuran. When the



Scheme 1

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Table 1. Physical data of photo-crosslinkable polyester before and after UV irradiation

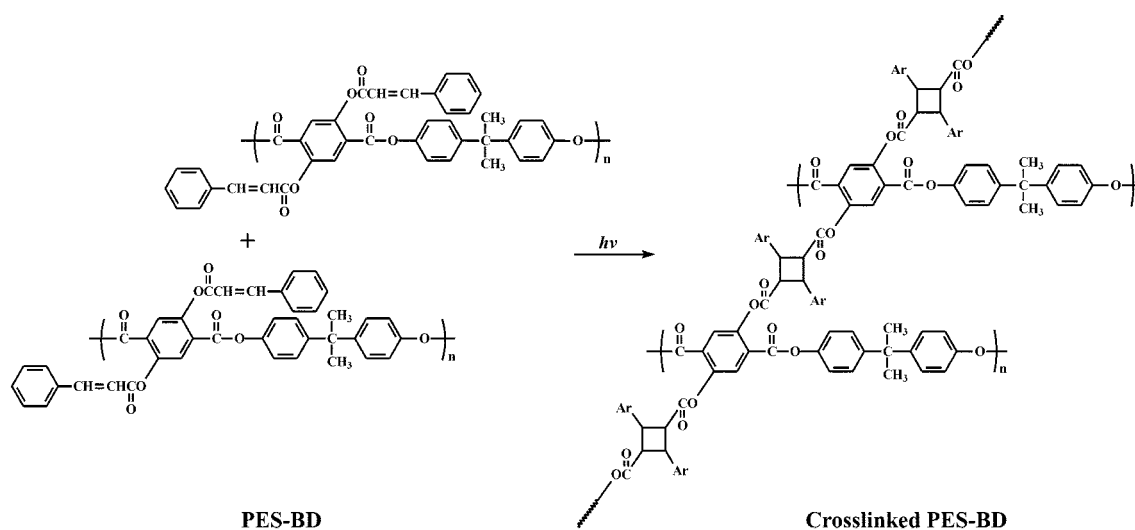
Samples	M_n	M_w	T_g (°C)	T_{fd} (°C)	Char Yield at 800 °C (N ₂) (%)	λ_{max}^a (nm)	λ_{max}^b (nm)
PES-BD (Before irradiation)	8,640	21,300	142	276	35	299	287
Crosslinked PES-BD (After irradiation)	–	–	153	310	40	–	–

^aabsorption maximum of polymer solution in CHCl₃. ^babsorption maximum of polymer thin film on a quartz glass.

polymer is dissolved in chloroform. good optical quality films were obtained by spin coating. The molecular weights and some physical data are listed in Table 1. The number average and weight average molecular weights of polymer determined by gel permeation chromatography were $M_n = 8,640$ and $M_w = 21,300$ ($M_w/M_n = 2.5$), respectively. From DSC thermogram performed under nitrogen atmosphere at a heating rate of 10 °C min⁻¹, the glass transition temperature (T_g) was 142 °C, and no crystalline melting transition was detected for PES-BD indicating that the polymer was amorphous. Initial decomposition temperature (T_{fd}) was determined by using TGA (temperature range 25–800 °C). It showed initial decomposition at 276 °C due to thermal breaking of the cinnamoyl group (>C=C<), a 10% weight loss at about 377 °C, and the residual weights of more than 35% at 800 °C in nitrogen atmosphere due to the presence of high aromatic rings in the polymer structure. These thermal studies have shown that this photosensitive polymer possessed a very good thermal stability. According to UV absorption spectrum, this polymer exhibited a typical absorption band at 299 nm due to the π - π^* transitions of >C=C< of the pendant cinnamoyl moiety in CHCl₃ solution. The absorption maximum of polymer thin film on a quartz glass was 287 nm, thus indicating slightly blue-shifted compared with that of the solution.

