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ARTICLE

Thermally Stable UV Crosslinkable Copolyesters: Synthesis, Crosslinking, and Characterization of Poly(1,4-cyclohexylenedimethylene–1,4-cyclohexane dicarboxylate-*co*-4,4′-stilbene dicarboxylate)

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ABSTRACT: We report a rare occurrence in polymers where a photoreactive group has been incorporated into the backbone of an engineering thermoplastic polyester resulting in a polymer stable at 250 °C that is highly UV crosslinkable at room temperature. Poly(1,4-cyclohexylenedimethylene–1,4-cyclohexane dicarboxylate) (PCCD) copolymers containing *trans*-4,4′-stilbene dicarboxylate structural units were synthesized, and their thermal stability was confirmed by parallel plate rheometry and the absence of crosslinks upon melt processing (melt extrusion and melt-blowing processes) at 250–300 °C. The glass transition temperature of the copolymers increased linearly with *trans*-4,4′-stilbene dicarboxylate units in the backbone which further enhanced with the crosslinking of films resulting from exposure to UV light. The fluorescence emission spectrum revealed that the majority of stilbene units formed ground-state dimers or aggregates, and dynamic mechanical analysis indicates that most of the stilbene units can form crosslinks upon UV irradiation. The group contribution method predicts that the 1,4-cyclohexane dicarboxylate repeating unit and the *trans*-4,4′-stilbene dicarboxylate repeating unit should have a strong tendency toward dimerization or aggregate formation. The crosslinking mechanism is attributed to the face-to-face dimerization and subsequent [2 + 2] cycloaddition of the stilbene moieties in the copolymers.

Introduction

crosslinking has wide commercial usage in applications such as coatings, paints, adhesives, etc., to impart properties such as superior chemical and scratch resistance, which cannot be easily met by uncrosslinked polymers.[1−3] Because of the commercial importance, various aspects of thermal and photochemical crosslinking have been under continuing focus.

Most commercial photochemically crosslinkable polymers are essentially oligomers and are either liquid or low melting solids.[4] These characteristics would facilitate reactive groups orientation and proximity for further reaction to produce crosslinking. Inclusion of crosslinkable moiety in a controllable manner that is amenable to engineering thermoplastics has met with limited success. This is largely due to the fact that many commercial engineering polymers are synthesized via melt polymerization at temperatures between 200 and 300 °C with high residence times. Additionally, such materials are further melt-processed for compounding with additives to form molded parts or extruded films within the same temperature range. In this work, we report a rare occurrence in polymers where a photoreactive group has been incorporated into the backbone of an engineering thermoplastic polyester, resulting in a polymer stable at 250 °C that is highly UV crosslinkable at room temperature.

Despite the many investigations of the physical and photophysical properties of polymers containing the stilbene moiety in the backbone[5,6] or in a side chain,[7,8] relatively little has been reported in the literature regarding the thermal stability and UV crosslinking of this moiety in engineering thermoplastic polyesters. In this work, we have copolymerized *trans*-4,4′-stilbene dicarboxylate as a chromopore into poly(1,4-cyclohexylenedimethylene–1,4-cyclohexane dicarboxylate) (PCCD) in order to impart UV crosslinking. Aliphatic polyester made from 1,4-cyclohexanedimethanol (CHDM) and 1,4-dimethylcyclohexane dicarboxylate (DMCD) is a commercial engineering thermoplastic polyester, PCCD, and utilized in applications requiring a combination of clarity, ductility, and chemical resistance.[9]

Dimethyl-*trans*-4,4′-stilbene dicarboxylate (DMSDC) has been utilized as a monomer in several main chain liquid crystalline polyesters[5] and has demonstrated thermal stability.[10] The stilbene moiety is well-known for [2 + 2] photocycloaddition in the presence of ultraviolet light[11] (Scheme 1). However, stilbene units in liquid crystalline polymers may result in only surface crosslinking since UV light cannot penetrate into the bulk due to light scattering on crystalline domains. In the present study, amorphous PCCD was chosen to achieve UV crosslinking in the bulk as well as the surface of polymeric articles including films, fibers, and molded parts. PCCD-SD is not UV transparent before UV exposure. However, UV exposure converts stilbene units (UV-absorbing) to non-UV-absorbing moiety, further allowing deeper UV penetration.

Experimental Section

Materials. DMCD and CHDM were supplied by Eastman Chemical Co. DMCD was received as a 95/5 trans/cis isomer mixture and CHDM was received as a 70/30 trans/cis isomer mixture. Tetraisopropyl titanate (TPT) was supplied from DuPont Chemical Co. DMSDC was synthesized and purified by Dalian Research and Development Institute, China. All chemicals were used as supplied without further purification.

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Polymer Synthesis. Typical polymerization of DMCD, CHDM, and DMSDC at various molar compositions was carried out in presence of tetraisopropyl titanate catalyst (175 ppm of Ti relative to polymer) in a glass reactor equipped with an overhead stirrer and torque gauge at 170 °C under nitrogen for 2 h until the distillation of methanol ceased (Scheme 2). The reaction was then heated to 230−250 °C while the pressure was slowly reduced to below 1 Torr over the course of 1 h. The mixture was held at temperature while the agitation rate was gradually decreased until the torque on the stirrer at low speed ceased to increase or the polymer separated from the walls of the reactor. The reaction vessel was flushed with nitrogen and cooled to room temperature resulting in a water white to slightly yellow transparent copolyester. All reactions were carried out with the molar feed ratio of dicarboxylate:diol = 1.003:1. In the first stage of polymerization, a Dean−Stark apparatus with an overhead condenser was used to distill methanol generated from the ester interchange reaction. In the second stage of reaction, the Dean−Stark apparatus and condenser was replaced by a heated glass overhead line connected to a cold trap was used to complete the distillation and drive the polymerization to completion.

