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Approaches to Conjugated Polymers via Solid State Polymerization

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Summary: Topochemical solid state polymerization is a method of obtaining fully crystalline macromolecules. Herein, approaches to conjugated polymers via new solid state polymerizations and the properties of materials, especially polydiacetylenes(PDA), obtained via solid state polymerization are discussed. Our attempts to polymerize cyanoalkynes and to define the thermal reaction product of a dicyanodiazepine are presented. Certain PDA exhibit absorption, likely charge-transfer, at energies below the exciton. Nanocrystals of PDA-DCH react with liquid bromine to give the mixed polyacetylene PDA-$DCHBr_6$ whose visible spectrum exhibits structure not observed in spectra of bulk crystals of PDA- $DCHBr_6$. The thermochromic PDA of the dialkylurethanes of 5,7-dodecadiyn-1,12-diol were studied by variable temperature solid state ^{13}C nmr. The upfield shift of the acetylene carbons as the temperature is raised above that of the thermochromic phase transition indicates the role of mechanical strains in achieving thermochromism.

Introduction

Conjugated polymers have attracted considerable interdisciplinary scientific interest for over thirty years. The 2000 Nobel Prize in Chemistry[1-3], awarded to H. Shirakawa, A.G. MacDiarmid, and A.J. Heeger for "doping", via electron transfer chemistry, of polyacetylene, $(CH)_x$, to a metallic state may be taken as a recognition at the highest level of the scientific, technological, and commercial results of an extremely large body of work. Nevertheless, much of this work has been carried out on materials that are partially crystalline at best, and hence many properties, especially electronic transport, are limited and do not reach their intrinsic limit. Hence, it will be argued herein that there are still many important challenges remaining in the area of conjugated polymers, and materials with very high degrees of three dimensional order are key to several desirable advances. It is in this context that we note that G. Wegner's studies[4] of the topochemical and topotactic diacetylene (DA, **1**) polymerization predate the "doping" of $(CH)_x$.

As examples of fully ordered macroscopic polymer single crystals, polydiacetylenes (PDA, **2**) have structural and physical properties that provide far more detail and insight than those of

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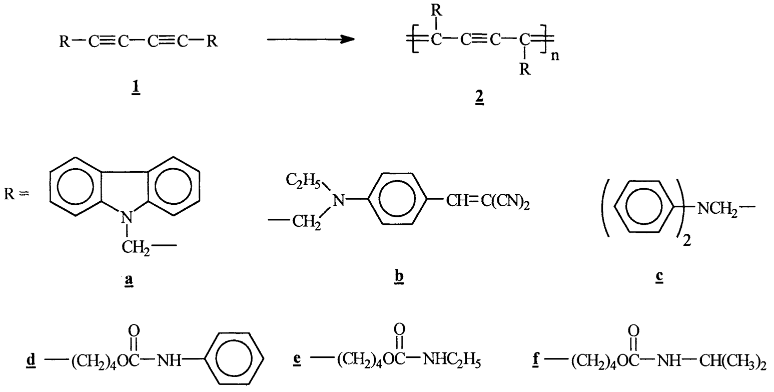
less ordered systems. Scheme 1 illustrates the DA polymerization and gives the structures of the side group substituents under discussion herein. Let us provide two examples to illustrate that point chosen from the areas of odd order non-linear optics (NLO) and studies of exciton binding energy. The third order NLO coefficient, $X^{(3)}$, is related to the light intensity-dependent refractive index, the key parameter for all-optical signal processing. The studies[5] of $X^{(3)}$ in both PDA single crystals and related thin films have revealed magnitudes of $X^{(3)}$ comparable to the best inorganic semiconductors with temporal responses in the transparent spectral region in the subpicosecond time frame. Recently, the dispersions of $X^{(5)}$ and $X^{(7)}$, higher order NLO coefficients, have been obtained[6] from electroabsorption spectroscopy using spin-cast thin films of soluble PDA. Hopefully, the extension of these studies to single crystal PDA will occur in the near future.



