

Investigations of Chromatic Transformations of Polydiacetylene with Aromatic Compounds

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ABSTRACT: Thermochromic changes of 10,12-pentacosadiynoic acid (PCDA) were investigated in combination with four aromatic compounds, benzene, furan, thiophene, and cyclopentadiene, with subsequent exposure to UV radiation. Using Raman spectroscopy and solid-state Fluorometry, no differences were observed between benzene, furan, or thiophene from the PCDA itself, with respect to the blue to red color change, which took place from 80°C to 100°C. However, the addition of cyclopentadiene exhibited the color change at a significantly higher temperature, ranging from 180°C to 200°C. Lack of new products formed during the initial mixing period was ruled out by analysis using solid-state NMR MAS and differential scanning calorimetry (DSC), with only monomer peaks at 69.61°C for the PCDA and 72.37°C for PCDA in combination with cyclopentadiene, as recorded by the DSC. It is believed that a chemical bond between PCDA and cyclo-

pentadiene is formed after polymerization from catalysis by the UV radiation. Solid-state NMR MAS revealed a chemical shift peak of 131.55 ppm for the PCDA and a much larger peak at 130.84 ppm for the PCDA and cyclopentadiene. The DSC exhibited melting point peaks at 193.26°C and 194.88°C for PCDA and PCDA with cyclopentadiene, respectively. Because the color change involves C—C bond rotation of side groups, stressing π -bond overlap, the cyclopentadiene bond is thought to prevent rotation by steric hindrance until a higher temperature or melting occurs at the DSC stated temperature of 194.88°C. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 2809–2820, 2011

Key words: photopolymerization; differential scanning calorimetry (DSC); fluorescence; Raman spectroscopy; NMR

INTRODUCTION

There has been an ongoing search for materials that possess certain chemical, mechanical, and optical properties for use in biological sensors,^{1–12} nanoscale sensors,^{13–22} and other optical-electronic devices.^{23–27} These materials should, in principle, be sensitive to changes in environmental stimuli, such as chemical, heat, and mechanical stress in their role as nanosensors. Materials that show particular potential in these areas are known as polydiacetylenes (PDAs), which demonstrate strong optical and UV absorption and fluorescence emission when exposed to heat, mechanical stress, and chemical solvolysis.^{28–33} One of the most widely used PDAs is 10,12-pentacosadiynoic acid (PCDA), which possesses two conjugated triple bonds along its backbone resulting in extended π -electron delocalization along this distance. When exposed to UV or γ radiation, the PCD

monomers (Fig. 1a) undergo a 1,4 addition polymerization to form ene-yne alternated polymers, which results in a blue color (Fig. 1b), and an absorption of light at ~ 650 nm, thereby functioning as a nanosensor. When subjected to heat, mechanical stress, or chemical solvents, it shifts to the red-colored polymer (Fig. 1c), which now absorbs light at 550 nm and undergoes fluorescence at 640 nm.^{4,28,34}

Early studies attributed the blue to red color change to a change in the backbone from a PDA to a polybutatriene structure.^{35–37} Later, however, ¹³C NMR studies showed no butatriene structure but rather changes in the side arms from the blue to red phase, suggesting a backbone change from planar to nonplanar with a consequent change in the conjugation length of the π bonds and a shift in the absorption spectrum from blue to red.³⁸ Saito et al.³⁹ attributed this color change to a two-step polymerization process. In the first step, as the blue polymer forms, it maintains a regular trans-zigzag structure of its side chains and in the second step, it converts to an irregular structure made up of gauche conformations of its side chains when converting to the red form. Ji et al.⁴⁰ have proposed that the extended conjugation of p-orbitals in the polymer chain become twisted or distorted when subjected to heat, mechanical stress, or chemical stimuli, whereas Carpick et al.⁴¹

Additional Supporting Information may be found in the online version of this article.

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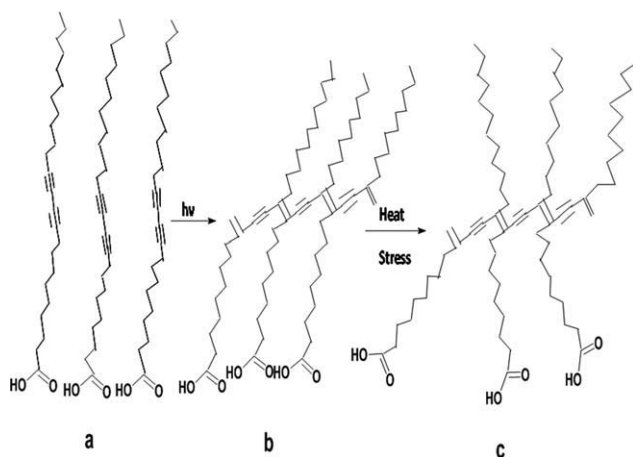


Figure 1 Forms of PCDA (a) monomeric, (b) polymeric-blue, and (c) polymeric-red.

considered that the side-chain packing, ordering, and orientation induce stress to the polymer backbone, altering its configuration and thereby changing the electronic states and subsequent absorption. Similarly, Burns et al. considered the blue form to represent a planar form with all *trans*-geometry and with unbroken π -electron overlap. When stressed, side-chain rotation occurs, disrupting the π overlap, shortening conjugation length and consequently shifts the absorption spectrum from blue to red.⁴² Some researchers have taken the opposite approach to an ordered to a disordered structure and side-chain entanglement when the polymers undergo a blue to red color change and have found, using AFM images, that the red form displays a higher degree of ordered side chains than the blue form.^{38,43,44} In addition, IR and ¹³C NMR data indicate side-chain rotation in the red form, which stresses the backbone of the polymer and induces rotation around the C—C bond of the backbone, changing its planarity.^{29,37} Orchard et al. have calculated that a rotation of only 5° around the C—C bond would significantly change the π -orbital overlap and a corresponding shift of the blue absorption spectrum to red.³⁶

Our investigations studied the thermochromatic behavior of monomeric and polymeric forms of PCDA and the effects of aromatic compounds, such as benzene, furan, thiophene, and cyclopentadiene, on the transition temperature from the blue to red phases. The analysis and characterization involved Raman spectroscopy, solid-state fluorometry, ¹H and ¹³C NMR MAS, and differential scanning calorimetry (DSC).

EXPERIMENTAL

Materials

PCDA was purchased from GFS Chemicals (Powell, OH) and was subsequently dissolved in a small amount of chloroform and filtered through double

filter paper. The clear filtrate was then tested for purity using ¹H NMR with D-chloroform as the solvent. Aromatic compounds, such as thiophene, furan, benzene, dicyclopentadiene, and chloroform were purchased from Sigma-Aldrich (Milwaukee, WI) and similarly tested for purity.

Synthesis

Samples were prepared by first weighing ~ 1.25 g of PCDA and then placing it onto a Buchner funnel with double filter paper and then placed into the sidearm of a previously evacuated 100 mL round-bottomed flask with stirrer, under an Argon flow. Repeated 2.0 mL portions of chloroform were pipetted into the PCDA to dissolve it and also separate the PCDA from the polymer contaminants until a volume of 30mL remained. Sample SS154M-B was prepared with PCDA and cyclopentadiene that was freshly cracked but without chloroform. After removal of the funnel and filter paper, specific amounts of benzene, furan, thiophene, or cyclopentadiene were added to the experimental flask and stirred for 2 h, as shown in Table I below.