Various compositions of DMCD, CHDM, and DMSDC copolyester have been synthesized. Typical example include PCCD-SD10 where 10 mol % of the total dicarboxylate monomer is comprised of DMSDC. Similar PCCD-SD20 and PCCD-SD30 corresponds to 20 and 30 mol % of DMSDC as a comonomer (Table 1).

Polymer Processing. *Extrusion and Molding*. The polymers were extruded on a 28 mm Werner Pfleiderer twin-screw extruder with a vacuum vented mixing screw, at a barrel and die head temperature between 250 and 270 °C and 150−300 rpm screw speed at a maximum rate of 30 kg/h.[12,13] The extrudate was cooled through a water bath prior to pelletizing. Test parts were injection molded on a van Dorn molding machine with a set temperature of approximately 250 and 270 °C. The pellets were dried for 3−4 h at 60−120 °C in a forced air-circulating oven prior to injection molding.

Film Extrusion. Films of 250 μm thickness were made on a film extruder which was manufactured by Randcastle Extrusion Systems Inc. It consists of two RCP0625 (1.8 cm screw) extruders and one RCP1000 (2.5 cm screw) extruder, two Randcastle modular feed blocks, and a 15.2 cm die with a custom-made three-roll vertical takeoff system. The pellets were dried for 3−4 h at 60−120 °C in a forced air-circulating oven prior to film extrusion. Films were extruded with a set temperature of approximately 250−270 °C.

Melt-Blown Fibers. The copolymers were processed to form melt-blown fibers at TANDEC at The University of Tennessee. The copolymers were melted at ~300 °C in a 150 mm melt-blown extruder at 16 rpm. The melt temperature was higher than typical extrusion processes since the melt-blowing process requires very low viscosity polymers. The melt was pushed though 121 circular holes with 0.45 mm diameter. The melt was then further thinned by hot air at a speed of 170−300 m/s. The thinned strands were finally collected on a roll with melt-blown fiber layers of 30−60 g/m^2.

Polymer Characterization. The ^{1}H NMR spectra of PCCD-SD copolymer, model compounds and raw materials were recorded using Varian 400 MHz NMR. A 70/30 (volume/volume) mixture of deuterated chloroform and deuterated trifluoroacetic acid was used as the solvent. The ^{1}H NMR spectra were obtained at 25 °C with a flip angle, pulse delay, and number of scans being 90°, 10 s, and 32, respectively.

Differential Scanning Calorimetry (*DSC*). DSC experiments were performed using a Perkin-Elmer DSC 7. Samples were scanned from 40 to 250 °C at a scanning rate of 20 °C/min. Glass transition temperatures (T_g) were measured using data generated during the second heating cycle by the inflection point method calculated by the Perkin-Elmer Pyris software package.

Dynamic Mechanical Analysis(*DMA*). DMA analyses of the samples were performed with a TA Instruments TA 2980 or TA Q800. Copolymers were extruded into thin films and then cut into a strip to fit into a tensile fixture. The films were tested before and after UV curing. A small-amplitude tensile deformation at a frequency of 1 Hz and a temperature scan from room temperature to 200 °C at a ramp rate of 2 °C/min were used.

Scheme 1. [2 + 2] Photocycloaddition of *trans*-4,4′-Stilbene

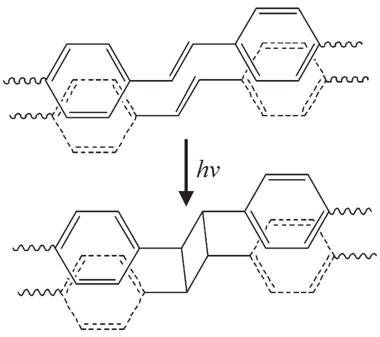
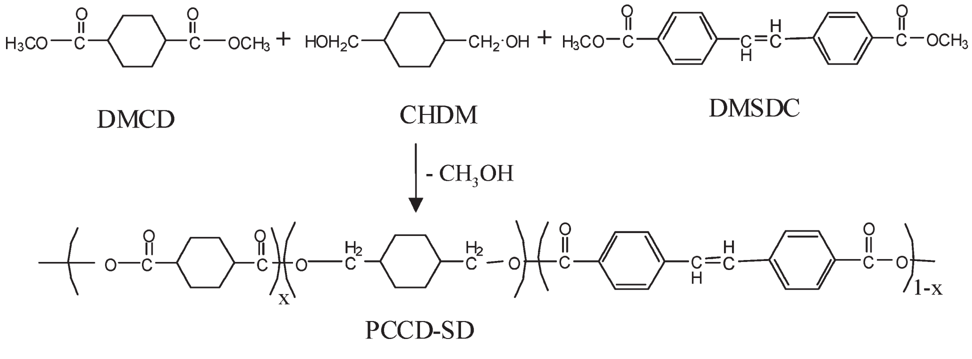


Table 1. Composition, Intrinsic Viscosity, and Glass Transition Temperature of PCCD-SD Copolymers

	composition of dicarboxylate in the copolymer			
sample identification	DMCD (mol %)	DMSDC (mol %)	intrinsic viscosity (dL/g)	T_g (°C)[a]
PCCD	100	0	0.84	65
PCCD-SD10	90.2	9.8	0.85	74
PCCD-SD20	79.2	20.8	0.82	85
PCCD-SD30	67.8	32.2	0.83	94

[a] Glass transition temperature of the copolymers with various DMSDC fractions. The glass transition temperature was registered at the inflection point in the DSC scan at 20 min/°C. Linear model indicates T_g = 0.98 × (DMSDC mole fraction) + 64.9 with R^2 = 0.998.

