Thermochromism in Liquid Crystalline Polydiacetylenes

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ABSTRACT: The thermochromic behavior of diacetylene-containing hydrogen-bonding thermotropic liquid crystalline monomers and a semirigid main chain thermotropic poly(ester−diacetylene) were examined. These materials were successfully designed to undergo dramatic, first-order thermochromic transitions at the onset of their characteristic mesogenic transitions, as exhibited by changes in the shapes and locations of their polydiacetylene absorption bands and the corresponding visually observed color changes. Two different types of chromic response have been observed: one case, the diacid monomer 5,7-DODBA, in which the polydiacetylene chain responds to the liquid crystalline transitions of its host monomeric lattice, and two cases, the 10,12-DHDP monomer and 10,12-DHDP/TC polyester, in which the side chains covalently bonded to the polydiacetylene chain undergo mesogenic transitions that drive the thermochromic transition. It was found that the thermochromic transition is not reversible beyond the melting points of the partially polymerized monomers, whereas the poly(ester−diacetylene) exhibited partial reversibility above the polyester melting point. In all cases, a new absorption curve at higher energies represented the liquid crystalline phase above the mesogenic melt transition.

Introduction

The thermochromic behavior of the conjugated polydiacetylene backbone is well-documented in the literature;[1] however, this phenomenon has yet to be exploited in any major practical applications. Useful engineering applications based on the chromic behavior of the polydiacetylenes are not likely without the ability to in some way define and predict thermochromic behavior. Thus, the ability to design or tailor the polydiacetylene chain to produce color changes at specific temperatures is necessary to realize the potential of these materials in the development of thermal sensors, thermally controlled optical filters and modulators, and other smart systems.

The polydiacetylene backbone can undergo chromic transitions that correspond to a first- or second-order transition of its host environment; this knowledge makes it possible to design materials that exhibit a phase transition at a desired temperature range, and thus induce a thermochromic transition. Liquid crystalline monomers and polymers are clearly ideal host materials for the tailoring of the chromic response of the polydiacetylene backbone. Due to the multiphasic nature of these materials, significant changes in ordering are exhibited at two or more mesogenic transitions; in the simplest case these transitions are the melting point and isotropization temperatures present in most liquid crystals. Because the relationships between chemical structure and thermal behavior of liquid crystals and liquid crystalline polymers are well understood, these materials are natural choices for exploring the concept of controlling thermochromic behavior.

We have recently reported the design and synthesis of a series of small molecule functionalized diacetylene-containing liquid crystals[2] and a corresponding group of aromatic diacetylene-containing polyesters derived from these monomers;[3] these materials were specifically designed to undergo chromic transitions at their mesogenic transition temperatures. The liquid crystalline behavior of these diacetylene materials is discussed in separate publications.[2,3] In this paper, we report the thermochromic behavior and general optical characteristics of these new polydiacetylene systems.

A brief review of previous studies of chromism in polydiacetylene-based systems indicates that even the slightest conformational changes in the side chains of some polydiacetylenes can cause significant chromic transitions. This is true for poly-ETCD, which has a diacetylene substituent $R = (CH_2)_4OCONHC_2H_5$.[4] Some of the first observations of thermochromism involved changes in the reflectance spectra of insoluble single crystals of poly-ETCD. This transition was discovered to be due to the rearrangement of alkyl side chains, a change that disrupts the planarity of the polydiacetylene backbone.[5,6] On the other hand, large scale changes in the conformation of the conjugated chain will also trigger chromism. For example, chromic changes have been induced by the gradual loss of hydrogen bonding in soluble urethane-substituted polydiacetylenes such as the ACMU ([(alkoxycarbonyl)methyl]urethane) series of polydiacetylenes.[7−9] The thermo- and solvatochromic changes observed in the solutions of these polymers have been attributed to a rod-to-coil conformational transition.

More recent studies on the chromism of polydiacetylenes have centered on the optical properties of diacetylene macromonomers, such as segmented diacetylene−polyurethanes[10−12] and polyamides.[13] The host polymers in such systems provide an environment rich in varied morphological and conformational behavior to which the polydiacetylene backbone may respond. In the case of the segmented polyurethanes, the unique phenomenon of mechanochromism occurs when the elastomers are strained. These chromic transitions have been attributed to a disordering of polydiacetylene chains in the hard domains, and in certain cases, to a mechanically induced phase transition.[11] Solid state NMR

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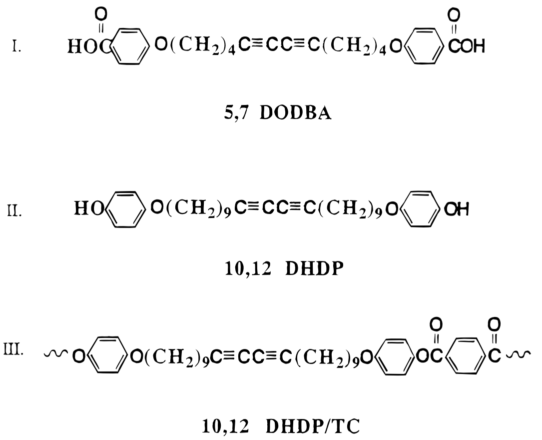


Figure 1. Chemical structures of the thermochromic mesogenic diacetylene monomers and poly(ester−diacetylene) macromonomer.

studies of the diacetylene-containing aliphatic polyamides revealed that the thermochromic transition was due to conformational changes of methylene spacers in the side chains from gauche to trans isomers.[13] Studies such as these demonstrated the use of the visible absorption spectra of polydiacetylene systems as a means of determining physical changes that occur in the host environment on a molecular level.

This paper marks the first attempt to actually design polydiacetylenes to undergo phase transitions and corresponding thermochromic responses at specific temperatures. In this investigation, first-order thermochromic transitions are induced by the mesogenic behavior of the liquid crystalline side chains of the polydiacetylene. Various mesogenic structures have been used to incur the transitions at different temperatures, and both small side chain mesogens and thermotropic polyester macromonomers serve as hosts to the polydiacetylene chain.