Scheme 1. Diacetylene polymerization and the structures of side groups R.

Exciton binding energy (E_b) is the energy that must be exceeded for electron-hole formation, and subsequently carrier transport, to occur. Carrier transport is especially critical in polymeric light emitting diodes (LEDs). PDAs have a large E_b[7], approximately 1 eV, and this value is significantly larger than other conjugated polymers, such as polyphenylenevinylenes (PPVs), where the E_b is estimated to range from close to zero to 0.9 eV. An extensive literature[8] discussing experimental and theoretical aspects of this topic exists. Recently, the E_b in PPV was determined[9] to be 0.060 eV from studies of photoconductivity excitation profile spectroscopy as a function of light polarization, applied electric field, and temperature.This contrast between PDA and other less ordered conjugated polymers is illustrated[10] in the difficulty of observing photoinduced electron transfer from PDA to C_{60} versus the ease of the process with PPV.

PDA exhibit electronic carrier mobilities (μ) greater than 1 cm^2/volt-sec[11], slightly larger than molecular crystals at room temperature. Values of μ greater than 10^3 cm^2/volt-sec are an important aspect of the functioning of crystalline semiconductors such as Si and GaAs. The room temperature mobilities of crystalline PDA are 3-4 orders of magnitude larger than those of partially crystalline or amorphous conjugated polymers. Recent experiments by H. Schön and coworkers at Lucent Technologies Bell Laboratories reveal[12] carrier mobilities in molecular crystals in excess of 10^4 cm^2/volt-sec, at liquid helium temperatures in a field effect transistor (FET) device configuration. As a consequence of such large values of μ, electrically pumped laser action[13] and superconductivity[14]have been observed in molecular crystals such as anthracene, tetracene, and pentacene, and PPV oligomers[15]. In addition, the FET device configurations have been used to observe[16] superconductivity in a specimen of partially crystalline regioregular poly-3-hexylthiophene (P3HT) with T_c approx. 2°K. It is most likely that a more crystalline specimen of P3HT would exhibit a higher value of T_c. It is very likely that a full assessment of the scientific and technological potential of the phenomena dependent on large values of μ will require fully crystalline rigorously purified samples of conjugated polymers beginning with PDA.

The literature of approaches to conjugated polymers via solid state polymerization is overwhelmingly dominated by PDA[7,17-24] and closely related systems. Lauher, Fowler, and coworkers have recently reported[25] the topochemical and topotactic 1,6-addition polymerization of a triacetylene where the required monomer crystal structure is achieved by means of a host-guest strategy involving hydrogen bonding. There are a number of reports of studies of solid state reactivity and polymerization, especially of monoacetylenes. B.M. Foxman and coworkers have studied[26] the crystallography and solid state reactivity of numerous metal propiolates, $HC{\equiv}C\text{-}CO_2^-M^+$. The crystallographic information provides a compelling case that these polymerizations are topochemically initiated. Nevertheless, to date, the solid state chemistry of the overall reaction is single crystal monomer-to-amorphous polymer. Other acetylenes such as 10-undecynamide and the cyclohexyl urethane of 5-hexyn-1-ol display[27] intermolecular contacts between potentially reactive acetylenic carbons less than 3.70Å, yet these melt stable compounds appear to be unreactive to ionizing radiation due to a facile fluorescence process. In the interest of enhancing the reactivity of a crystalline monoacetylene by means of a heavy atom effect, 11-Bromo-10-undecynamide was synthesized.[28] This compound is reactive to ultraviolet light and ^{60}Co γ-radiation; the latter converts the crystalline monomer to an amorphous polymer.