Scheme 2. Copolymer Synthesis of Poly(1,4-cyclohexylenedimethylene-1,4-cyclohexane dicarboxylate-co-4,4′- stilbene dicarboxylate) (PCCD-SD)



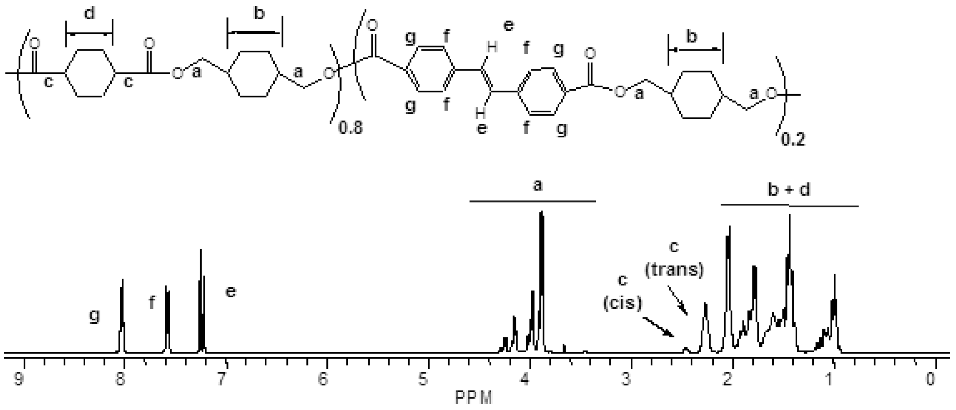


Figure 1. ^{1}H NMR of PCCD-SD20 copolymer.

Rheology. A TA Instruments rheometer (Advanced Rheometric Expansion System, ARES) operated with a parallel fixture was used for viscoelastic measurements. These measurements were used to determine the melt stability of the materials by evaluating the time dependence of the viscosity. A frequency of 10 rad/s and a strain amplitude of 15% were used at 250−280 °C for 30 min.

Ultrathin Film. Ultrathin films were spin-coated from 0.1 wt % of PCCD-SD20 in toluene. A spinning speed of 1000 rpm produced a thin film with a peak intensity of 0.73 in UV spectra. The thickness of the film was calculated to be 120 nm, based on UV extinction coefficient obtained from UV spectrum of dilute solution.

Fluorescence Spectroscopy. Stilbene steady-state fluorescence spectra were measured with a Fluorolog 3-21 from Horiba Jobin Yvon equipped in the front-face geometry with 1.2 mm excitation and emission slits with a data collection interval of 1.0 nm. Unless otherwise specified, all fluorescence measurements were obtained at room temperature under an air atmosphere. The fluorescence intensity is expressed as the ratio between the sample cell and reference cell. For films, a spectrum of air was obtained before a thin film. In most fluorescence measurements, background fluorescence intensity due to electronic noise and substrate is less than 10%.

crosslinking Density. The degree of crosslinking density was measured by swelling experiments. The crosslinked films were immersed in chloroform or dichloromethane, and then the length of swelling film (L) was measured over time until it did not change further. Chloroform or dichloromethane was chosen as a solvent since it has a solubility parameter close to the copolymer, and it was found experimentally to dissolve uncrosslinked copolymers.

UV Curing. A Fusion UV F300S curing system equipped with a cold reflector was used in conjunction with a Fusion UV LC6 benchtop conveyor for UV radiation experiments. The light source was a Fusion D bulb with a cutoff of ~300 nm. 250 μm thick films were cured at a conveyor rate of 1.5 m/min. A typical radiation profile for each pass as measured by a radiometer would be UVA = 4.1 J/cm^2, UVB = 1.4 J/cm^2, UVC = 0.13 J/cm^2, and UVV = 1.8 J/cm^2. UV doses were approximated to be cumulative and simply multiplied by the number of passes to which samples were subjected. The pass length of the conveyor under the UV source was 0.3 m. Therefore, at 1.5 m/min, samples experienced 12 s of UV exposure per pass. Additionally, a high-energy glass light filter with a cutoff at ~300 nm was used to prevent damage to materials being irradiated.

Intrinsic Viscosity. The viscosity (IV) measurements were made using an automated Viscotek Y501C capillary rheometer and a mixture of 60/40 phenol/tetrachloroethane as a solvent.

Mechanical Properties. Tensile properties were tested on 3.2 mm type I tensile bars at room temperature with a crosshead speed of 5 cm/min using ASTM D648. Notched Izod testing was done on 116 × 12.7 × 3.2 mm bars using ASTM D256. The flexural strength test specimens were tested as per ASTM 790. Heat deflection temperature (HDT) at a load of 1.8 MPa was determined by ASTM D648. For density measurement, Izod parts were molded in dimensions of 63.5 mm length, 12.7 mm width, and 3.2 mm thickness.

Optical Properties. Transmission (%) was obtained on Gretag Macbeth CE7000. Films and parts of PCCD and PCCD-SD copolymers with thickness of 3.2 mm or less showed greater than 95% transmission at wavelength of > 400 nm.