Experimental Section

Materials Synthesis. The design and synthesis of the diacetylene-containing liquid crystalline monomers and host macromonomers are described in separate papers.[2,3] These materials include 4,4′-(5,7-dodecadiynediyl-1,12-dioxy)dibenzoic acid (5,7-DODBA), 1,22-bis(4-hydroxyphenoxy)-10,12-docosadiyne (10,12-DHDP), and the polyester formed from polycondensation of 10,12-DHDP with terephthaloyl chloride (10,12-DHDP/TC); the respective chemical structures are shown in Figure 1.

Differential Scanning Calorimetry. The thermal characterization of all materials discussed in this paper is presented in separate publications, and DSC and other thermal analysis techniques are described in detail in these papers.[2,3] The thermograms shown in this paper were taken with a Perkin-Elmer DSC 4 at 20 °C/min.

UV/Visible and Infrared Spectroscopy. UV/visible absorption spectra were measured using an Oriel Instaspec System 250 multichannel analyzer with a quartz halogen light source and a continuous spectral wavelength range of 350−900 nm. The temperature of thin film samples cast onto potassium bromide plates was varied using a heated precision cell equipped with a Fenwal Model 550 temperature controller with a temperature range of 25 to 200 °C. Spectra were recorded at each temperature after a 2 min equilibration period.

Polymer and monomer samples for spectroscopy were prepared by casting from various solvents to obtain a uniform thin film on a potassium bromide cell. These films were then exposed to 250 nm UV light at 5 mW/cm^2 power density. The length of time required for UV exposure varied considerably, depending on the material, and sometimes on the solvent from which it was cast. For most cases, a series of films cast from different solvents were exposed for different time intervals. The samples that exhibited the lowest energy absorption peaks obtainable, as well as absorption strong enough to be easily detected, were those chosen for thermochromism studies. This was done to enable the observation of the full range of thermochromic behavior possible for each material. In the case of 10,12-DHDP/TC polyester, the films had to be annealed for a 48−72 h period to obtain optimal absorption spectra.

Heat/cool cycles were measured in the UV/visible spectrometer by heating a film to a desired temperature, taking its optical spectrum in the heated state, then allowing the film to cool in air down to 50 °C, and measuring the absorption spectra in the cooled state. The sample was then taken to successively higher temperatures by repeating this cycle.

Infrared spectra were obtained using a Fourier transform infrared spectrometer with the Fenwal temperature controller and a nitrogen purge. IR samples were made by solvent casting thin films of monomer onto potassium bromide plates. The heated and cooled infrared data were obtained from a simple heat ramp from 25 to 200 °C, which was stopped at various temperatures to record the IR spectra of the sample. The sample was then cooled to specific temperatures to record the spectra in the reverse cycle from 200 °C down to room temperature.

Results

The diacetylene monomers and macromonomers that were synthesized for this study and exhibit thermochromic behavior are shown in Figure 1. All details regarding synthesis and characterization of these materials are reported elsewhere.[2,3] The diacetylene monomers, 5,7-DODBA and 10,12-DHDP, are small mesogenic molecules that can react upon exposure to UV or electron beam irradiation to produce highly colored polydiacetylene chains with mesogenic side groups. On the other hand, 10,12-DHDP/TC is a polyester that cross-polymerizes upon irradiation to form a network of LC polyester chains interconnected with polydiacetylene backbones. Figure 2 is a schematic illustrating the structures that result from the topochemical polymerization of the LC monomers and the LC polyester.

Optical Properties and Thermochromism in 5,7-DODBA. The DODBA film, cast from either acetone or chloroform, exhibits a deep pink color in appearance following UV irradiation. The polymerized film was easily soluble in acetone, chloroform, and other organic solvents, indicating a low to moderate degree of conversion.

Figure 3 contains the visible absorption spectra of 5,7-DODBA taken at temperatures ranging from 30 to 200 °C in a single ramp mode. The shape of the absorption curve at 30 °C is typical of the polydiacetylene backbone. The strongest peak at 572 nm corresponds to the excitonic transition of the conjugated polydiacetylene chains and its position is dependent on the effective conjugation length of the polymer. The secondary peaks at 532 and 495 nm represent a broad distribution of conjugation lengths present in the DODBA polydiacetylene, overlaid on the vibronic sidebands of the polydiacetylene due to stretching frequencies associated with the double and triple carbon−carbon bonds. The primary and secondary bands are broadened by the presence of a distribution of conjugation lengths caused by slight differences in the local ordering of the chains; this results in a corresponding distribution of excitation energies, which is seen in the visible absorption spectrum.

For ease of reference, the differential scanning calorimetry (DSC) thermogram of the nonirradiated monomer is also shown in the inset of Figure 3. The peaks