Reaction flasks were subsequently evacuated over a warm water bath at 37°C until contents appeared dry, as judged by the appearance of a white solid and cessation of spinning by the stir bar. A rigorous evacuation followed over a 30°C water bath an additional 5–15 min. To judge the effect of evacuation times, sample SS129M-B was evacuated an additional 5 min, and sample SS131M-B was evacuated an additional 15 min.

The flasks with stirrers and stoppers had been previously weighed empty and were now weighed after evacuation. The masses were then subtracted to ascertain the amount of aromatic compound that remained. Because a small amount of chloroform also remained, typically about 0.0200 g, as ascertained by the control sample SS129M-A PCDA, the exact amount of aromatic compound that remained after evacuation was not precisely known except in sample SS154M-B where no chloroform was used.

TABLE I
Reactant Materials

Sample Number	Mass (g) PCDA	Mass (g) Aromatic	Mole Ratio Aromatic : PCDA
SS74M-B	2.1177	Benzene 0.8760	1.9876 : 1
SS80M-B	1.2508	Furan 1.4288	6.2909 : 1
SS113M-B	2.0830	Thiophene 2.6275	5.6164 : 1
SS129M-B	1.2661	Cyclopentadiene 0.1098	0.4911 : 1
SS131M-B	1.2499	Cyclopentadiene 0.6325	2.8693 : 1
SS154M-B	0.9853	Cyclopentadiene ^a 6.5068	37.485 : 1

Amounts that were added before evacuation.

^a No chloroform used.

The amount of cyclopentadiene that remained in this sample was 0.3060 g, which was a larger amount than in samples SS129M-B and SS131M-B because of the multiple filtering and increased polymer concentration of this sample, as described below.

Normally cyclopentadiene is cracked from dicyclopentadiene, in a distillation process by simply heating the dicyclopentadiene at 170°C and condensed into a long-term storage Schlenk flask. The last three studies, SS129M, SS131M, and SS154M, used the Birmingham process, which uses a high boiling point oil, such as mineral oil, with heating of the dicyclopentadiene at temperatures of 250°C to 260°C to avoid the reaction of cyclopentadiene with dicyclopentadiene forming unwanted tri, tetra, and higher cyclopentadiene polymers and thereby producing a higher yield of the cyclopentadiene monomer.⁴⁵

A portion of each sample of ~ 0.65 g was withdrawn from each flask and placed in a 30 mL beaker with Teflon stirrer and then placed on a stir plate 10 cm under an 8 watt UV lamp and allowed to stir for 1.5 h. The beakers were removed every 10 min, and any large clumps were crushed and stirred with a spatula. Sample SS154M-B was irradiated for 30 min, removed, filtered, and the filtered solution allowed to dry and irradiated for another 30 min to increase the polymer concentration. The two filtrates were combined and then characterized with MAS (Magic Angle Spinning) NMR and DSC. Finally, the contents of each of the other samples were loaded into two NMR tubes, connected to a vacuum manifold, and the air very carefully removed and refilled with helium to 0.5 atmospheres and sealed with a micro torch. The samples were removed and placed in either test tubes suspended into a hot oil bath or into an aluminum block with predrilled holes and heated for 15 min at various temperatures, in 5° increments, from 70° to as high as 230°C in some instances. After each 5°C heating, duplicate tubes were removed and tested: one in a Raman spectrometer and the other in a solid-state fluorometer.

Equipment

Raman spectrometry for solid samples was undertaken, using a DeltaNu Advantage 220A Raman Spectrometer and for solid-state fluorometry, a FluoroMax-2 Solid-State Fluorometer was used. Several of the samples were analyzed with a 7.05 T Bruker DPX 350MHz NMR spectrometer, with cross-polarization/magic-angle-spinning (CP/MAS) probes using 7 mm ZrO rotors for a total of 6000 scans at a speed of 6000 rps. Chemical shifts are reported using adamantane as an external reference (38.56 ppm) with an uncertainty of ±0.2 ppm. Some of the samples were heated, from 40°C to 300°C, in a model

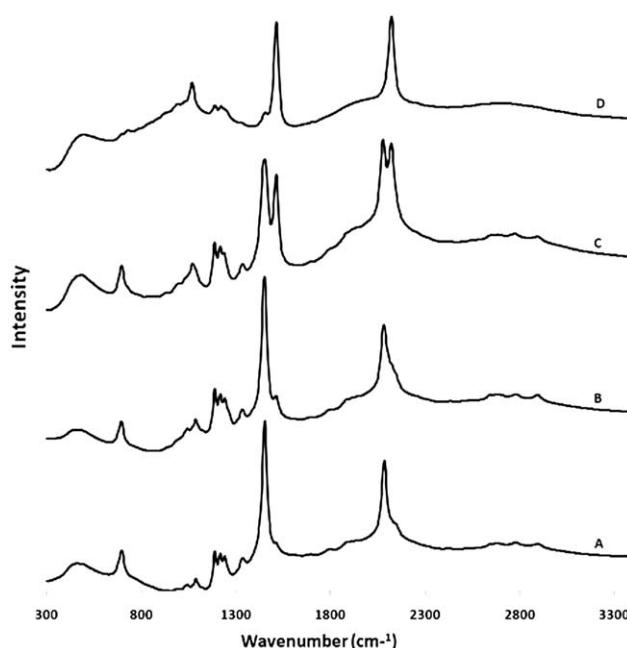


Figure 2 Raman spectra of SS129M-A PCDA: A, 70°C; B, 80°C; C, 90°C; and D, 100°C.

DSQ DSC to look for monomer and polymer endotherms, as well as melting points of the monomers and polymers.

RESULTS

The reaction of PCDA with four different aromatic compounds has yielded several interesting differences, with respect to the blue to red color conversion temperature of PCDA. After polymerization, using UV radiation, this compound exhibits Raman peaks at 2080 (caused by C≡C stretching) and at 1453 (caused by C=C stretching). If the temperature is increased beyond 353 K, the absorption maximum is shifted from 650 to 550 nm, giving it a red color and new Raman peaks at 2121 (C≡C stretching) and 1515 (C=C stretching).^{46,47} O-H stretch bands, at 2675, 2784 and 2903 cm⁻¹ decrease in intensity with an increase in temperature, as do out-of-plane bending of ring C-H bonds at 700 cm⁻¹ and in-plane bending of C-H bonds at 1190, 1218 and 1243 cm⁻¹.⁴⁸ Only an in-plane C-H bending, at 1090 cm⁻¹ appears to increase with an increase in temperature. Figure 2 below shows Raman spectra of the control PCDA, at temperatures ranging from 70°C for the blue form to 100°C for the red form.