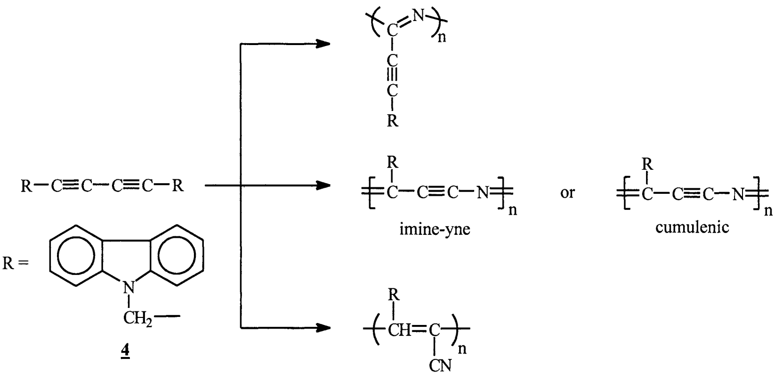
As a result of these studies on monoacetylenes and other work it should be apparent to the casual reader and beginning researcher that solid state reactivity and polymerization can be very complex subjects. Not only must potentially reactive molecules have atoms that will form covalent bonds within about 4.20 Å of each other in accord with the topochemical postulate[17], but there must also be viable reaction mechanisms for thermal, ultraviolet light, and ionizing radiation to initiate and propagate a chain whose growth must also be compatible with the initial lattice. Just as William Shakespeare tells us in *The Merchant of Venice* that "all that glisters is not gold", so every colorless organic compound that becomes a dark reflective solid in response to thermal, uv light, and ionizing radiation stimuli is not necessarily experiencing processes analogous to the optimal DA-PDA conversion.

Herein, we summarize recent initial studies of the solid state reactivity of cyanoalkynes, compounds iso-π-electronic to DA, the definition of the initiation process and structure of the black reflective solid product of the solid state reaction of 2,3-dicyano-5,7-dimethyl-6H-1,4-diazepine (**3**), our initial observation of charge-transfer transitions in PDA, our observation of vibrational structure in the brominated product of PDA-DCH (**2a**) nanocrystals, and our deduction of the role of mechanical strains in thermochromic PDA via solid-state ^{13}C cross polarization magic angle spinning (CPMAS) NMR.

Cyanoalkyne Reactivity

Pursuant to the identification of other solid-state reactions that might be related to DA polymerization, we identified cyanoalkynes because they are iso-π-electronic to DA. Just as DA reactivity involves diradical and dicarbenes as intermediates, qualitatively, in principle, cyanoalkynes should be able to form analogous intermediates, as shown in Figure 1. Just as the observed en-yne form of a PDA chain is lower in energy than the butatriene form, so the imine-yne product of 1,4-addition polymerization of a cyanoalkyne is calculated to be lower in energy than a cumulene form (Scheme 2). The calculations were performed on pentamer oligomeric structures of both PDA and polymerized cyanoalkyne chains using the AM1 semiempirical method in the Hyperchem suite of programs. As shown in Scheme 2, reaction at either the acetylene or cyano groups of a cyanoalkyne is conceivable.

The first cyanoalkyne that we synthesized was N-(3-cyanoprop-2-ynyl)carbazole, **4**. This compound was found[29] to be relatively unreactive to uv light and ^{60}Co γ-radiation. Compound **4** exhibits m.p. 91-93°C, and it was heated at 80°C for an extended period of time.

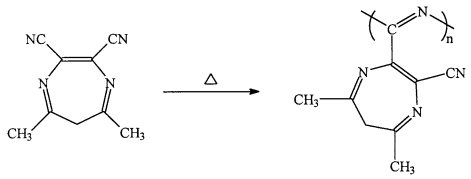


Scheme 2. Possible reaction pathways for reactions of cyanoalkynes.

The initially colorless crystals become light brown on heating. The crystal structure[29] reveals relatively short contacts between cyano groups with a N----C intermolecular distance as short as 3.339Å, but this structure is not one that allows the desired 1,4-addition polymerization. The characterization[29] of the thermal product reveals only reactivity between the cyano groups. Our further studies of cyanoalkynes will involve systems designed to bring about 1,4-addition.