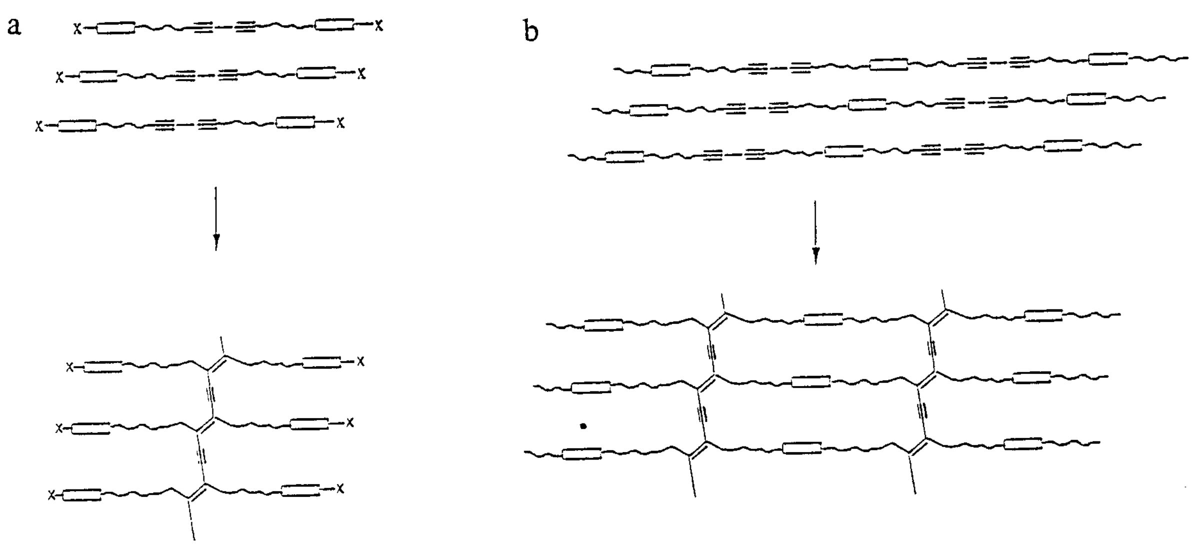


Figure 2. Schematic of (a) the diacetylene polymerization and (b) cross-polymerization processes. X indicates a functional group (−OH or −COOH). The open rectangle represents a rigid mesogenic unit. The squiggled line represents the flexible alkyl spacer.

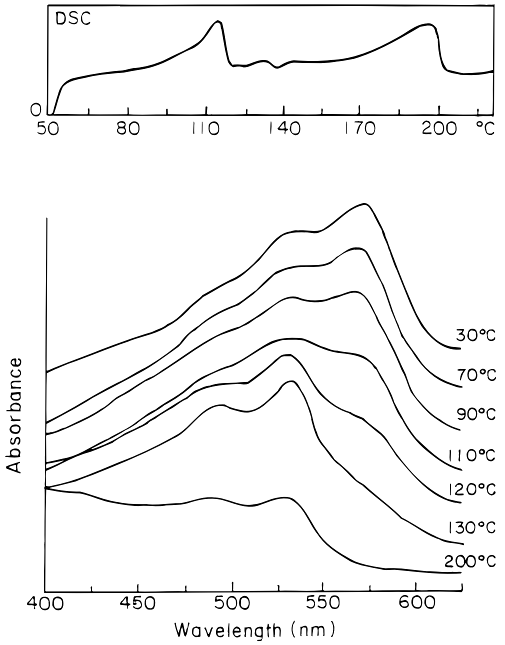


Figure 3. Visible absorption results of 5,7-DODBA, single ramp heating experiment. The inset shows the DSC thermogram of the monomer. Spectra have been offset for clarity.

in the inset indicate each of the endothermic mesogenic transitions of the monomer, including the first transition from the crystalline to the smectic phase at 113 °C and a smaller endotherm at 132 °C. As discussed in a previous paper[2] that addresses the thermal properties of the diacetylene monomers, this second transition is assumed to be due to the melting of a second crystalline form of 5,7-DODBA, which is present in a smaller quantity than the first crystalline phase. Finally, a broad clearing transition at 195 °C is observed, spanning from 180 to 205 °C.

When 5,7-DODBA is heated, its visible absorption spectra remain relatively unchanged up to temperatures as high as 90 °C. However, at 110 °C, the excitonic peak at 572 nm undergoes a sharp drop in intensity, and a second excitonic peak arises at 538 nm. Thus, it is at a temperature near the center of the melting endotherm that this new peak appears, representing a second population of polydiacetylene chains residing in the smectic mesophase. This liquid crystalline phase has a lower effective conjugation length than the crystalline phase that it replaces, and therefore, the primary excitation appears at lower wavelength. At 120 °C, just above the first endotherm, the sideband of this second phase becomes much more evident; however, some absorption is still present at 572 nm, indicating that not all of the crystalline material has disappeared. It is not until 130 °C, as the small, second melt endotherm is reached, that the remainder of the crystalline excitonic transition and sidebands are eliminated. At this point, a typical ordered polydiacetylene spectrum is observed, with a strong excitonic transition at 538 nm and a broad vibronic sideband at 490 nm; the shape is nearly the same as that of the crystalline phase, and in fact, the bands are somewhat sharper and narrower, suggesting that the distribution of conjugation lengths in the smectic phase is narrower than that in the polycrystalline state. This is consistent with the fact that the monomer exhibits more than one stable crystalline form, each of which melts to form a single smectic A mesophase, as evidenced by WAXD and optical microscopy results.[2] The layered structure of the smectic A phase involves a simple but regular spacing of the fully extended monomer, which may allow for more uniformity in the ordering of polydiacetylene chains situated in the monomer lattice. Hydrogen bonding of the dimerized acid groups is in part responsible for this uniformity, as will be discussed presently.

Finally, at 200 °C, the isotropic clearing point is reached, and the intensities of the liquid crystalline visible absorption peaks become weaker and less well-defined and a high energy tail develops at 400−450 nm. Because the temperature device used in this study does not heat beyond 200 °C, it was not possible to obtain visible absorption data at higher temperatures. It is expected that the peaks at 538 and 490 nm will continue to decrease as they are replaced by a broad, featureless peak at low wavelengths. The visible spectra and the infrared results indicate that some features of the liquid crystalline phase are not completely lost at 200 °C, although DSC indicates a clearing point at 200 °C. This discrepancy may be due to a number of factors. The heat/cycling experiments and stepwise heating done for the spectroscopy studies expose the diacetylene to different thermal histories, which may result in an increased degree of conversion of the 5,7-DODBA to polydiacetylene. In the previous paper,[2] it was found that polymerization increased and broadened the clearing point peak. There is also as much as ± 5% error in the accuracy of the hot stage at high temperatures.