To investigate the photo-crosslinking reaction of PES-BD, a thin film of polyester prepared from a 5% solution in chloroform was irradiated with a high pressure mercury lamp in air (Scheme 2). The polymer thin film coated on quartz plate was kept at a distance of 10 cm from the UV

lamp and it was irradiated with different time intervals of 10 to 60 min. The FT-IR and UV-vis spectra of the polymer film were recorded immediately after each exposure time. Figure 1 shows the changes in the FT-IR spectra of PES-BD in the range from 1370–2000 cm⁻¹, observed as a function of UV exposure time at room temperature. The intensity of >C=C< stretching vibration at 1633 cm⁻¹ decreased rapidly. However, the peak at 1633 cm⁻¹ was not disappeared quantitatively due to the aromatic C=C stretching vibration. Also, the intensity of conjugated C=O stretching mode at 1735 cm⁻¹ decreased and moved to a higher frequency of 1745 cm⁻¹. This indicates that conjugated cinnamoyl groups are gradually crosslinked through [2 π +2 π] cycloaddition of the carbon-carbon double bond upon irradiation with UV light, and they consequently form non-conjugated cyclobutane rings as shown in Scheme 2. In addition, the changes in the UV spectral pattern during the photo-crosslinking of the PES-BD polyester at various intervals of time are shown in Figure 2. Initial irradiations show the formation of an isobestic point at about 332 nm caused by the *cis-trans* isomerization of the double bond in cinnamoyl moiety. The absorption band at 287 nm decreases very rapidly with increasing irradiation time, disappearing almost completely within 60 min of irradiation. The polymer on irradiation for about 10 min was rendered insoluble in the solvents, in which it was soluble before irradiation, and this is due to the crosslinking of the polymer chains. The crosslinking efficiency was determined by the rate of disappearance of the >C=C< in the cinnamoyl moiety of the polyester PES-BD using the following expression:

**Scheme 2**

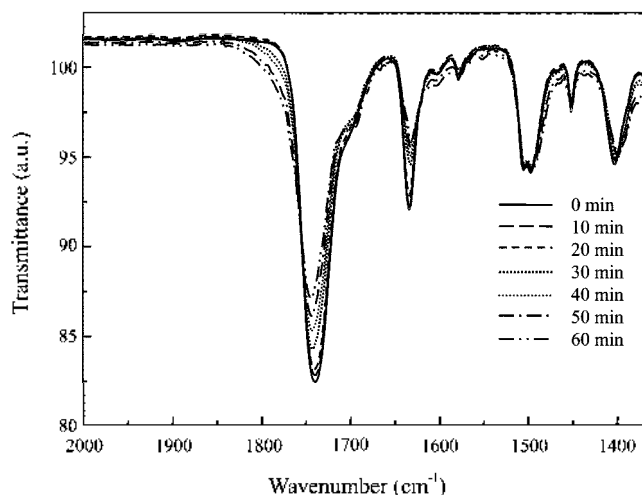


Figure 1. Infrared spectra of the photo-crosslinkable polyester film before and after UV irradiation.

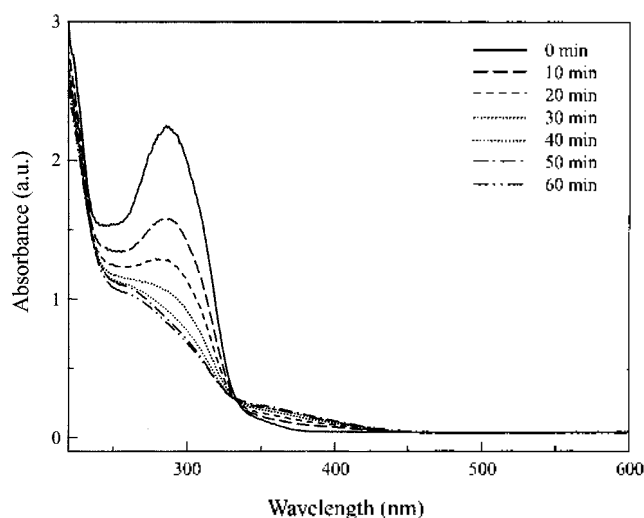


Figure 2. Absorption spectral changes of the polyester film irradiated with UV light.

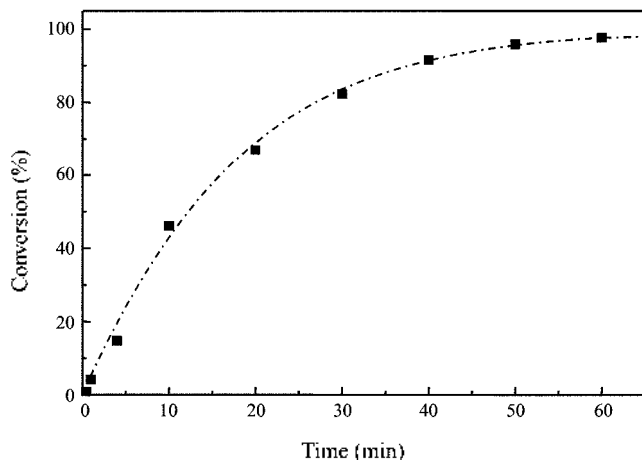


Figure 3. Conversion of photo-crosslinking reaction of the polyester PES-BD with the UV exposure time.