Solid State Reaction of 2,3-Dicyano-5,7-dimethyl-6*H*-1,4-diazepine

We began the study of 2,3-dicyano-5,7-dimethyl-6H-1,4-diazepine (**3**) in connection with our studies of polymerization[30] and cyclotetramerization[31] of dicyanoalkenes and –arenes initiated by unprotected sugar reagents. This compound was hoped to be a cyclic analog of *bis* (dimethylamino) maleonitrile which reacts[32] with alkaline glucose to give a low yield of cyclotetramer. The original synthesis of **3** reported[33] melting at 199-200°C with decomposition. Of the dicyanoalkenes and –arenes that we have studied to date, **3** is the only compound that does not exhibit reversible melting behavior. The process of decomposition attracted our attention, and we observed that heating the colorless **3** at 150°C for one week resulted in formation of a black reflective solid (45% yield) accompanied by sublimation of **3** out of the reacting crystal. The solid product was amorphous, and its IR spectrum revealed that its average chain structure involved formation of a conjugated polymer via reaction at one of the two cyano groups, similar to that found in solution polymerization[30] involving sugars. The solid state reaction of **3** is illustrated in Scheme 3.



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Scheme 3. Molecular structure of diazepine **3** and a possible structure of the product of its thermal solid state reaction.

As noted above, the key to understanding solid state reactivity is the reactant crystal structure and the intermolecular relationships of monomer molecules. Examination of the crystal structure[34,35] of **3** did not reveal a linear pathway for polymerization. The structure also exhibits an intermolecular N---C contact of 3.425Å between –CN groups. This experimental observation coupled with lack of other thermally reactive dicyano compounds raises the question as to how the thermal reaction initiates and how the chain grows. Our current understanding of these issues comes largely from solid state nmr studies of ^{13}C, ^{15}N, and ^{1}H nuclei.

The ^{15}N spectrum exhibits resonances in regions that allow assignment to tertiary amine and quaternary ammonium (R_3NH^+). The ^{1}H spectrum of partially reacted monomer reveals resonances assignable to olefinic H atoms. These observations may imply the involvement of tautomeric forms of the monomer. Some tautomers of **3** are illustrated in Figure 1. If reaction initiates from a tautomer such as **3b** by addition of the –NH group to a cyano group in an adjacent molecule, this process would involve a defect site because the NH is not found in the crystal structure[[34,35] and its creation would involve formation

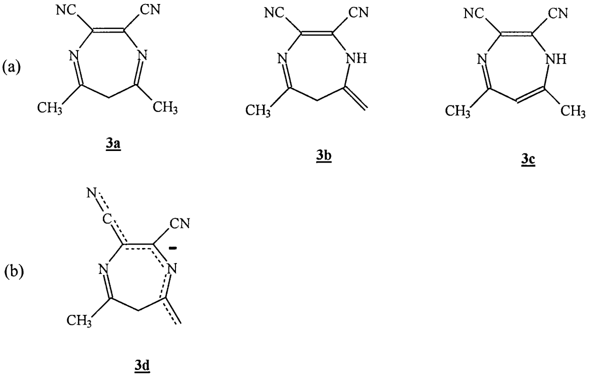

Figure 1. (a) Some tautomers of **3**. Tautomer **3c** is an 8π antiaromatic system. (b) **3d** is a delocalized anion derived from **3**.

of the NH bond which would have a length of approximately 1Å. This situation describes creation of a defect site, and the initiation may be topochemically controlled. It is apparent that the lattice does not control the chain growth process. If **3** can lose a proton in the solid state, the anion **3d** (or an equivalent group of resonance structures), also illustrated in Figure 1, would form. The presence of excess negative charge on a cyano nitrogen[30] in **3d** offers a rationalization as to why one cyano group is unreactive in this solid state reaction.