In the isotropic phase, all ordering of the side chains is lost, and the polydiacetylene chains become free to assume nonplanar conformations in the randomized melt. The color changes that are observed during the heating experiment correspond to the changes in the visible absorption spectra. The dark pink color gives way to a lighter peach (orange-pink) color in the liquid crystalline phase above 110 °C. Films heated above the clearing point on a hot plate appear yellow, a color which corresponds to absorptions at 400−500 nm. The yellow color, indicative of low conjugation lengths, is often observed in the highly disordered states of many polydiacetylene systems.

It is apparent that the conjugated polydiacetylene chains undergo conformational changes triggered by the phase changes of the predominant nonpolymerized diacetylene monomer. There exist two basic means by which polydiacetylene chains are produced within a solid monomer crystalline lattice.[14−16] The diacetylenes may polymerize homogeneously, in which case the polymer chains formed are evenly dispersed in a solid solution with the monomer. At low conversions, the monomer crystalline lattice acts as the solvent, surrounding the individual polydiacetylene chains. The alternative kinetic model involves nucleation of polydiacetylene chains at sites where preformed polymer already exists, thus resulting in a heterogeneous polymerization in which phase-separated monomer and polymer domains are formed. In this second case, the absorption wavelength of the polydiacetylene chains residing in the monomeric domains is generally different from that exhibited in the polymeric domains. The visible absorption spectrum of 5,7-DODBA has been observed to exhibit a single excitonic transition regardless of the length of irradiation exposure time at both low to moderate conversions. This indicates that no phase separation occurs during solid state polymerization of 5,7-DODBA. Assuming homogeneous solid state polymerization of the monomer, the poly-DODBA should be dispersed evenly throughout the monomer crystalline lattice.[14] For this reason, at relatively low degrees of conversion, the side chains of the polydiacetylene conjugated backbones are directly influenced by surrounding monomer via hydrogen bonding of the carboxylic acid groups. The reordering of the three-dimensional crystalline lattice to form a layered smectic liquid phase involves changes in the conformations of the side chains and, consequently, adjustments in the planarity of the conjugated backbone. It is possible that these changes produce periodic disturbances in the planar arrangement of the π orbitals of the polymer.

To observe the reversibility of the thermochromic transition, a 5,7-DODBA irradiated film was exposed to a series of heat/cool cycles, in which each cycle was taken to progressively higher temperatures. The UV/visible spectrum was measured in-situ at the temperature of interest and then cooled to 50 °C, where it was measured once again. It was found that the visible absorption spectra were irreversibly changed when heated beyond 110 °C, the melting point of the monomer. This irreversibility is not surprising in this case, as recrystallization of 5,7-DODBA has been observed to be slow and incomplete within the time scale of DSC and optical microscopy experiments, with indications of some recrystallization to higher melting crystalline forms, as well.

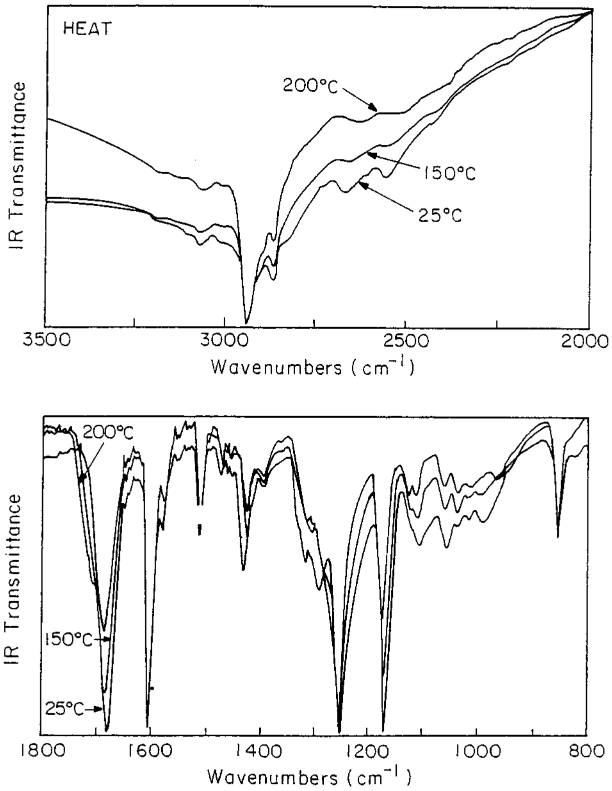


Figure 4. Results of the FTIR in-situ heating experiment for the 5,7-DODBA monomer.

The role of hydrogen bonding is central to the smectic nature of the 5,7-DODBA diacid. Like all *n*-(alkyloxy)-benzoic acids that show nematic and smectic liquid crystalline phases,[17,18] this symmetrical carboxylic diacid is thought to be dimerized in the mesophase. The mesogenic stability is increased by the fact that the dimerization can take place on either end of the molecule, encouraging stacks of alternating rigid aromatic hydrogen bonded units with aliphatic spacer segments containing the diacetylene group. It is no wonder that the smectic phase of 5,7-DODBA is well ordered or that it has such a high clearing point. To verify that hydrogen bonding does indeed persist in the liquid crystalline melt, and to observe potential structural differences in the mesophase, in-situ temperature variation infrared spectroscopy studies have been used to further characterize the mesogenic transition of 5,7-DODBA. Historically, analysis of the vibrational spectra of liquid crystals has been used as an additional means of characterization of many classic mesogens.[19] Differences between crystalline and liquid crystalline spectra include decreases in the intensity of C−H stretches and broadening of peaks due to increased rotational and translational freedom of the molecules and, certain, more subtle differences unique to a given family of compounds. There are considerable data available on the IR spectra of the (alkyloxy)benzoic acids,[19,20] which are ideal for comparison with DODBA.