$$\text{Rate of Conversion (\%)} = (A_0 - A_t) / A_0 \times 100$$

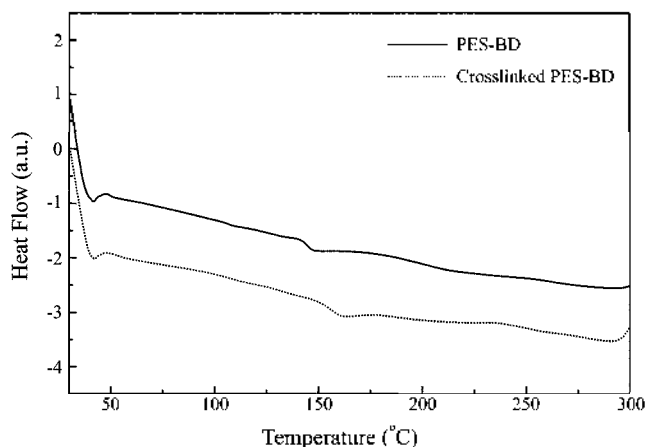


Figure 4. DSC thermograms of the PES-BD and photo-crosslinked polyester. Photo-irradiation was carried out by using a high pressure mercury lamp for 60 min in air.

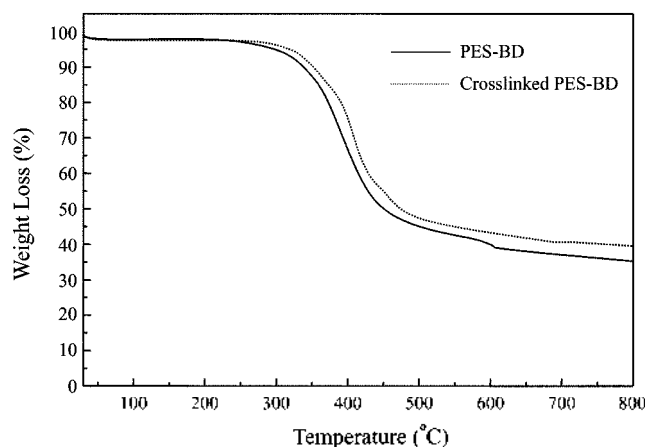


Figure 5. TGA curves of the PES-BD and photo-crosslinked polyester. Photo-irradiation was carried out by using a high pressure mercury lamp for 60 min in air.

where A_0 and A_t are the absorption intensities of $>C=C<$ after irradiation times $t = 0$ and $t = t$, respectively. The rate of conversion was plotted against the UV irradiation time as shown in Figure 3. The conversion to the cyclobutane from the cinnamoyl group was estimated to be over 90% based on the absorbance change at 287 nm after 60 minutes of UV irradiation. This behaviour is superior to that reported for photoreactive polymers containing pendant chalcone moieties which are observed to have photoconversions of a range between 60% and 87%.¹⁵ The crosslinked PES-BD polyester treated during 60 minutes of UV irradiation was found to have a T_g of 153 °C and T_{id} of 310 °C under the same condition as measured by DSC and TGA, respectively, for the untreated PES-BD with UV light (Figures 4 and 5). The reason for this increases of glass transition temperature and initial decomposition temperature of photo-crosslinked PES-BD polyester are due to the photodimerization in cinnamoyl moiety.¹⁶

In conclusion, we have successively prepared the photo-crosslinkable aromatic polyester having cinnamoyl moiety (PES-BD) by the step-reaction polymerization of 1,4-(2,5-

dicinnamoyloxy)terephthaloyl chloride (DCOTPC) and bisphenol-A. Due to good physical properties including highly photo-crosslinking activities of PES-BD, this polymer might be used for photoresist as well as photo-alignment applications for liquid crystals.

Experimental Section

Pyridine (Junsei) was purified by refluxing, distilling from calcium hydride, and drying on 4 Å molecular sieves. All other solvents and reagents, of analytical-grade quality, were commercial products and used as received.

The ¹H-NMR spectral data were obtained on a Bruker AM 300 (300 MHz) spectrometer. Chemical shifts were given in ppm using tetramethylsilane (TMS) as internal standard. The FT-IR spectra were recorded on a Bio-Rad FTS-20B80 spectrometer and UV-vis absorption spectra were measured using a Shimadzu UV-240 spectrophotometer. The average molecular weights of the PES-BD were estimated by gel permeation chromatography (GPC) (column: styragel HT6E6E3, solvent: THF). Elemental analysis was performed with a Fisons EAGER 200. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed with a Dupont 2100 analyzer. The melting points of the monomers were measured by Fisher-Johns melting apparatus.