Results and Discussion

^{1}H NMR Spectroscopy. A representative ^{1}H NMR spectrum of the PCCD-SD copolymers, namely PCCD-SD20, is shown in Figure 1. The aromatic ring protons of stilbene are observed at 7.6 and 8 ppm while the $-CH{=}CH-$ is detected at 7.2 ppm. The $-CH_2-$ and the $-CH-$ peaks from the cyclohexyl portion of the backbone are found as multiplets between 0.9 and 2.5 ppm, respectively. Multiple signals for the $-OCH_2-$ protons (3.8−4.4 ppm) are due to two reasons: (a) commercial CHDM monomer exist as an isomeric mixture of 70% *trans* and 30% *cis* form and (b) two different ester linkages, i.e., cyclohexyl and stilbene. Both the factors together compound and create varied configurational splitting (refer to Supporting Information for detailed analysis). Lastly, the $-CHCO-$ protons were identified at 2.3 and 2.5 ppm for the ester attached to *trans* and *cis* CHDM, respectively. All of the signals of PCCD-SD copolymers have been identified by comparing with the NMR spectra of the monomers (DMCD, CHDM, and DMSDC) and commercial PCCD (refer to Supporting Information). Table 1 displays the composition and intrinsic viscosity of the copolymers. The monomer feed ratios are closely reflected in the resulting copolymers of PCCD-SD10 to PCCD-SD30, indicating both DMCD and DMSDC have similar reactivity toward CHDM. Analysis of the copolymer sequence by ^{1}H NMR and comparison to a statistical prediction indicated that the copolymers were statistically random in nature (details provided in the Supporting Information).

Glass Transition Temperature. The polymers were analyzed by DSC to determine the glass transition temperature, T_g. As shown in Table 1, the copolymer composition affected the thermal properties of the copolymers. Incorporation of stilbene comonomer into PCCD increased the T_g by ~1 °C/mol % stilbene. The increase in T_g is attributed to the rigidity of the stilbene units as compared to cyclohexyl units.

Thermal Stability. Thermal stability is a key requirement for the utilization of polymers in industrial applications that involve processing at elevated temperatures. Processes that involve injection molding as well as film and fiber formation

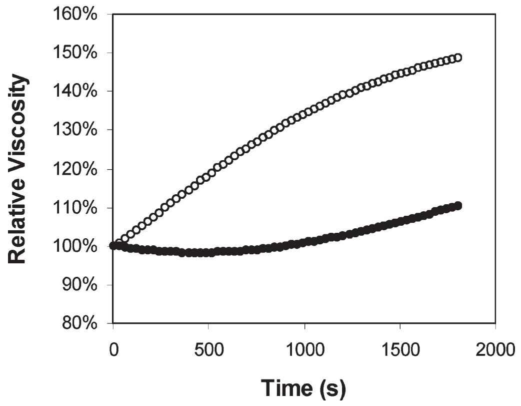


Figure 2. Melt viscosity of PCCD-SD20 at 250 °C (closed circles) and 280 °C (open circles) as a function of time by parallel plate rheometry experiments.

Table 2. Gel Content, Mechanical, and Thermal Properties[a]

polymer	gel content (%)	flexual strength (MPa)	notched Izod impact strength (J/m)	HDT (°C)
PCCD	0	45	1175	57.2
PCCD-SD10	0	51	956	64.6
PCCD-SD20	0	53	662	69.5
PCCD-SD10	50	55	977	69.8
PCCD-SD20	50	61	593	77.2

[a] Gel content is a result of UV exposure.

extrusion are examples of such industrial applications. Parallel plate rheometry experiments (Figure 2) were carried out to investigate the melt stability of PCCD-SD20 at 250 and 280 °C. The change in melt viscosity was negligible at 250 °C for 15 min (within 3%). At an elapsed time of 30 min, the melt viscosity increased by only 10%, indicating the copolymer to be thermally stable in melt processes such as extrusion and molding. At 280 °C, a gradual increase in melt viscosity of 50% above the initial viscosity was observed after 30 min. Most of the melt processing in the present study was conducted at 250 °C; melt stability, i.e. thermal crosslinking for PCCD-SD20, is not expected to occur substantially. Furthermore, typical melt processes such as molding and extrusion occur in the order of 1 min or less, i.e., much faster than residence time used in Figure 2.

Mechanical Properties. As displayed in Table 2, the polymers were extruded by a twin-screw extruder and injection-molded (see Experimental Section) for the evaluation of typical engineering properties such as flexural strength, notched izod impact strength (room temperature), and heat deflection temperature (HDT). An increase of rigid stilbene moiety from 10 to 20% in the backbone resulted in increase in flexural strength as well as HDT. The increase in HDT also correlates with increased T_g of PCCD-SD20 compared to PCCD-SD10. Upon crosslinking of the molded parts as a result of exposure to UV light, the gel content of the copolymers in dichloromethane solvent was found to be 50%. The crosslinked molded parts showed even higher flexural strength and HDT compared to the uncrosslinked samples of the same composition which can be explained by the increase of stiffness or decreased mobility of the polymer chains resulting from crosslinking. Notched Izod impact testing showed that all samples had ductile failure mechanism with impact strength of > 500 J/m (Table 2). A typical polymer with brittle failure mechanism for a polymer would typically be observed to have an impact strength of 50−100 J/m or less by notched Izod testing.

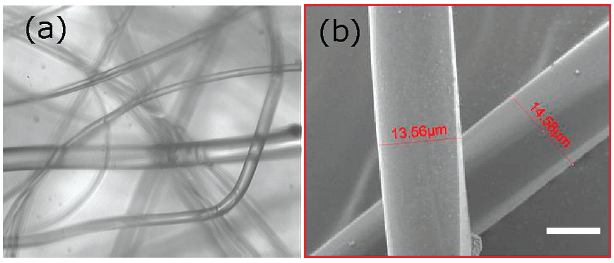


Figure 3. PCCD-SD20 melt-blown fibers. The average fiber diameter was 14 ± 3 μm: (a) Optical microscopy. (b) Scanning tunneling microscopy with scale bar of 10 μm.