The FTIR spectra of 5,7-DODBA recorded at 25, 150, and 200 °C are shown in Figure 4. The hydrogen-bonded carboxylic O−H stretch is the broad band from 2500 to 3500 cm^{-1}; the methylene stretches are superimposed on this band at 2980 and 2850 cm^{-1}. At room temperature, two clearly defined peaks that are also due to the hydrogen-bonded OH are visible at 2550 and 2650 cm^{-1}. In the mesophase, at 150 °C, the O$-$H stretch and the two smaller peaks remain present, although they have broadened considerably, suggesting an increasing number of variations of hydrogen-bonding strengths present in the melt. The peaks have also shifted to lower energies due to the increased O$\cdots$H distance with increased temperature. The intensity of these peaks has also decreased somewhat, suggesting a decrease in hydrogen bonding. The O$-$H stretch is still very much intact in the liquid crystalline state. Upon melting of the crystalline structure, hydrogen bonding is retained, as stable dimerized structures are formed. As the isotropization point is reached at 200 °C, the hydroxyl peaks broaden considerably but are still only slightly distinguishable as individual peaks. Again, at the limit of the temperature controller, the clearing point is reached, but not surpassed, and a truly isotropic melt cannot be observed using this technique. The behavior of the carboxylic acid stretch at 1682 cm^{-1} confirms the above conclusions. This peak undergoes only a small drop in intensity in the mesophase, verifying the retention of hydrogen bonding in the mesophase. At 200 °C, the intensity decreases further, and the band broadens as it begins to split into two absorption bands: one at the original 1682 cm^{-1} position and the other at a non-hydrogen-bonded acid position at approximately 1700 cm^{-1}. This is an indication that free acid is forming at the isotropization temperature, as the hydrogen bonding of the smectic liquid breaks up. As observed with the UV/visible data, the data at 200 °C appear to be at or near the clearing transition; however, characteristic features of the liquid crystal phase have not completely disappeared. This observation is thought to be due to the prolonged heating and resulting polymerization of the monomer and a 5% error in the heating stage.

Other changes in the IR spectra are quite characteristic of liquid crystalline phase transitions. The decrease in intensity of the CH_2 bending vibrations at 1450 cm^{-1} and the merging of CH_2 bands at 1250$-$1300 cm^{-1} (two shouldered peaks along the edge of the C$-$O stretch at 1250 cm^{-1}) are especially characteristic of mesophases of *n*-alkoxybenzoic acids.[17] The existence of many rotational isomers in the methylene spacer groups is the cause of this broadening. This is further evidence that the chromic transition occurring in 5,7-DODBA is activated by the increased mobility of side chains packed in the smectic phase. Other areas of change in the IR spectra also correspond to rearrangements or increased mobility of C$-$C and C$-$H bonds, including the single C$-$C stretch region at 950$-$1050 cm^{-1} and the aromatic C$-$H deformations at 1165 and 1100 cm^{-1}.

The infrared spectroscopic data are quite consistent with the visible absorption spectra of lightly cross-polymerized 5,7-DODBA monomer. It appears that the solid solution of polymerized DODBA in monomer produced upon solid state polymerization undergoes changes that can be accurately followed by observing the thermochromic behavior of the conjugated polydiacetylene backbone. The fact that the visible absorption peaks of the liquid crystalline phase show relatively high degrees of order are consistent with the presence of directional hydrogen bonding found in the smectic mesophase. The high-temperature stability of the hydrogen bonding is also corroborated by the retention of an ordered visible absorption peak at 200 °C. Finally, the fact that the infrared spectral changes upon cooling were subtler than those observed on heating suggests quenching of the mesophase, along with the possibility of the formation of higher melting crystalline phases that retain some of the hydrogen bonding and ordering characteristics of the smectic phase. This is reflected in the irreversibility of the poly-DODBA thermochromic transition.

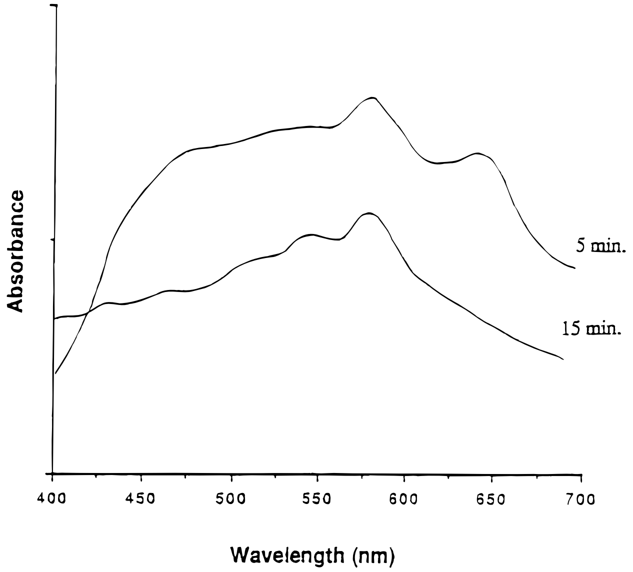


Figure 5. Visible absorption spectra of the 10,12-DHDP monomer samples at two irradiation times.

Optical Properties and Thermochromism of 10,12-DHDP Derivatives. 10,12-DHDP. The 10,12-DHDP monomer was highly reactive to UV light, and at very short exposure times of up to 5 min, blue-purple films were formed; however, further cross-polymerization resulted in a gradual shift to a red color. The visible absorption spectra of 10,12-DHDP taken at two different irradiation times are shown in Figure 5. At very short irradiation times, two excitonic transitions are visible at 640 and 575 nm; the sidebands of the smaller 650 nm peak are shouldered into the transition at higher energy. Comparison with the sample irradiated for 15 min shows that the red-shifted peak at 640 nm is no longer present after longer exposure times. The disappearance of the lower energy peak, as well as the color change with further irradiation, has been observed in other polydiacetylenes, including PTS-12 (dodeca-5,7-diyn-1,12-diylbis(*p*-toluenesulphonate) and 12-8 PDA (substituents $R = C_{12}H_{25}$, $R' = (CH_2)_8COOH$)).[21,22] In both of these examples, two absorption peaks appear at low conversions, and the peak at higher energy gradually increases at the expense of the lower energy transition. For PTS-12, Siegel et al.[21] label these peaks P1 and P0, respectively. The authors explain that the peaks are due to the differences between the monomer lattice in a solid solution of polydiacetylene at low conversions and the polymer lattice that exists at higher conversions (greater than 2$-$5% conversion). Unlike polydiacetylenes formed in single-phase reactions, monomers such as PTS-12 and 12-8 PDA undergo a polymerization-induced phase transition at a given level of conversion, at which point regions of polydiacetylene chains rearrange, shifting the monomeric lattice spacings so as to better accommodate the packing requirements of the polymer, and thus creating a new polymeric crystalline lattice with a different characteristic conjugation length. The presence of both peaks in the visible absorption spectra illustrate the fact that the polymerization is taking place in two different re-