The above graph, in Figure 2, shows that the 70°C curve exhibits peaks solely at 1453 and 2080 cm⁻¹, which indicate only the blue form of PCDA. Increasing the temperature to 80°C, produces a small shoulder at 1515 and 2121 but the preponderance of the two peaks remains at 1453 and 2080. At 90°C each peak is split into nearly equal halves indicating

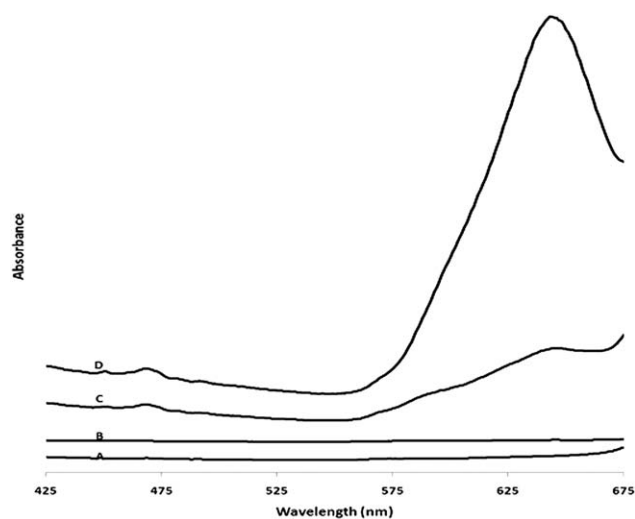


Figure 3 Solid-state fluorometry spectra of sample SS129M-A: PCDA—A, 70°C; B, 80°C; C, 90°C; and D, 100°C.

a blue to red transition, whereas at 100°C, both peaks at 1515 and 2121 indicate nearly total color change from the blue to red form. Further evidence for the color transition is shown below by solid-state fluorometry, in Figure 3.

Because only the red form of PCDA exhibits fluorescence, the peaks at 640 nm are a direct indicator of the red form of PCDA.⁴¹ As can be seen from Figure 3, the 70°C and 80°C spectral curves show little fluorescence, as predicted by the Raman peaks of 1453 and 2080 cm^{-1} in Figure 2, which is almost entirely indicative of the blue form, which also does not undergo fluorescence. Conversely, the 90°C peak in Figure 3 shows a larger degree of fluorescence, as exhibited by its Raman peaks of 1515 and 2121 cm^{-1} in Figure 2. Finally, the 100°C peak on Figure 3 shows very strong fluorescence at 640 nm, which is predicted by its two Raman peaks of 1515 and 2121 cm^{-1} in Figure 2, which consist almost entirely of the red form.

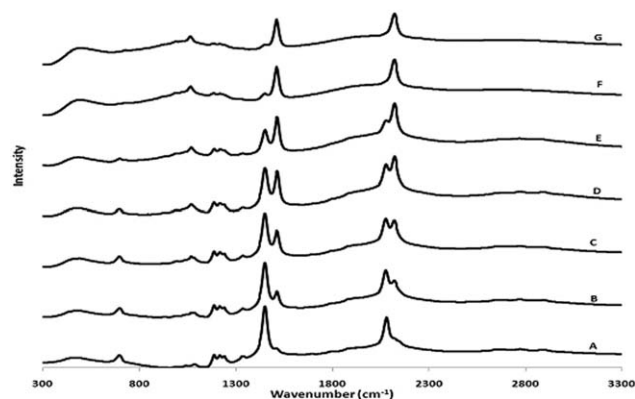


Figure 4 Raman spectra of sample SS129M-B: PCDA and cyclopentadiene—A, 160°C; B, 170°C; C, 180°C, D, 185°C, E, 190°C; F, 195°C; and G, 200°C.

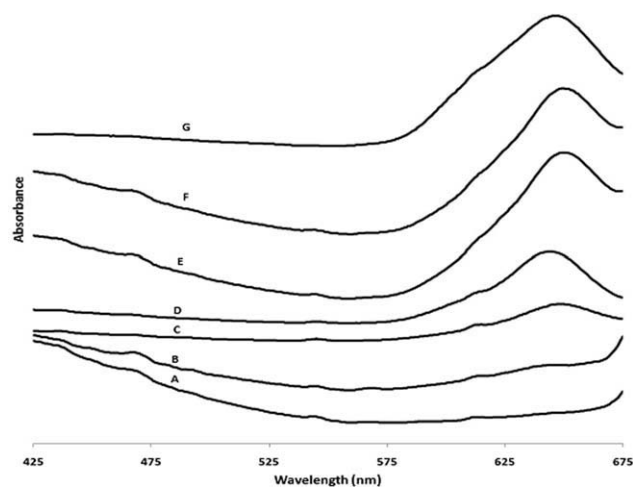


Figure 5 Solid-state fluorometry spectra of sample SS129M-B: PCDA and cyclopentadiene—A, 160°C; B, 170°C; C, 180°C, D, 185°C, E, 190°C; F, 195°C; and G, 200°C.

Of the four aromatic compounds that were separately combined with PCDA in a chloroform solution, benzene, furan, and thiophene had Raman and solid-state fluorometry spectra very similar to the control PCDA. Their spectra are included in the Supporting Information Figures 21–26.

The fourth aromatic compound to be combined with the PCDA was cyclopentadiene, sample SS129M-B. The Raman spectra ranges from 160°C to 190°C are shown below in Figure 4.

It may be observed that the spectra in Figure 4 are 90°C to 95°C higher in temperature than the control PCDA in Figure 2 or of any of the other three aromatic samples in the Supporting Information Section. The small shoulders at 1515 and 2121 cm^{-1} at 160°C are the beginnings of a blue to red color transition. In

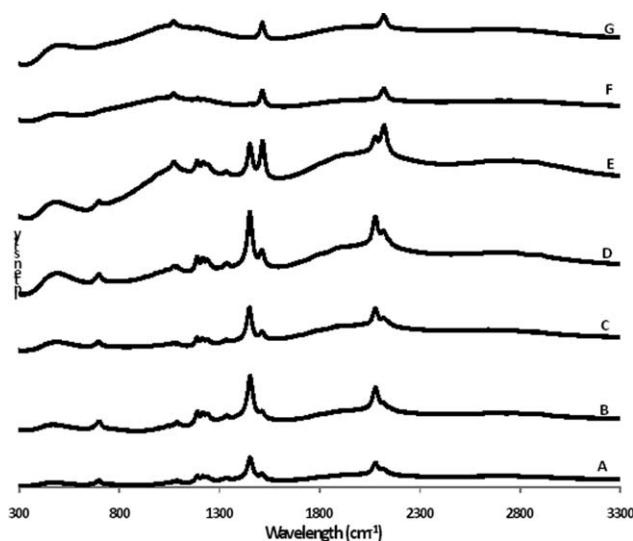


Figure 6 Raman spectra of sample SS154M-B: PCDA and cyclopentadiene—A, 160°C; B, 170°C; C, 180°C, D, 185°C, E, 190°C; F, 195°C; and G, 200°C.

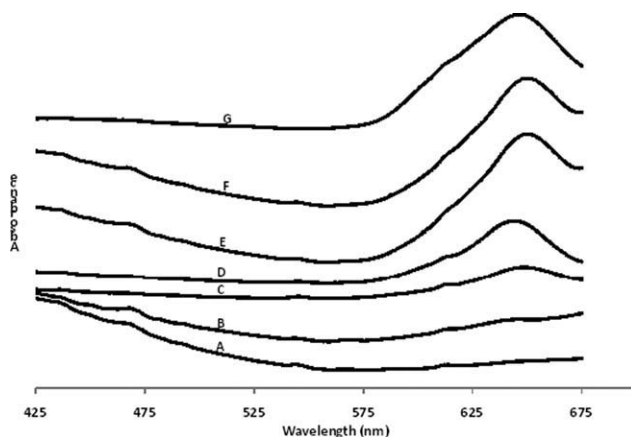


Figure 7 Solid-state fluorometry of sample SS154M-B PCDA and cyclopentadiene—A, 160°C; B, 170°C; C, 180°C, D, 185°C, E, 190°C; F, 195°C; and G, 200°C.

addition, the 40°C range of color change is larger than the 20°C range for the PCDA control and the other three aromatic spectra. The change from blue to red appears to be almost complete at 200°C. The fluorometry spectra appear to agree with the Raman spectra, as shown in Figure 5 below.