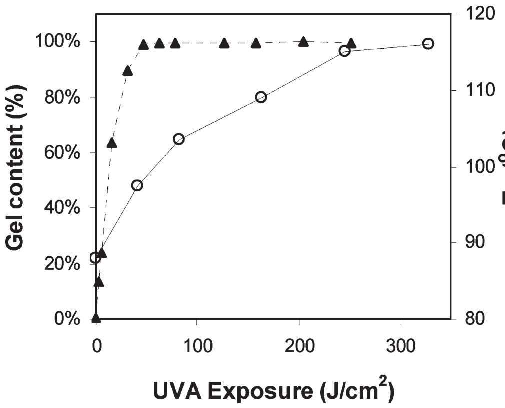


Figure 4. Gel content (solid triangles) and glass transition temperature (open circles) of PCCD-SD20 as a function of UV exposure.

Film Extrusion and Melt-Blown Fibers. Film extrusion was carried out at 250 °C for PCCD-SD20. The copolymer was extruded to form 250 μm thick film. The high-temperature thermal process did not introduce any noticeable amount of crosslinking to the film as confirmed by swelling experiments in dichloromethane. In another application, a melt-blown extrusion was carried out to make micrometer size fibers from the copolymers. The copolymers were melted with zone temperatures of 200−300 °C in the extruder without resulting in any processing issues. The processing temperature was relatively high since melt-blown process requires low-viscosity material to form micrometer fibers. The melt was then thinned by high-speed (170−300 m/s) hot air to form 10−15 mm melt-blown fibers as shown in Figure 3. Even after this high-temperature fiber processing, the fiber did not have noticeable gels, indicating the residence time was not long enough to form substantial amount of crosslinking. The fibers completely dissolved in chloroform without leaving any gels after filtration.

UV crosslinking. A 250 μm thick PCCD-SD20 film was crosslinked under UV light as described in the Experimental Section. Films with varying amounts of UV exposure were dispersed in dichloromethane, and the gel contents were measured. Figure 4 shows that the amount of gels increased from 0% at no exposure to nearly 100% at 50 J/cm^2 UVA dose.

DMA Analysis. The glass transition temperature of the copolymer was measured on strips of thin films by DMA. The peak in loss modulus correlated to the glass transition temperature. T_g of the film considerably increased after UV radiation (Figure 4). Although the gel content reached 100% at ~50 J/cm^2, T_g was monotonically increased until ~240 J/cm^2, indicating further reaction occurring between stilbene units to form tighter crosslinks. crosslinking of the polymer chains is known to increase T_g of polymers since it reduces conformational entropy of the polymers.[14−16]

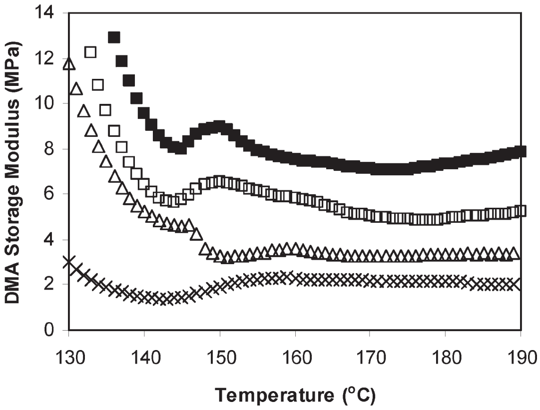


Figure 5. Plateau modulus of crosslinked PCCD-SD20 (■, 80 cycles; □, 60 cycles; △, 40 cycles; ×, 20 cycles).

Table 3. Crosslinking Density of PCCD-SD20 as a Function of UV Exposure[a]

UV exposure (cycles)	plateau modulus at 180 °C (MPa)	crosslinking density (mol/m^3)
10	0.9	42
20	1.8 ± 0.5	83 ± 23
40	3.6 ± 0.4	167 ± 19
60	5.5 ± 1.2	254 ± 56
80	7.3 ± 1.4	337 ± 65

[a] The standard deviation of experiments was calculated on 3−5 DMA measurements.

Ueberreiter and Kanig[17] found that the change in glass transition temperature, $\Delta T_{g,c}$, of a crosslinked polymer is *linearly* proportional to the crosslinking density (moles/volume), μ: $\Delta T_{g,c} = Z\mu$, where Z is a proportionality constant given for a polymer. Based on Ueberreiter's observation, Figure 4 implies that the crosslinking reaction proceeds rapidly at the early times follwed by gradual slow down at higher exposure levels to reach the saturation point around 250 J/cm^2. Beyond 60 exposure cycles (246 J/cm^2 UVA dose), no substantial increase in T_g was observed most likely due to either all the stilbene units already formed crosslinks or some unreacted stilbene units were not close enough to undergo crosslinking.

The crosslinking density of PCCD-SD20 is determined using the rubber elasticity theory.[14] The plateau modulus as measured by DMA is related to crosslinking density of polymers through rubber elasticity theory: $E = 3nRT$, where E is Young's modulus, R is the gas constant, T is absolute temperature, and n is the number of active chains. Since two stilbene units are assumed to form a crosslink through [2 + 2] cycloaddition, a tetrafunctional crosslinking model was assumed to estimate the crosslinking density. In a tetrafunctional crosslinking model

$$E = 6\mu RT \qquad (1)$$

where μ is crosslinking density (moles/unit volume).

After UV exposure, the copolymers demonstrated distinct plateau regimes at temperatures considerably higher than T_g, as shown in Figure 5. The plateau modulus at 180 °C was used to estimate the crosslinking density of the films (Table 3). The crosslinking density at the highest UV exposure (80 exposure cycles in Table 3) was ~90% of the theoretical maximum crosslinking density.[18]

UV/vis and Fluorescence Spectroscopy.[19,20]**.** The UV/vis spectra for a dilute solution of PCCD-SD20 in chloroform and a film are shown in Figure 6. No substantial absorption was found beyond wavelength 400 nm. The UV spectrum of the film is marginally broader than the dilute solution. The broadening of UV spectra in thin film may be due to the stilbene aggregation.