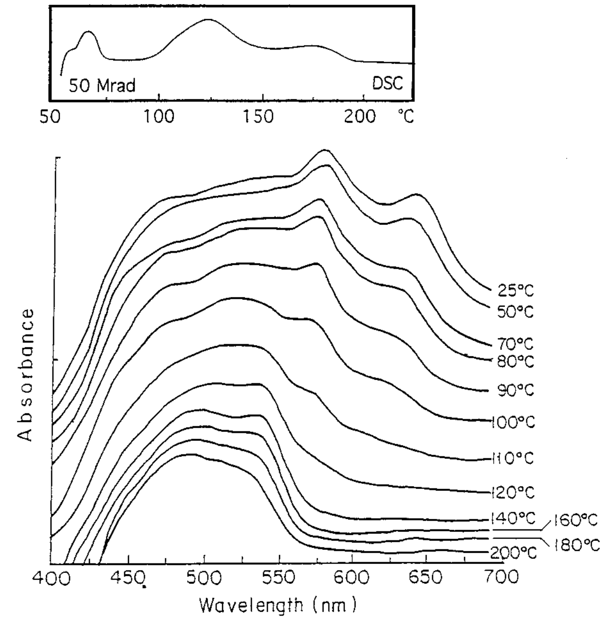


Figure 6. Visible absorption spectra of the 10,12-DHDP monomer, single ramp heating experiment. The inset shows the DSC thermogram of the polymerized monomer. Spectra have been offset for clarity.

gimes: the monomer with polydiacetylene dispersed in a solid solution and domains consisting predominantly of growing polydiacetylene chains in a polymer lattice. Therefore, when thermochromic changes in 10,12-DHDP are examined, it must be kept in mind that the first transition at 640 nm is representative of polydiacetylenes in a monomeric matrix but the second, much stronger peak at 575 nm corresponds to poly-10,12-DHDP in its own polymeric lattice. For this reason, the thermochromic shifts exhibited by the 575 nm peak are expected to correspond to the phase transitions of the polydiacetylene chains themselves, and not necessarily to those of the monomer. The absorption bands shown in Figure 5 are relatively broad and ill-defined in the 5 min sample due to the presence of two very different polydiacetylene environments. The 15 min sample has a more defined absorption curve, although the absorption is still broad, reflecting the distribution of conjugation lengths present in the polymeric lattice.

Figure 6 shows the visible absorption spectra of 10,-12-DHDP films, irradiated for 5 min with UV light, taken during a simple heat ramp experiment. Due to light scattering of crystals in the monomer film, a large degree of scattered intensity is visible at lower wavelengths in those spectra taken below the melting point of the polydiacetylene. For general reference, the DSC thermogram of the partially polymerized monomer (after 50 Mrad electron beam irradiation) is shown in the inset. The DSC data shown are an example of a typical 50 Mrad sample; the residual unpolymerized monomer melts at 60−70 °C, and the polymerized monomer exhibits melt transitions ranging from 100 to 120 °C, and clearing transitions centered at 160−180 °C. It should also be noted that the pure unpolymerized DHDP monomer exhibits endothermic transitions at 70 and 90 °C, respectively.[2]

From 70 to 90 °C, the peak at 640 nm decreases in intensity, disappearing completely at 90 °C. Because the polydiacetylene chains represented by this peak are surrounded by monomer units, it is not surprising that they undergo a chromic transition at low temperatures corresponding to the transitions found in the unpolymerized 10,12-DHDP monomer. The resulting order−disorder chromic transition probably occurs as flexible methylene spacers of the polydiacetylene chains in the monomeric lattice gain rotational freedom. These polydiacetylene chains, now free from the original monomer lattice, can gradually take on the preferred disordered conformations of polymer in solution at 90−100 °C; this is seen as an increase in absorption at higher energies (a very broad peak centered at 520 nm).

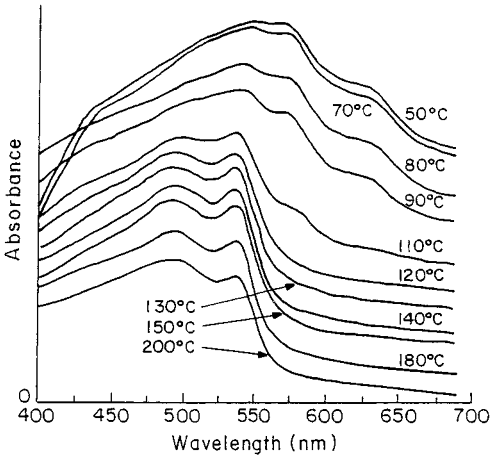


Figure 7. Cooled state visible absorption spectra of 10,12-DHDP from the heat/cool cycle experiment. Spectra have been offset for clarity.

On the other hand, the polydiacetylene chains that exist in a polymer lattice are still present at 90 °C, as illustrated by the presence of the 575 nm peak. The 575 nm peak undergoes a sharp decrease in absorption between 100 and 110 °C; between 120 and 140 °C, this peak completely disappears and a new band appears at about 540 nm. This very broad transition is reflective of the breadth of the DSC endotherm from approximately 100 to 135 °C that marks the melting range of the polymerized 10,12-DHDP. What remains is a fully developed, broad excitonic transition at 545 nm, with an equally broad high-energy shoulder. The spectrum is representative of the liquid crystalline phase of polymerized 10,12-DHDP, which has been characterized as a smectic phase.[2] The appearance of a distinct, albeit broad, excitonic transition suggests that a moderate degree of ordering exists in the mesophase.