An examination of Figure 5 above will indicate that the fluorometry data are in good agreement with the Raman data in Figure 4. One will notice that the lack of fluorescence at 160°C and 170°C are predicted by the large blue Raman peaks at 1453 and 2080 cm^{-1} compared with the small red peaks at 1515 and 2121 cm^{-1} . As the temperature increases to 200°C, the blue Raman peaks decrease substan-

tially, whereas the red peaks increase dramatically and show even larger fluorescence. Raman spectroscopy of sample SS154M-B, with PCDA and freshly cracked cyclopentadiene, but without chloroform, is shown in Figure 6 below.

It follows the same blue to red color conversion behavior as sample SS129M-B in Figure 4, starting at 160°C, with a large blue peak at 1453 cm^{-1} and a small red shoulder at 1515 cm^{-1} and ends with a single large red peak at 1515 cm^{-1} , indicating complete conversion to the red form at 200°C, with respect to double bond stretching. Triple bond stretching shows a large blue peak at 2080 cm^{-1} and a very small red shoulder at 2115 cm^{-1} beginning at 160°C with a continual decrease of the 2080 cm^{-1} peak and increase of the 2115 cm^{-1} peak until complete conversion to the red form at 200°C. Solid-state fluorometry data, in Figure 7 below, once again supports the Raman data shown in Figure 6 above for sample SS154M-B.

It may be observed that no fluorescence is detected at 160°C or 170°C, which is characteristic of the blue form of PCDA but as the temperature increases to 180°C, a small red peak at 640 nm becomes evident. This peak increases in intensity at higher temperatures, with the largest peak occurring at 200°C, indicating total conversion to the red form, in agreement with the Raman data in Figure 6 above.

DSC scans were run on the control Sample SS129M-A PCDA at the end of the 2 h mixing and evacuation period, as described in the Experimental section. Scans were also run on Sample SS129M-B

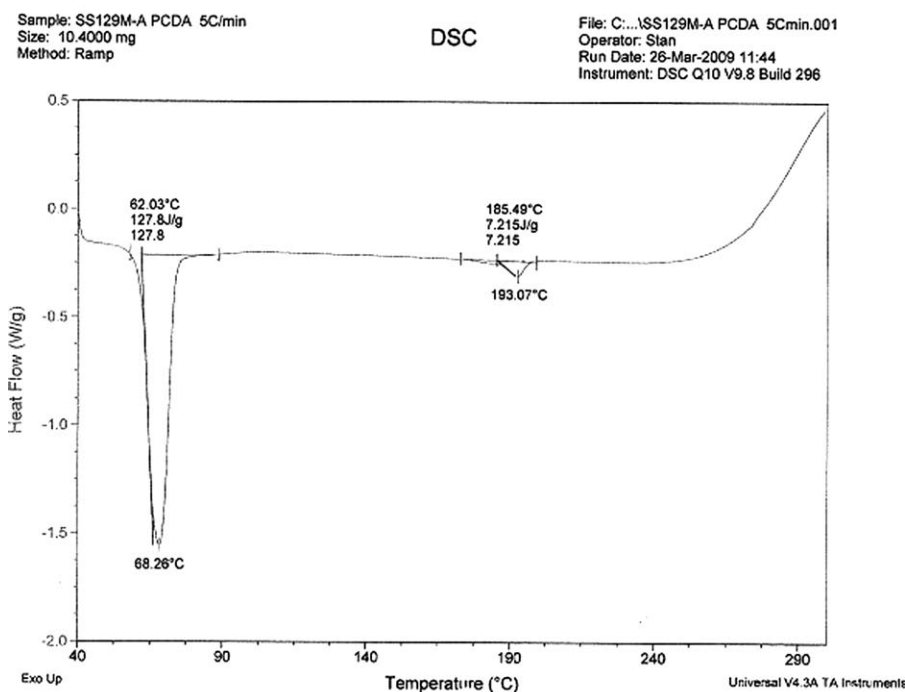


Figure 8 DSC Spectra of Control Sample SS129M-A PCDA Polymers (UVed).

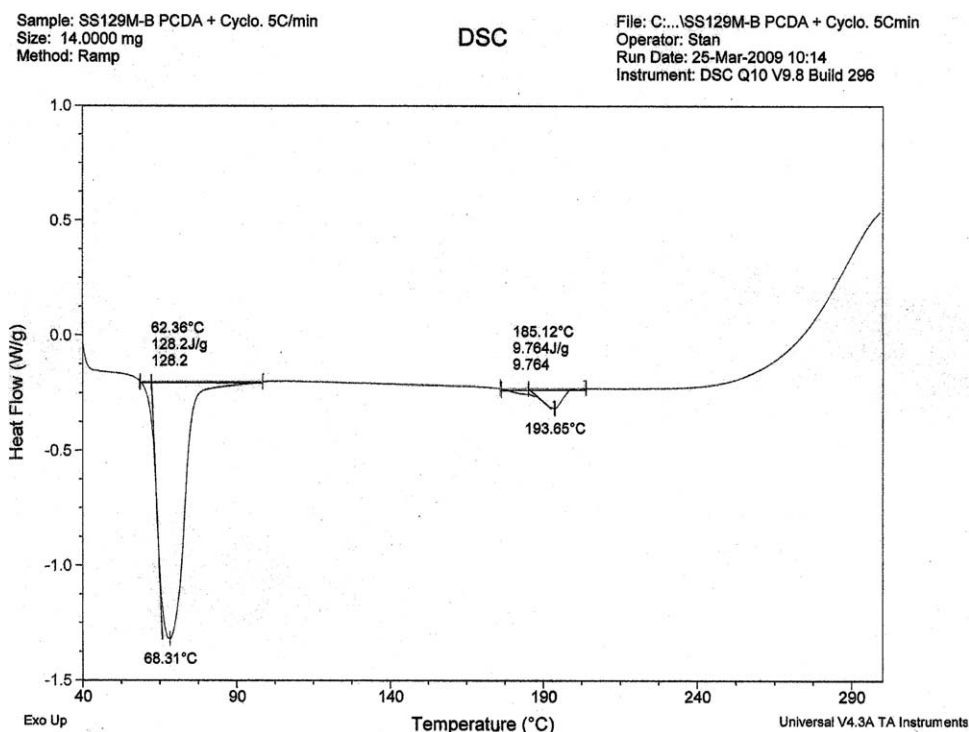


Figure 9 DSC spectra of sample SS129M-B PCDA and cyclopentadiene polymers (UVed).

PCDA and cyclopentadiene, also at the end of the same period to determine whether a new polymer species was formed. Because they had the sample monomer melting points of 71.29°C with no other differences between them, they were placed in the Supporting Information Figures 26 and 27.