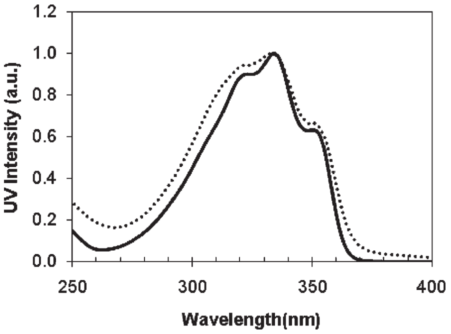


Figure 6. Normalized UV/vis spectra for a dilute solution of PCCD-SD20 (solid line) in chloroform (10^{-6} g/mL) and a thin film (dotted line). Before normalization, absolute intensities at peak were 1.0 for the dilute solution and 0.73 for the thin film.

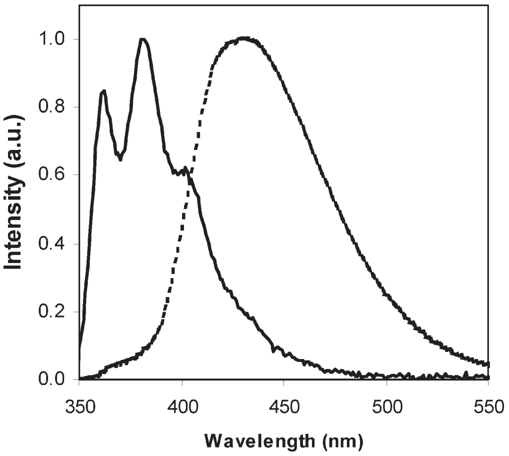


Figure 7. Fluorescence emission spectra of neat PCCD-SD20 before UV crosslinking (dashed line) and 10^{-6} g/mL PCCD-SD20 before UV crosslinking in chloroform.

The fluorescence spectra for a solution of PCCD-SD20 in chloroform and neat PCCD-SD20 film are shown in Figure 7. A structured emission peak at shorter wavelength is assigned to a single excited state of stilbene unit or monomer state, and the broad structureless emission at longer wavelength is due to excimer or aggreagate of stilbene units.[19] Monomer fluorescence at short wavelength is originated from single excited stilbene returning to a ground state. Excited stilbene could attract neighboring stilbene unit in the ground state to form an excited state dimer, i.e., excimer. The excited state dimer emits excimer fluorescence at a longer wavelength. Since the excimer is originated from the same excitation mechanism as the excited monomer, the excitation spectrum of dynamic dimers should be the same as the monomer fluorescence. In another case, stilbene units may form ground state dimers due to aggregation even without light. Since the ground state dimer should absorb light at a different wavelength from the monomer, the excitation spectrum of static dimers should be different from the monomer fluorescence.[19] A good review of the use of excitation spectra for distinguishing the presence of *static* dimer from *dynamic* dimer formation is found in ref 20.

Stilbene units in very dilute solution (e.g., 10^{-6} g/mL PCCD-SD20 in chloroform) are expected to be spatially separated, and interactions, if any, would primarily be

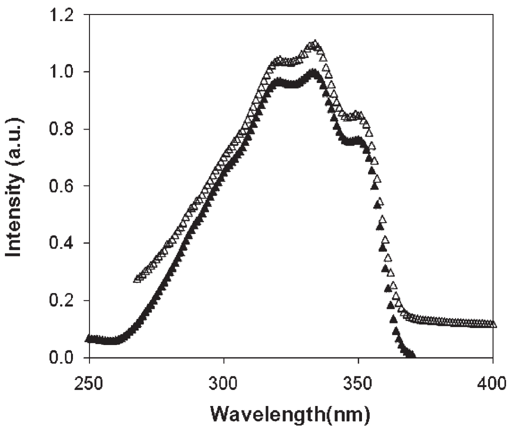


Figure 8. Excitation spectrum of dilute solution (10^{-5} g/mL) of PCCD-SD20: Excitation spectrum of dilute solution observed at 380 nm (solid triangles); excitation spectrum of dilute solution observed at 460 nm (open triangles). Open triangles were shifted by 0.1 in *y*-axis for easy comparison with solid triangles.

expected to be intramolecular rather than intermolecular in nature. Hence, fluorescence at longer wavelength is due to excimer formation in excited state rather than aggregation in ground state. In Figure 8, the dynamic nature is confirmed by measurement of excitation spectra at two emission wavelengths: one characteristic of monomer fluorescence (363 nm) and the second characteristic of excimer fluorescence (460 nm). For a very dilute solution of PCCD-SD20 in chloroform, the two excitation spectra were identical within error, indicating that essentially all excimer fluorescence originates with the excited state monomer. In this case excimers were formed by dynamic interaction of a second ground state stilbene unit with the excited state stilbene monomer during its excited state lifetime.

In the present study, the intensity ratio between excimer or aggregate to monomer is characterized by I_E/I_M, where I_E represents intensity at 436 nm and I_M represents monomer intensity at 363 nm. The fluorescence emission spectrum of the 10^{-6} g/mL PCCD-SD20 in chloroform solution showed structured peaks at short wavelength, indicating that stilbene units were mostly in monomer state with low I_E/I_M ratio of 0.1. In contrast, the emission spectrum of neat PCCD-SD20 film showed structureless broad peak at longer wavelength. The high I_E/I_M ratio of 38.5 indicates that most of stilbene units in the neat film were not in monomer state. Broadening of UV spectra and the fact that glass transition temperature of PCCD-SD20 (85 °C) is much higher than the experimental temperature further indicates that stilbene monomer in PCCD-SD20 should form ground state dimers or aggregate rather than excimer.