Polydiacetylenes: Electronic Transitions Below the Exciton

In the absence of oxidation[36] of a PDA backbone, PDA crystals are typically transparent at energies lower that of the excitonic absorption. We synthesized[37] a series of 2,4-hexadiyne DA monomers that have the characteristic that they absorb light at longer wavelengths than carbazole such that, on polymerization, they would provide an environment that would shift the excitonic absorption of the PDA to longer wavelengths than found in **2a**. The first monomer to give suitable single crystals for crystallographic study was 1,6-diethyl-(1,6-bis-*p*-benzylidenemalononitrile)-2,4-hexadiyndiamine, **1b**. This monomer is relatively inert to ionizing radiation and was thermally polymerized in a topotactic process[38] to **2b**. Polarized specular reflection spectra were obtained from the (001) face of crystals of **2b**. The reflection peak is found near 571 nm for pseudo-long-axis polarization, and significant anisotropy is apparent from the spectrum in the perpendicular direction. This reflection peak is in a similar position as that found[39] in the PDA of 1,1,6,6-tetraphenylhexadiyndiamine (THD, **2c**). In addition, heretofore unobserved structure for PDAs is observed in both principal directions from approximately 833 to 625 nm. The observation of a band at lower energy than the usual PDA absorption, its width, lack of vibronic structure, and apparent polarization suggest[38] that the band arises from one or more charge-transfer transitions. The donor would be the conjugated backbone of one polymer chain with the side group of an adjacent chain serving as acceptor. Such features to the red of PDA excitonic absorption had not been previously observed. Figure 2 displays the low energy portion of the reflection spectrum of **2b**. Subsequently, another PDA was reported[40] to have such absorption.

Polydiacetylenes: Bromination of PDA-DCH Nanocrystals

Single crystals of the PDA of 1,6-di-N-carbazolyl-2,4-hexadiyne (**2a**) react[41] with bromine in a crystal-to-crystal transformation that allows the material to gain 3-9 Br atoms per repeat unit. A particularly interesting member of this family is the material that has gained 6Br atoms per repeat unit. Here, bromine adds to each carbazole unit at the 3 and 6 positions and then proceeds to add to the triple bond. The brassy appearance of **2a** is changed to a copper bronze. Thus, the PDA backbone structure is converted largely to a mixed polyacetylene structure, as initially[42] deduced from ^{13}C CPMAS NMR studies. Evidence[43] supporting the mixed polyacetylene structure also came from Raman spectra. While the material is intensely colored, its visible spectrum was recorded[44] by diffuse reflectance. The reflectance was not particularly informative as a distinct visible maximum associated with the conjugated backbone was not observed.

In 1993 Nakanishi and coworkers described[45] the preparation of nanometer sized crystals of a variety of organic molecular compounds, some of which were DA monomers. Of particular interest to the present work, nanocrystals of **2a** obtained by uv photopolymerization have been extensively studied.[46] Specimens of **2a** in programmed[47] electrostatic assemblies formed by layer-by-layer deposition with polydiallyldimethyl- ammonum chloride (PDADMAC) as polycation were assesssed[48] for their third order NLO properties.

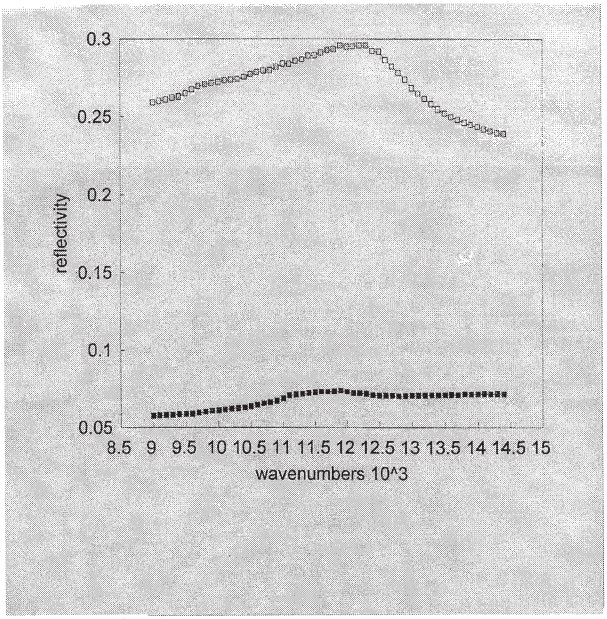

Figure 2. Polarized specular reflection spectra of **2b** in the infrared region. The upper spectrum is obtained with light polarized along the chain axis, and the lower spectrum is taken with light polarized perpendicular to the upper spectrum.