For the Control UV'd sample, the melting points for monomers was 68.26°C for the PCDA and

193.07°C for the PCDA polymers, as shown below in Figure 8. All values were very close to the literature values of 72.8°C for the monomer and 196°C for the polymer melting point.⁴³

For the UV sample of PCDA and Cyclopentadiene, the melting points for monomers was 68.31°C and 193.65°C for the polymers, as shown below in Figure 9. Sample 154M-B shown below in

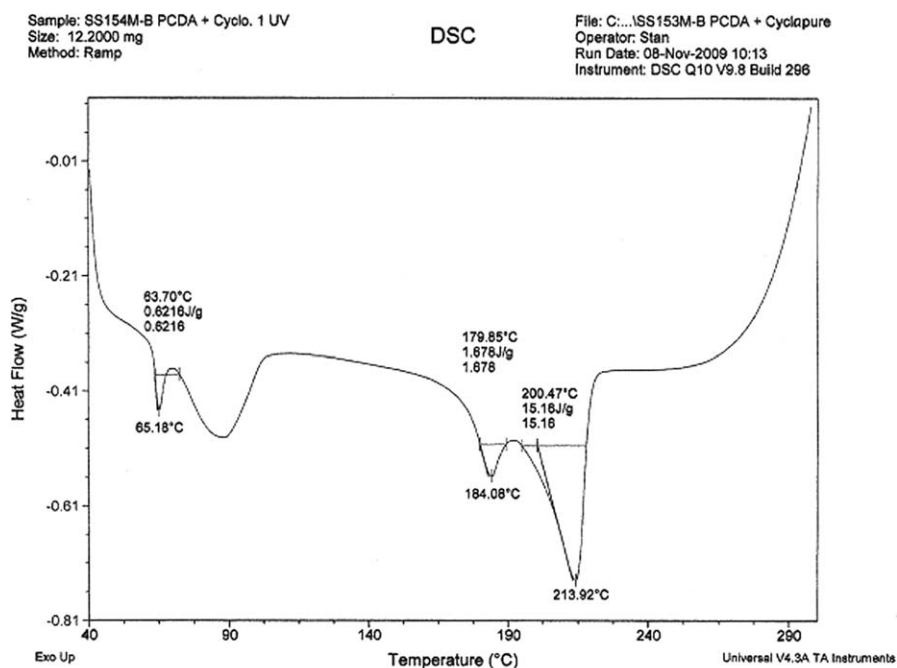


Figure 10 DSC spectra of sample SS154M-B PCDA and cyclopentadiene polymers (UVed).

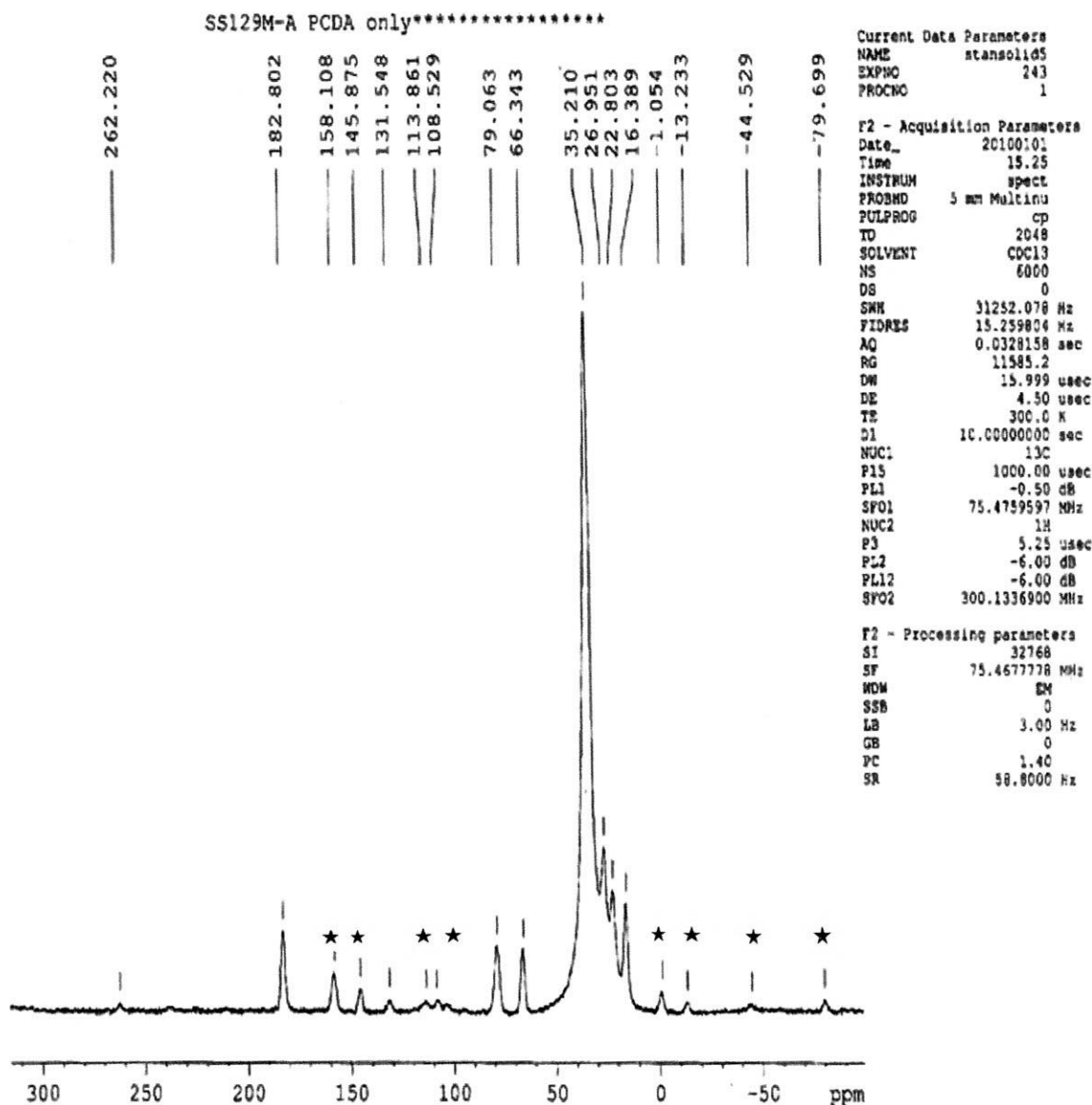


Figure 11 Solid-state CP NMR MAS of polymers SS129M-A PCDA (UVed). ★ indicates spinning sidebands.

Figure 10, containing freshly cracked cyclopentadiene but no chloroform and a more concentrated polymer fraction, as described in the Experimental section, shows a monomer melting point at 65.18°C. Two separate melting points, 184.08°C and 213.92°C, are observed, which are 9 degrees below and 20 degrees above the melting points in the previous sample scans in Figures 8 and 9, representing two different polymer species.

Solid-state CP NMR MAS runs were undertaken for both the control PCDA and PCDA combined with the cyclopentadiene in the monomer states, after the 2 h mixing and evacuation process to determine whether a reaction between the PCDA and cyclopentadiene had taken place. The results indicate no differences and were therefore placed in the Supporting Information Figures 28 and 29.

CP NMR MAS scans of polymerized samples SS129M-A PCDA and SS129M-B PCDA and cyclopentadiene were run to look for new products, as shown in Figures 11 and 12 below. The results above show major differences at 131.548 in Figure 11, which has increased in size in Figure 12 at 130.841 ppm, indicating a possible norbornadiene (NBD) peak. The triple bond peaks at 66 and 78 are smaller but the sidebands at 101 and 107 ppm are readily evident. A CP NMR MAS scan was run of the UV sample SS154M-B PCDA with Cyclopentadiene (without chloroform).