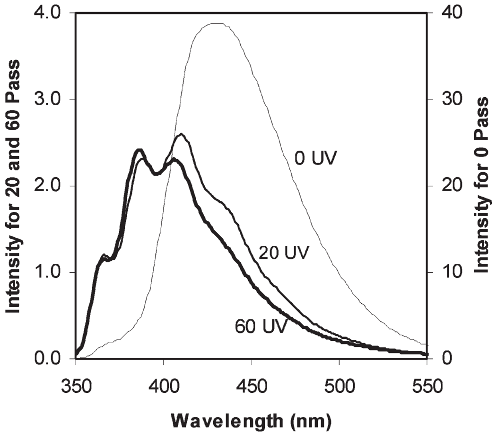


Figure 9. Fluorescence emission spectra of PCCD-SD20 as a function of UV irradiation during the crosslinking reaction. The spectra were normalized to 1.0 at 363 nm. The film without UV irradiation (labeled as 0UV) is plotted in a different scale from other two UV-irradiated samples (20 UV cycles and 60 UV cycles) due to its much higher I_E/I_M ratio. UV irradiation induced a lower I_E/I_M ratio and structured peaks at shorter wavelength.

Table 4. Excimer to Monomer Intensity Ratio of Neat PCCD-SD20 and PCCD-SD20 in Chloroform[a]

concentration	UV exposure	I_E/I_M
10^{-7} g/mL $CHCl_3$	none	0.19
10^{-6} g/mL $CHCl_3$	none	0.17
10^{-5} g/mL $CHCl_3$	none	0.20
neat	none	38.5
neat	20 cycles	1.75
neat	40 cycles	1.62
neat	60 cycles	1.30

[a] Neat PCCD-SD20 films exposed to UV lamp at various exposure time before fluorescence spectra measured.

Table 5. Solubility Parameters (δ) of Repeating Units by Group Contribution Methods[a]

	1,4-cyclohexylene-dimethylene−1,4-cyclohexane dicarboxylate)	1,4-cyclohexylene-dimethylene−4,4′-stilbene dicarboxylate
δ $(cal/cm^3)^{0.5}$ by Small's method	8.3	9.4
δ $(cal/cm^3)^{0.5}$ by Hoy's method	9.3	10.2
δ $(cal/cm^3)^{0.5}$ by Krevelen's method	8.6	9.4

[a] The density and molar volumes of 1,4-cyclohexylenedimethylene−1,4-cyclohexane dicarboxylate are 1.12 g/cm^3 and 280 cm^3/mol, respectively, by Krevelen's group contribution calculation.[24] The density and molar volumes of 1,4-cyclohexylenedimethylene−*trans*-4,4′-stilbene dicarboxylate are calculated to be 1.17 g/cm^3 and 321 cm^3/mol, respectively.

UV irradiation to the films containing stilbene units is expected to induce [2 + 2] cycloaddition of the stilbene in an excimer-like state.[21,22] Since [2 + 2] cycloaddition of the stilbene units only consumes stilbene dimers and the majority of stilbene units are aggregates or ground state dimers, the I_E/I_M ratio is expected to decrease as the reaction occurs. In fact, in Figure 9, samples with UV irradiation (20 UV cycles and 60 UV cycles) had structured peaks at shorter wavelength and substantially reduced I_E/I_M while the sample before UV irradiation had a broad and structureless peak at longer wavelengths and a high I_E/I_M ratio. Table 4 summarizes the intensity I_E/I_M ratios in solution as well as films with varied UV irradiation levels. The dramatic decrease in the intensity of I_E/I_M ratio from 38.5 in the unexposed film to 1.3 in the UV-irradiated film confirms that majority of stilbene excimers (97% for 60 cycles[23]) formed crosslinks upon UV exposure. The strikingly high crosslinking efficiency indicates that the stilbene dimers or aggregates in poly(1,4-cyclohexylenedimethylene−1,4-cyclohexane dicarboxylate-*co*-4,4′-stilbene dicarboxylate) are well aligned for [2 + 2] cycloaddition in the bulk which is likely driven by van der Waals force or repulsion between the stilbene moiety and the cyclohexyl moiety. It is also worth pointing out that the crosslinking reaction should occur at the surface first and then gradually move to deeper bulk phase. Stilbene at the surface initially blocks UV penetration to bulk before being converted to non-UV-absorbing crosslinker, i.e., aliphatic four-membered ring structure.

Origin of Stilbene Aggregation. The fluorescence emission spectra and DMA data indicated that majority of stilbene units in PCCD-SD20 were dimers or aggregates. Group contribution methods by Small,[24] Hoy,[25] or van Kreveken[26] were used to calculate the degree of interaction between 1,4-cyclohexylenedimethylene−1,4-cyclohexane dicarboxylate repeating unit and 1,4-cyclohexylenedimethylene−4,4′-stilbene dicarboxylate repeating unit. All three methods provide similar results on $(\delta_1 - \delta_2)^2$, where δ_1 and δ_2 are solubility parameters for repeating unit 1,4-cyclohexylenedimethylene−1,4-cyclohexane dicarboxylate and 1,4-cyclohexylenedimethylene−4,4′-stilbene dicarboxylate, respectively. The large difference (i.e., ∼1.0) in $(\delta_1 - \delta_2)$ indicates that two repeat units in polymer chains have a strong tendency for phase separation. In the presence of chain connectivity in the copolymer, two repeat units cannot form macroscopic phase separation. However, microscopic aggregation in nanometer scale, i.e., size of a repeat unit, is likely to occur. Furthermore, planar structure of stilbene may induce close proximity between −CH=CH− double bonds in dimers or aggregates.