In our studies, nanocrystals of **1a** were prepared as described[46] by Nakanishi and coworkers. These specimens were polymerized with UV light and thermally, and their sizes were studied by transmission electron microscopy and dynamic light scattering. The optical properties, including vibronic structure, of these materials were in agreement with previous reports.

Bromination of **2a** nanocrystals was carried out in multilayers with PDADMAC and **2a** obtained by uv polymerization. The absorbance at 647 nm of these assemblies increased in a linear fashion with the number of bilayers. Ten bilayers of this assembly were exposed to bromine vapor. After 22 hours exposure to bromine vapor, the spectrum of the assembly was not significantly changed. Bulk crystals of **2a** are relatively unreactive[41,42] to bromine vapor. When these assemblies were exposed to liquid bromine for 10 seconds, the visible spectrum of **2a** was replaced by a new spectrum with maxima at 540 and 497 nm. The separation between these two peaks is 1605 cm^{-1}. The Raman spectrum[49] of crystals of PDA-$DCHBr_6$ reveals a shifted line at 1518 cm^{-1}. This shift is characteristic of an extended polyene chain. The broad agreement between the splitting in the optical spectrum of the assembly and the Raman spectrum of bulk crystals suggests that the assembly bromination converted it to a mixed polyacetylene structure. In addition, the carbazole absorption in the polymer shifted to the longer wavelength of 362 nm. This spectral information is displayed in Figure 3 along with spectra of the PDA-DCH assembly exposed to bromine vapor.

Polydiacetylenes: Thermochromic Phase Transitions

The PDA of the *bis*-alkylurethanes of 5,7-dodecadiyn-1,12-diol exhibit thermochromism. At 25°C, single crystals of these materials exhibit peaks in their reflection spectrum between 635-650 nm with light polarized along the polymer chain. When heated at temperatures in the range 120-150°C, the reflection spectrum shifts to higher energy. The issue of changes in the macromolecular structure[8] that occur in the course of this color change has concerned researchers since 1976.

In 1976, it was suggested[50] that the spectral shift was associated with a change in the number of delocalization lengths. Another proposal[51] suggested a change from the acetylenic structure at room temperature to a butatrienic structure above the temperature of the phase transition. Crystallographic data and quantum chemistry calculations ruled out this suggestion. Moreover, a ^{13}C CPMAS NMR study[52] of the PDA of the *bis*-phenyl urethane of 5,7-dodecadiyn-1,12-diol (TCDU, **1d**) showed its backbone to be acetylenic and not butatrienic. An additional proposal[53] involved the formation of an orbital-flip defect or backbone planar-nonplanar transition as temperature is increased. Such a process demands a change in the backbone repeat distance and was excluded[54] by variable temperature X-ray powder diffraction studies of PDA-ETCD, **2e.** Local dielectric effects were proposed[55] to be involved in the transition. While this proposal was not quantitated and the possibility of mechanical strains was not excluded, it has been criticized.[56] The possibility of mechanical strains[57] involving side group and backbone during polymerization to maintain intramolecular hydrogen bonding was advanced. To maintain these hydrogen bonds, the methylene groups would distort resulting in a mechanical strain on the backbone. From theoretical calculations[58] it was deduced that such side group strain could induce a change in PDA electronic structure. Possibly, thermal stimulus during the transition gives the side group sufficient energy to release the mechanical strain by rotation around the single bond