In Figure 13, a peak at 131 ppm appears much larger than the control sample SS129M-A PCDA in Figure 11, indicating a NBD peak. Two other possible NBD peaks are 49.3 and 52.6 ppm in which the peak at 51.3 ppm is a possible candidate. The triple

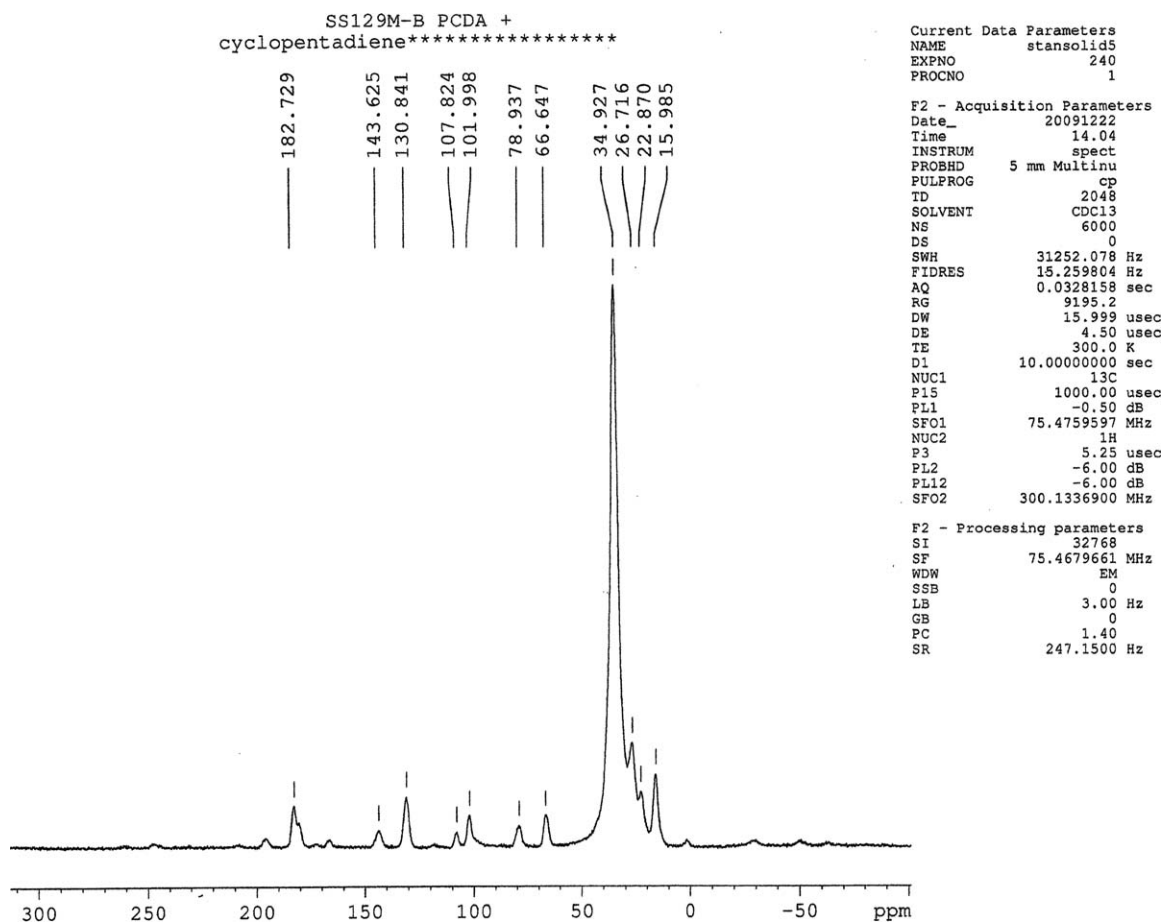


Figure 12 Solid-state CP NMR MAS of SS129M-B PCDA and cyclopentadiene (UVed).

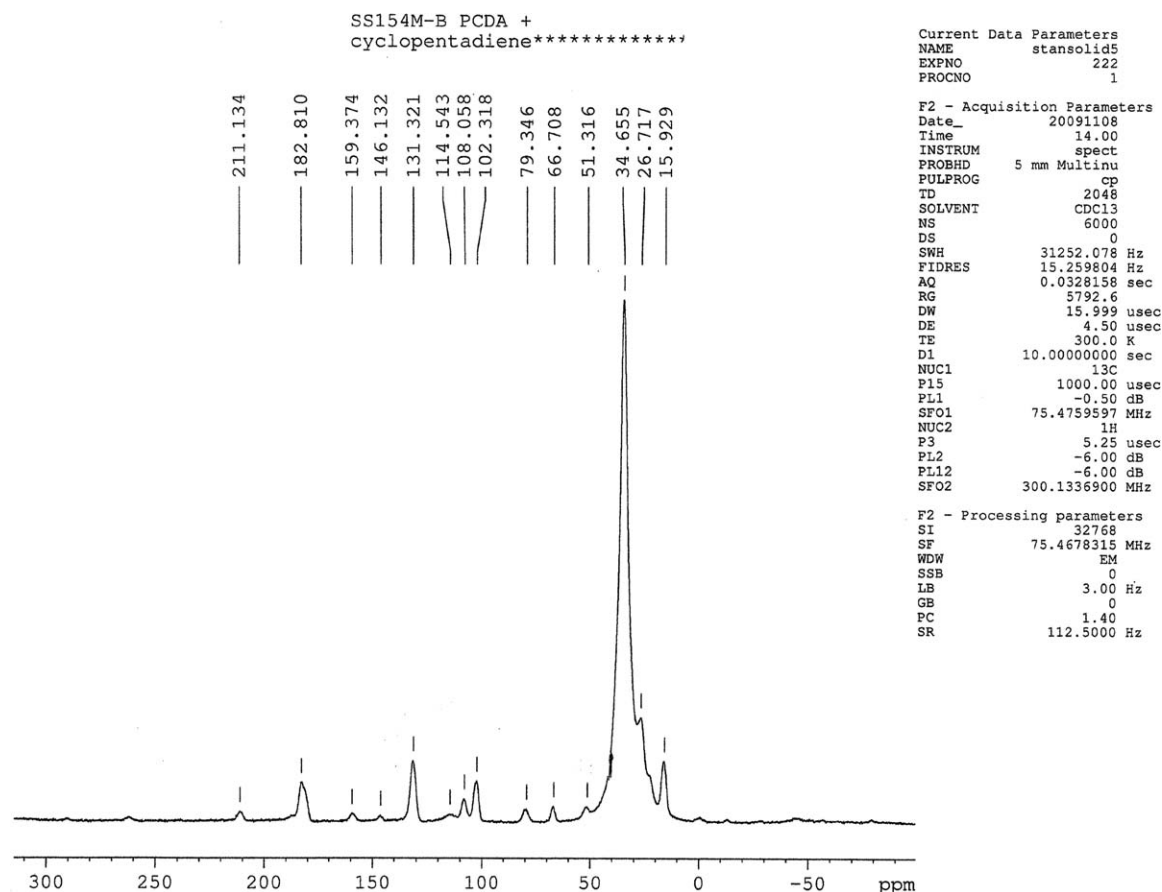


Figure 13 Solid-state CP NMR MAS of SS154M-B PCDA and cyclopentadiene (UVed).

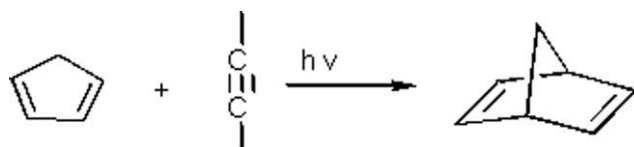


Figure 14 Diagram of conversion of cyclopentadiene to 2,3-NBD.

bonds peaks at 66 ppm and 79 ppm are smaller, whereas the sidebands at 102 and 108 ppm are also larger.