As the clearing transition from 160 to 180 °C is approached, the features of the peaks go away, and a wide band indicating a very large distribution of conjugation lengths in relatively disordered polydiacetylene chains is left in the isotropic melt. Abrupt color changes accompany each of the transitions described above. At the disappearance of the 640 nm peak, the film turns from blue-purple to violet-red, as described before. Upon entering the mesophase, the color becomes bright orange, and on entering the isotropic state, it turns yellow-orange or peach.

A heat/cool experiment was also completed for the 10, 12 DHDP irradiated monomer. Figure 7 contains the results from the cooled state portion of the 10,12-DHDP heat/cool experiment. The cooled state spectra indicate that the crystalline spectra are recovered up to 90 °C, just below the melting range of poly-DHDP. The 640 nm peak appears to be almost fully recoverable below this temperature, indicating that the disappearance of this peak is a reversible thermochromic transition. However, once the mesophase is approached at 110 °C, the polydiacetylene chains appear to become quenched

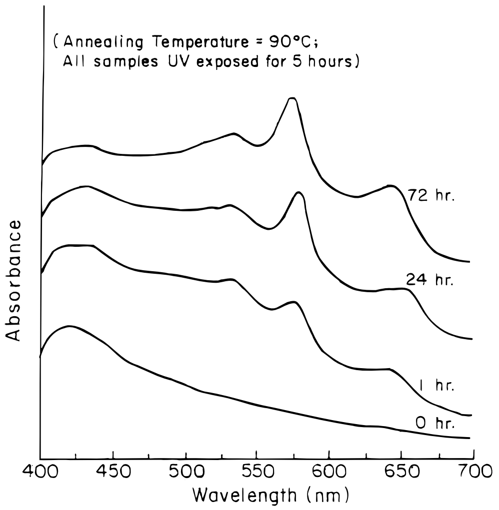


Figure 8. Visible absorption versus annealing times for the 10,12-DHDP/TC polyester.

into the conformational state of the mesophase. This quenched in structure is much more well-defined at room temperature and indicates a well-ordered polydiacetylene environment. This suggests that the isotropic to liquid crystalline transition is reversible in the UV/visible spectra, but not the liquid crystalline to solid state transition.

10,12-DHDP/TC. The optical properties of cross-polymerized 10,12-DHDP/TC are highly dependent on the morphology of the polyester prior to irradiation in the solid state. This fact is made clear upon observation of annealing effects on the visible absorption spectrum of 10,12-DHDP/TC. Thin films of the polymer were cast from toluene onto glass slides and annealed in an oven at 90 °C for varied amounts of time. Each of these films was then exposed to ultraviolet radiation for exactly 5 h. The visible absorption spectra of these films is shown in Figure 8. The overall intensity of the bands increases with annealing time. The degree of crystallinity is quite low in toluene-cast films prior to annealing, as evidenced by the transparency of the film. The reactivity of the diacetylene groups is lower in an amorphous morphology, which lacks the ordering needed to facilitate a solid state topochemical reaction. Those polydiacetylene chains that are produced have a low degree of polymerization and tend to exist in a broad distribution of highly nonplanar conformations, resulting in the observed "yellow" spectrum shown. Annealing prior to irradiation facilitates the development of an ordered semicrystalline structure in these films, and polydiacetylene chains are readily formed in the crystalline regions of the film, as seen by bands absorbing at 640 and 570 nm, respectively. Film samples appear blue to purple in appearance after long annealing times followed by irradiation, and the films become translucent as the degree of crystallinity is increased. The amorphous peak at 420 nm is decreased and background scattering from the semicrystalline film is seen at low wavelengths.

The polymerization processes discussed for 10,12-DHDP are applicable to the 10,12 polyester. For toluene-cast, annealed films with absorption spectra such as the one shown in Figure 8, the peak at 650 nm, indicative of homogeneously dispersed polydiacetylene chains in the original polyester lattice, does indeed disappear at longer irradiation times (e.g., 24 h). For the case of lightly cross-polymerized monomer, the peak at 570 nm represents domains of a cross-polymerized polyester matrix, in which unreacted polyester may be dispersed, with a peak at higher energies signifying the corresponding vibronic sideband.

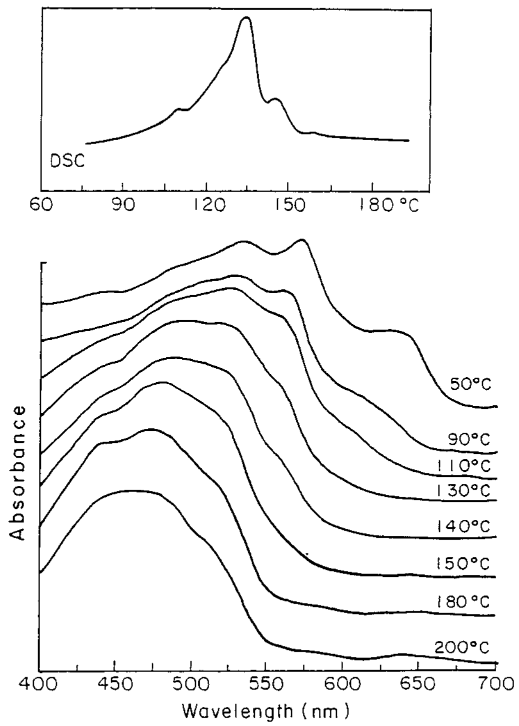


Figure 9. Heated state visible absorption spectra of the 10,12-DHDP/TC polyester from the heat/cool cycle experiment. The inset shows the DSC thermogram of the polyester. Spectra have been offset for clarity.