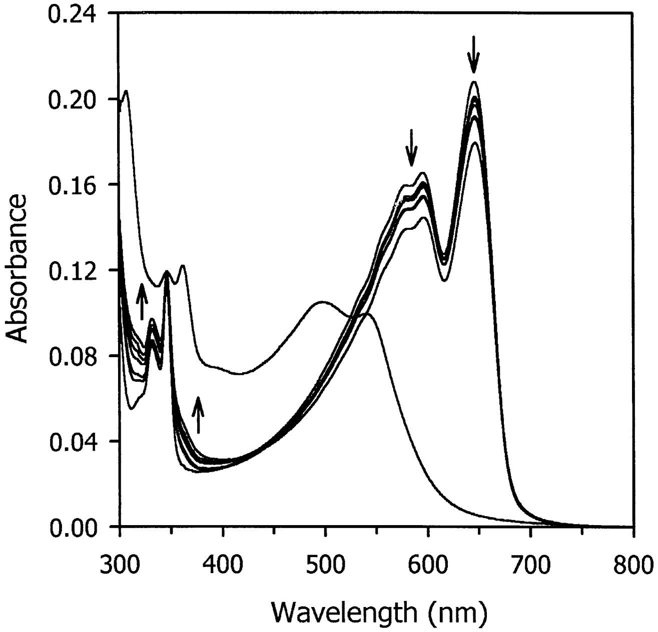

Figure 3. Electronic spectra of a nanocrystal assembly of **2a** exposed to bromine vapor and bromine liquid. The latter gives the maxima at 540 and 497 nm.

between methylene units although such movements of the side group seem somewhat restricted to maintain the necessary crystal unit cell parameters for reversibility. Side group movement decreases the strain on the backbone at the same time. The crystallographic unit cell increases in volume[54] during the transition, making the latter first order, and this results in a release of strain. The increase in unit cell volume[54] in the course of the transition is largely associated with distances involving the side chain and with interlayer features maintaining the backbone repeat distance. Infrared[59] and ^{13}C solid state NMR spectroscopy[60] revealed that the four methylene units between the backbone and urethane function undergo a change in the conformer population in the course of the transition. Change in methylene conformer population was also noted[61] in thermochromic cross polymerized diacetylene-functionalized polyamides. The thermochromic phase transition often occurs at a temperature close to the melting point of the corresponding monomer. The potential role of residual monomer in the transition was ruled out by a study of PDA-IPUDO, **2f**, which has a monomer to polymer conversion greater than 99%.

The availability[62] of a non-thermochromic form of **2e** allows a comparison of its properties to that of the thermochromic materials. The non-thermochromic form of **2e** is obtained by treating the thermochromic material with refluxing chlorobenzene. The chlorobenzene extracts monomer and oligomer, and the exposure to boiling solvent relieves potential mechanical strains. The resulting material retains crystallinity and maintains vibronic structure and anisotropy in its reflection spectrum.

We have recently[63] carried out a study of **2f** and the thermochromic and non-thermochromic forms of **2e** by a combination of thermal techniques and variable temperature ^{13}C CPMAS nmr spectroscopy. In this study, the chemical shift of the acetylenic carbons and its change with temperature and release of mechanical strain is particularly instructive. In general, the ^{13}C chemical shift of acetylenes is sensitive to the length of a conjugated chain[64] and the mechanical strain[65] on the acetylene group. In these cases, increased deshielding signifies a longer conjugation length or greater mechanical strain, as judged by distortion of a bond angle from 180°. Table 1 summarizes the ^{13}C acetylene shifts of these PDA. The increased shielding of the non-thermochromic form of **2e** indicates that mechanical strain has been decreased relative to the thermochromic forms. It follows then that the upfield shifts in going from the blue phase at ambient temperature to the red phase above the thermochromic transition is associated with a decrease in mechanical strain on the backbone. The ^{13}C shift of the acetylene in the non-thermochromic form does not change[63] significantly as temperature is increased. Figure 4 displays the ^{13}C CPMAS spectra of **2f** in a cooling cycle. In the spectrum recorded at 95°C, note the presence of acetylenic resonances corresponding to both the high and low temperature phases.