DISCUSSION

Cyclopentadiene seems to be responsible for the 90°C to 95°C increase in the blue to the red conversion temperature of the polymer PCDA to the polymer PCDA with cyclopentadiene. Because the energy barrier for the color conversion of PCDA at 90°C is $73.6 \pm 4.6 \text{ kJ mol}^{-1,40}$ a bond may form between cyclopentadiene and the polymer PCDA. Cyclopentadiene undergoes a Diels-Alder reaction with the triple bond of an alkyne to form a NBD,^{49,50} as shown in Figure 14 below. The reaction is very spontaneous, with a ΔG value of -65.31 kJ/mol , a $K_{eq} = 2.8 \times 10^{11}$ and energy of activation = $101.15 \text{ kJ/mol}^{51,52}$ that is easily catalyzed by 200 nm UV radiation with an energy of 598 kJ/mol.

Therefore, in the presence of UV radiation, cyclopentadiene may undergo a Diels-Alder reaction with the triple bonds of PCDA to form a 2,3-NBD adduct, as shown in Figure 15. The bonding process of cyclopentadiene and PCDA does not seem to occur when the cyclopentadiene is combined with the PCDA monomers, either initially or after the 2-hour stirring period, as evidenced by

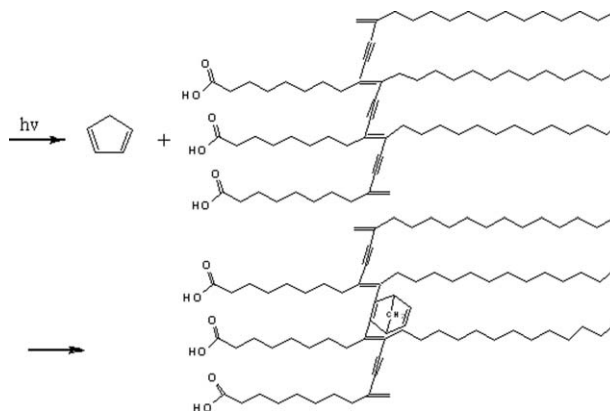


Figure 15 Possible bond of cyclopentadiene with PCDA to form 2,3-NBD.

the solid-state CP NMR MAS runs, as shown in Supporting Information Figures 28 and 29, as well as the DSC runs, as shown in Supporting Information Figures 26 and 27, which exhibit only monomer melting points, that are nearly identical to each other, both in melting point temperature and energy per unit gram.

When comparing the spectra of Supporting Information Figures 28 and 29, one will notice that they are identical in peak values, implying that new products were not formed with the addition of the cyclopentadiene. Instead, we consider the bonding reaction to be catalyzed by the UV light, either during the polymerization of the PCDA monomers or shortly thereafter.

Solid-State CP NMR MAS was subsequently run on the PCDA polymer samples, including PCDA only and PCDA combined with cyclopentadiene and were shown in Figures 11–13. It can be seen that new peaks at 131.55 and 130.82 ppm,

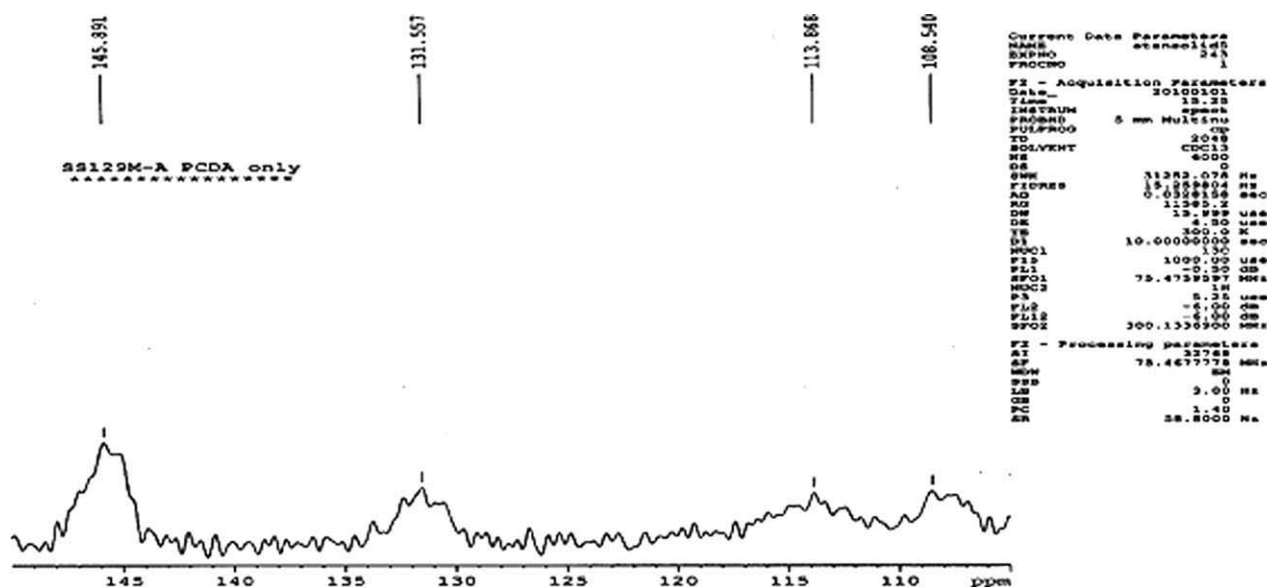


Figure 16 CP NMR MAS of SS129M-A PCDA polymers (UVed).