1,4-(2,5-Dicinnamoyloxy)diethylterephthalate (DCDT). To 12.7 g (0.05 mol) of 1,4-(2,5-dihydroxy)terephthalate dissolved in 80 mL of methylene chloride (MC), 10 mL of pyridine was added and the mixture was stirred for 3 hours in room temperature. 16.6 g (0.1 mol) of cinnamoyl chloride with 70 mL of MC was slowly dropped and stirred for 24 hours in the dark under the nitrogen atmosphere. The product was precipitated in water and filtered. The residue was twice washed with hexane and recrystallized with ethanol or toluene in 85% yield (21.8 g); mp 133–136 °C; IR (KBr) 1095, 1120, 1634, 1724, 1742, 2985 cm⁻¹; ¹H-NMR (CDCl₃, 300 MHz) δ 1.23 (6H, t, *J* = 5 Hz), 4.31 (4H, q, *J* = 7 Hz), 6.74 (2H, s), 7.42 (6H, m), 7.65 (4H, m), 7.88 (2H, s), 7.95 (2H, s). Anal. Calcd for C₃₀H₂₆O₈: C, 70.03; H, 5.09; O, 24.88. Found: C, 69.89; H, 4.95; O, 24.69.

1,4-(2,5-Dicinnamoyloxy)terephthalic acid (DCTA). 25.7 g (0.05 mol) of DCDT in 100 mL of 30% aqueous potassium hydroxide and 200 mL of ethanol was refluxed for 12 hours in the dark. After complete evaporation of ethanol and water under reduced pressure, the remaining solid was dissolved in 500 mL of water. The solution was neutralized with 0.1 M cold HCl to isolate the product. The precipitated solid product was filtered, washed with water, dried and recrystallized from ethanol/water (2/1) in 93% yield (21.3 g); mp 220–222 °C; IR (KBr) 1124, 1307, 1636, 1700, 1730, 2952, 3064, 3600 cm⁻¹; ¹H-NMR (CDCl₃, 300 MHz) δ 6.23 (2H, s), 7.22–7.45 (6H, m), 7.51–7.60 (4H, m), 7.71 (2H, s), 7.89 (2H, s), 10.43 (2H, s). Anal. Calcd for C₂₆H₁₈O₈: C, 68.12; H, 3.96; O, 27.92. Found: C, 68.44; H, 4.11; O, 27.59.

1,4-(2,5-Dicinnamoyloxy)terephthaloyl chloride (DCOTPC). The mixture of 200 mL of thionyl chloride (SOCl₂) and 18.33 g (0.04 mol) of DCTA was added a slight excess amount of pyridine as a catalyst. The solution was stirred for 12 hours at 80 °C in the dark under the nitrogen atmosphere. After complete evaporation of SOCl₂ under reduced pressure, the remaining solid was washed by dry petroleum ether and dried in 96% yield (19.0 g); mp 221–223 °C; IR (KBr) 1123, 1178, 1205, 1636, 1744, 1774, 3064, 3121 cm⁻¹; ¹H-NMR (CDCl₃, 300 MHz) δ 6.89 (2H, s), 7.52 (6H, m), 7.76 (4H, m), 8.04 (2H, s), 8.19 (2H, s). Anal. Calcd for C₂₆H₁₆Cl₂O₈: C, 63.05; H, 3.26; O, 19.38. Found: C, 61.59; H, 3.34; O, 19.99.

Polyester PES-BD. The mixture of 4.94 g (0.01 mol) of DCOTPC and 2.28 g (0.01 mol) was dissolved in 60 mL of tetrachloroethane, and stirred for 10 hours at room temperature in the dark under the nitrogen atmosphere. After 10 mL of pyridine was slowly added into the solution, the mixture was refluxed for 48 hours at 100 °C. After the reaction, the product was precipitated in hot methanol. The polymer of ash-colored solid was collected by filtration and then washed in a Soxhlet extractor with methanol for 3 days. 76% yield (4.94 g); IR (KBr) 1202, 1636, 1741, 2969, 3065 cm⁻¹; ¹H-NMR (CDCl₃, 300 MHz) δ 1.65 (6H, s), 6.90 (2H, s), 7.26 (6H, m), 7.44 (8H, m), 7.86 (2H, s), 8.21 (2H, s).

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