Table 1. ^{13}C Acetylene Chemical Shifts of Urethane Substituted PDA.

PDA	**^{13}C Acetylene Chemical Shifts, ppm**
2e(blue)	106.1
2e(red)	102.4
2e(non-thermochromic)	100.2
2f(blue)	105.6
2f(red)	101.7

Conclusion

Our studies of **3** and **4** again serve to emphasize the importance of an appropriate crystal structure for the reactant in a solid state polymerization. Our conclusion that a tautomeric form of **3** is involved in the initiation of the solid state reaction is not a common topic in the literature of organic solid state reactivity. The observation of charge transfer absorption in **2b** was not precedented and such spectral features may well be found in related systems. It is possible that such features may lead to new optical and electronic processes in PDA. The bromination of nanocrystals of **2a** led to the observation of spectral features that were not detected in earlier[42,44]studies of brominated bulk crystals of **2a**. Our variable temperature ^{13}C CPMAS nmr studies of the thermochromic PDA allowed study of these materials in both blue and red phases. The shifts of the acetylenic carbons were discussed in terms of contributions of conjugation lengths and mechanical strains. The availability of the nonthermochromic form of **2e** allows us to conclude that mechanical strains are important in the observation of thermochromism. Indeed, in the absence of mechanical strains, it would be expected that these PDA would have absorption maxima in the range 520-550 nm at ambient temperatures.

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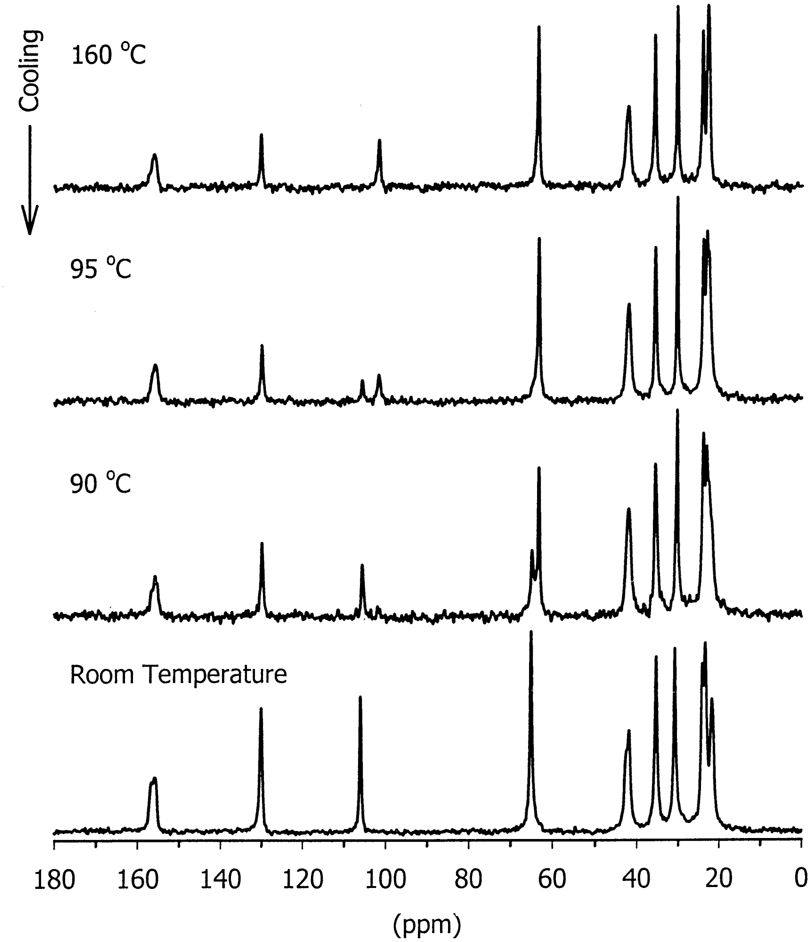

Figure 4. ^{13}C CPMAS spectra of **2e** in a cooling cycle.

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