Conclusions

We report a rare occurrence in polymers where a photoreactive group has been incorporated into the backbone of an engineering thermoplastic polyester resulting in a polymer stable at 250 °C that is highly UV crosslinkable at room temperature. Poly(1,4-cyclohexylenedimethylene−1,4-cyclohexane dicarboxylate) (PCCD) copolymers containing *trans*-4,4′-stilbene dicarboxylate structural units were synthesized, and their thermal stability was confirmed by parallel plate rheometry and the absence of crosslinks upon melt processing (melt extrusion and melt-blowing processes) at 250−300 °C. The glass transition temperature of the copolymers increased linearly with *trans*-4,4′-stilbene dicarboxylate units in the backbone which further enhanced the crosslinking of films resulting from exposure to UV light. The fluorescence emission spectrum indicated that the majority of stilbene units formed ground-state dimers or aggregates, and dynamic mechanical analysis indicates that majority of stilbene units can form crosslinks upon UV irradiation. The group contribution method predicts that the 1,4-cyclohexane dicarboxylate repeating unit and the *trans*-4,4′-stilbene dicarboxylate repeating unit should have a strong tendency toward dimerization or aggregate formation. The crosslinking mechanism is attributed to the face-to-face dimerization and subsequent [2 + 2] cycloaddition of the stilbene moieties in the copolymers.

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Supporting Information Available: Details of sequence analysis and end-group analysis by proton NMR spectroscopy. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Matthijs, G. *Prog. Org. Coat.* **2008**, *61*, 106–109.
(2) Ryntz, R. A.; Britz, D. *J. Coat. Technol.* **2002**, *74*, 77–81.
(3) Bhattacharya, A., Rawlins, J. W., Ray, P., Eds.; *Polymer Grafting and Crosslinking*; John Wiley & Sons, Ltd.: New York, 2009.
(4) Wicks, Z. W.,Jr.; Jones, F. N.; Pappas, S. P.; Wicks, D. A. *Organic Coatings Science and Technology*, 3rd ed.; Wiley-Interscience: New York, 2007.
(5) Somlai, A. P.; Cozad, R. A.; Page, K. A.; Williamns, H. R.; Creed, D.; Hoyle, C. E. *Photochem. Photobiol. Sci.* **2008**, *7*, 578–587.
(6) Leblanc, J. P.; Tessier, M.; Judas, D.; Friedrich, C.; Noel, C.; Marechal, E. *Macromolecules* **1993**, *26*, 4391–4399.
(7) Tsai, F.; Torkelson, J. M.; Lewis, F. D.; Holma, B. *Macromolecules* **1990**, *23*, 1487–1493.
(8) Ding, L.; Russell, T. P. *Macromolecules* **2006**, *39*, 6776–6780.
(9) Turner, S. R.; Seymour, R. W.; Dombroski, J. R. In *Modern Plastics: Chemistry and Technology of Polyesters and Copolyesters*; Scheirs, J., Long, T. E., Eds.; John Wiley & Sons, Ltd.: New York, 2003; Chapter 10, pp 267−292.
(10) Morris, J. C.; Jackson, W. J., Jr. US Patents 4728720, 4824931, 4414382, 4468510, and 4551520.
(11) Chen, Y.; Tsay, C. J. *J. Polym. Sci., Polym. Chem.* **1995**, *33*, 1319–1327.
(12) Kim, S. D.; Chakravarti, S.; Tian, J. *J. Appl. Polym. Sci.* **2008**, *110*, 2623–2633.
(13) Kim, S. D.; Chakravarti, S.; Tian, J.; Bell, P. *Polymer* **2010**, *51*, 2199–2206.
(14) Sperling, L. H. *Introduction to Physical Polymer Science*, 4th ed.; John Wiley & Sons, Inc.: Hoboken, NJ, 2006; p 394.
(15) DiMarzio, E. A. *J. Res. Natl. Bur. Stand.* **1964**, *68A*, 611.
(16) Dammert, R. M.; Maunu, S. L.; Mauer, F. H. J.; Neelov, I. M.; Niemelä, S. ; Sundholm, F.; Wästlund, C. *Macromolecules* **1999**, *32*, 1930.
(17) Ueberreiter, K.; Kanig, G. *J. Chem. Phys.* **1950**, *18*, 399.
(18) Theoretical maximum crosslinking density for PCCD-SD20 = (density) × (mole fraction of stilbene/2)/(molecular weight of an average monomer units) = $(1.15 \times 10^6\ \mathrm{g/m^3}) \times (0.2/2)/(300\ \mathrm{g/mol})$ = 383 mol/m^3, where the crosslinking density is calculated with the assumption that two stilbene units are combined to form a crosslinker.
(19) Kim, S. D.; Torkelson, J. M. *Macromolecules* **2002**, *35*, 5943–5952.
(20) Winnik, F. M. *Chem. Rev.* **1993**, *93*, 587.
(21) Ramamurthy, V.; Venkatesan, K. *Chem. Rev.* **1987**, *87*, 433–481.
(22) Lewis, F. D. *Acc. Chem. Res.* **1979**, *12*, 152–158.
(23) A simple assumption is used to calculate the efficiency: I_E/I_M is proportional to the concentration of excimers. Efficiency = $[1 - (I_E/I_M)_{\mathrm{after\_UV\_exposure}}]/(I_E/I_M)_{\mathrm{before\_UV\_exposure}}$ = 97% for 60 cycles. The assumption is based on the fact that UV irradiation should reduce the excimer due to [2 + 2] cycloaddition but it does not change monomer.
(24) van Krevelen, D. W. *Properties of Polymers*, 3rd ed.; Elsevier: Amsterdam, 1990; Chapter 12.
(25) Small, P. A. *J. Appl. Chem.* **1953**, *3*, 71–80.
(26) Hoy, K. L. *J. Paint Technol.* **1970**, *42*, 76–78.