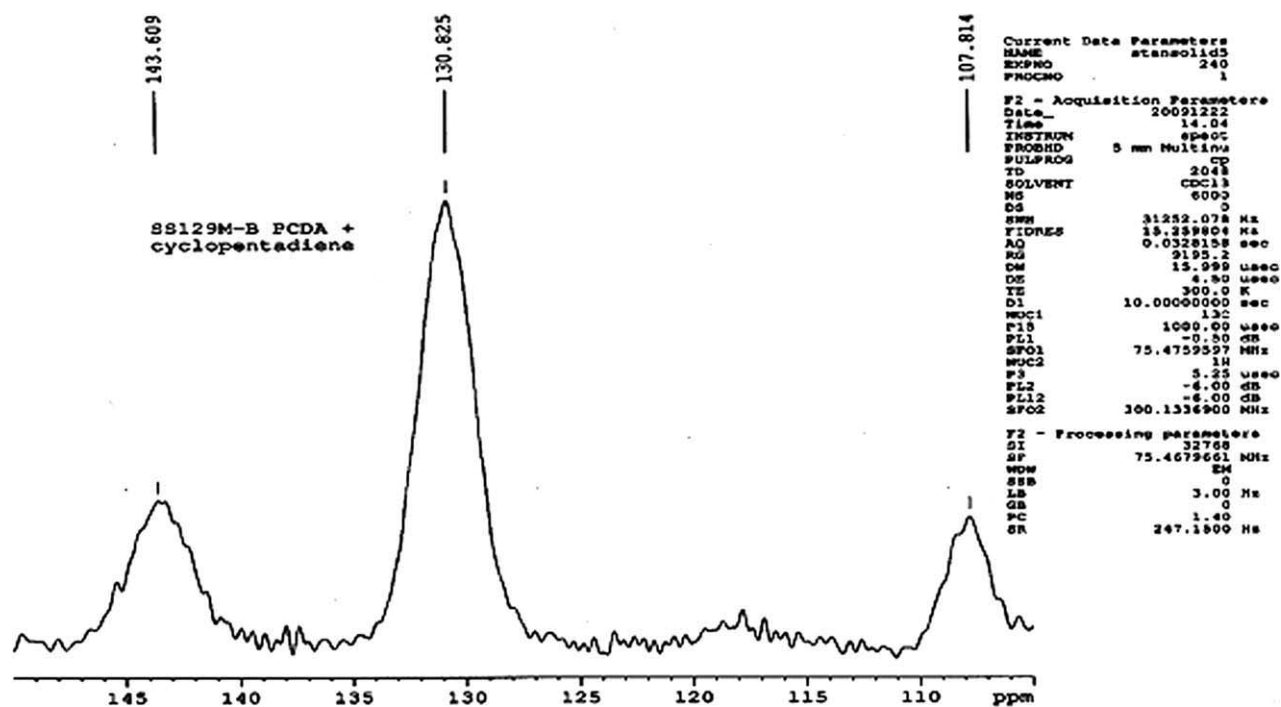


Figure 17 CP NMR MAS of SS129M-B PCDA polymers and cyclopentadiene (UVed).

respectively, were formed that were not present on the monomer spectra in Supporting Information Figures 28 and 29. The polymerization process, utilizing UV radiation, is normally performed on thin films not bulk powders and, therefore, a high percentage of monomers remain with only a low percentage of polymers formed because of a quenching of the excited monomers by the polymer chain just formed.⁵³ This can be seen in DSC runs of both polymers, PCDA and PCDA, combined with cyclopentadiene, as shown in Figures 8 and 9. On both DSC runs, it will be noted that the polymer endotherms are about one-tenth as large as the monomer endotherms. This is also in agreement with solubility separation experiments performed on these samples, which yielded polymer concentrations ranging from 9.29% to 12.9%, as shown in Table II in the Supporting Information. Expanded views of Figures 11 and 12 of

the peaks at 131.55 and 130.83 ppm are shown below in Figures 16 and 17.

The value of the peak in Figure 16, equal to 131.56 ppm, is the approximate value for the double bond of the 1,4 eneyne addition polymerization reaction in this experiment, as calculated from Chem Draw Ultra 11 and the value in Figure 17, equal to 130.83 ppm, is the value calculated for addition of cyclopentadiene bonded to the triple bond of PCDA, also using Chem Draw Ultra 11, and could possibly be the value for a Diels-Alder bond. Figure 13, which used PCDA and freshly cracked cyclopentadiene, was carried out without the use of chloroform. It will be observed in Figure 12 that the peak at 131.49 ppm is large, and the peak in Figure 13 at 131.32 ppm is even larger. Because of the equivalence of peak heights in Figures 12 and 13, therefore, it would seem that the presence of chloroform does

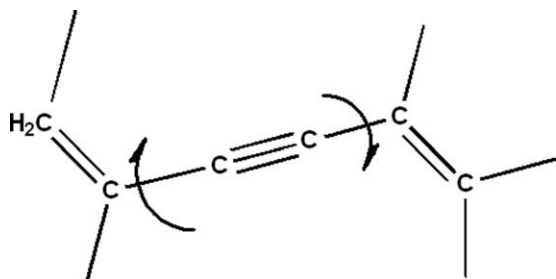


Figure 18 Diagram of C-C bond rotation around backbone of PCDA.

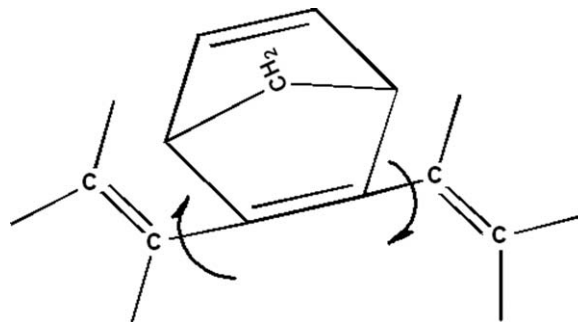


Figure 19 Inhibited rotation of C-C bonds by 2,3-NBD bonded to PCDA.

not block the triple bonding sites on the PCDA polymer from possibly bonding with cyclopentadiene. It is also of importance to note that the height of the triple bond peaks at ~ 66 and 79 ppm has decreased very significantly from their original height on the control PCDA polymer in Figure 11 to the PCDA-cyclopentadiene polymers in Figures 12 and 13. This can be explained only if a considerable number of triple bonds in the PCDA polymer are bonding with cyclopentadiene molecules thereby resulting in a much smaller number of unreacted triple bonds, and therefore smaller NMR peaks. Because triple bonds in acetylenic compounds may be used as dienophiles in the Diels-Alder reaction,^{49,50} it is certainly possible that cyclopentadiene is undergoing this type of reaction with the triple bonds of PCDA even though the closeness of the chemical shift values of the double bond in the polymer, and the possible Diels-Alder bond makes identification somewhat difficult.

As mentioned earlier,²⁸ studies have shown that the energy levels of the molecular orbitals of the overlapping π bonds in the backbone of the PCDA polymers is affected by rotation of C—C bonds in the tilted side chains around the backbone. A rotation of only 5 degrees causes significant stress of the π overlap thus producing a shift in the spectrum from blue to red, as shown below in Figure 18.

We believe that the bonding of cyclopentadiene to the triple bonds in the PCDA backbone inhibits rotation, perhaps by steric hindrance, as shown in Figure 19 and thus prevents the blue to red color change until the bond has sufficient energy to rotate from the higher temperatures. Further work in this area would involve studying a smaller conjugated diyne, such as 5,7-dodecadiynoic acid, which contains 13 less carbon groups and therefore causes less of a scaling problem, with fewer NMR peaks to interfere with smaller peaks, which might be formed with the cyclopentadiene. In addition, it appears important to investigate groups with inherently larger steric hindrances, such as anthracene or benzoquinone, to observe whether the blue to red conversion temperature is increased to a greater degree than that produced by cyclopentadiene in the present study. Finally, it would be advantageous to study these effects using ultrathin films, as others have done,^{41,46} which would yield polymers only without any effects because of large concentrations of surrounding monomers.

CONCLUSIONS

Aromatic compounds, such as furan, benzene, thiophene, and cyclopentadiene, were combined with PCDA and then subjected to UV radiation to form blue polymers. They were then heated from 70°C to 200°C in 5°C increments, and after each incre-

ment, they were analyzed by Raman spectroscopy and solid-state fluorometry. The results showed that three of the aromatics, furan, benzene, and thiophene, had no effect on elevating the blue to red conversion temperature. However the cyclopentadiene results demonstrated that the color conversion temperature was increased by 90°C to 95°C . Solid-state CP NMR MAS and DSC showed no new products at the end of the PCDA and aromatic compound mixing process, indicating that probable chemical bonding between PCDA and cyclopentadiene occurred after the UV polymerization process had occurred. It was then concluded that a possible Diels-Alder reaction had taken place between the cyclopentadiene and the conjugated triple bonds of PCDA that was catalyzed by the UV radiation. This is believed to prevent C—C rotation of side groups of the PCDA molecule by steric hindrance until sufficient energy at higher temperatures overcomes steric hindrance or until melting occurs.

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