Figure 9 contains the heated states of a heat/cool cycling experiment on an irradiated 10,12-DHDP/TC polyester film. Included in the inset is the DSC of the polyester, which indicates a shoulder at 110 °C and a broad melting endotherm centered at 129 °C, followed by a clearing point from 140 to 155 °C. The first spectrum at 50 °C illustrates the initial state of the polyester and is similar to the spectrum of the toluene-cast, annealed film described above. Upon heating to 90 °C, the 640 nm peak quickly drops off. It is interesting that the same effect was seen in the 10,12-DHDP monomer, in which case it corresponded to the melt transition of the monomeric lattice. It is likely that, although the ends of the original DHDP monomer are now tied down as part of a polymer repeat unit, the methylene spacer groups near the diacetylene monomer are far enough away from the rigid mesogenic units that their local motions remain uninhibited. The relaxations and increased rotational freedoms gained at 70−90 °C by the spacer units in the DHDP/TC polyester are probably quite similar to relaxations in the methylene groups of the monomer induced by melting. This sort of "localized melting" is made possible by the long flexible spacers of the 10,12-DHDP/TC polyester. Analogous to 10,12-DHDP, the thermochromism observed at these lower temperatures involves the rearrangement of the original polymer lattice (absorption at 640 nm) to the more stable expanded lattice form predominant in the cross-polymerized phase at higher conversion (i.e., the 570 nm phase).

At the low levels of conversion used for these experiments, the phase transitions of the original 10,12-DHDP/TC polyester should not be inhibited by cross-polymerization; therefore, thermochromic transitions

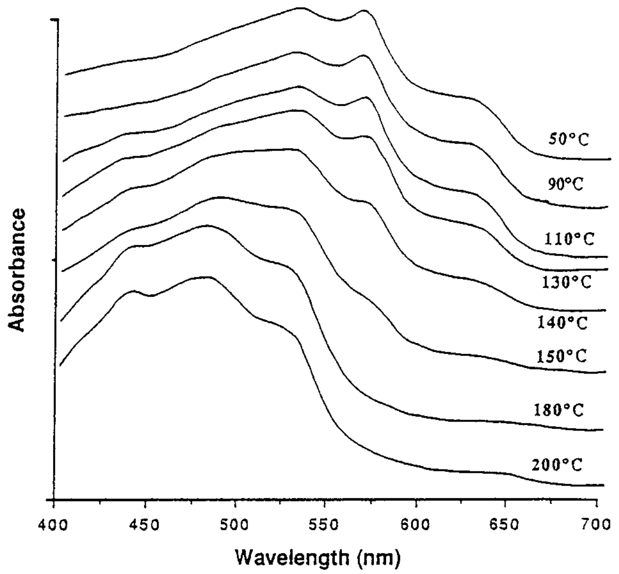
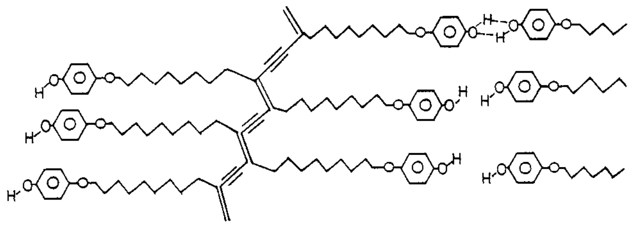


Figure 10. Cooled state visible absorption spectra of the 10,12-DHDP/TC polyester from the heat/cool cycle experiment. Spectra have been offset for clarity.

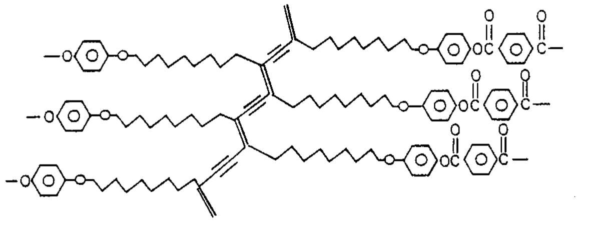
involving the 570 nm transition are expected to follow the phase transitions of the host polyester. In any case, at 110 °C, the peak at 570 nm remains, but a new absorption at 538 nm has just begun to rise out of the vibronic sidebands of the first transition. This transition corresponds to the shoulder at 110 °C in the DSC, and it is at this point that melting of the polyester first begins. The peak at 570 nm gradually drops off from 110 to 130 °C, which is approximately the temperature range of the broad melting endotherm for the polyester. In the meantime, the absorption that first appeared at 110 °C is visible as a disordered, but not featureless, broad absorption at 130−140 °C. These temperatures correspond to the presence of the liquid crystalline phase of 10,12-DHDP/TC, which is smectic and, from optical microscopy results, may exhibit both a smectic A and smectic C phase.[3] The broad absorption bands observed at 130−140 °C correspond to the relatively disordered polydiacetylene chains in the mesophase. The ill-defined appearance of the spectra is due to the more disordered nature of the polymeric mesophases. The absorption spectrum becomes completely featureless between 180 and 200 °C, well above the clearing point for the polyester. The higher apparent clearing point from the absorption study is probably due to the effects of small levels of heat-induced cross-polymerization at the clearing point during the cycling experiment. DSC data[3] illustrate that increasing cross-polymerization suppresses the clearing point of these materials, often pushing the transition to slightly higher temperatures.

Before heating, the polyester film was a light to medium purple color. Heating to 90 °C resulted in a bright red color, corresponding to the disappearance of the peak at 640 nm, and the color then changed once more to a peach color in the mesogenic temperature range. At higher temperatures, well above the isotropic clearing point, the color was light yellow.

The cooled states of the visible absorption spectra, corresponding to the heated states discussed above, are shown in Figure 10. It appears that the thermochromism of 10,12-DHDP/TC is fairly reversible up to 130 °C, which is 20 °C beyond the melting point. Unlike the monomeric diacetylenes, the crystalline peak is recovered up to temperatures as high as 150 °C, where only a small shoulder in the cooled state absorption spectra indicates where the 570 nm crystalline phase peak should exist. When the isotropic melt was cooled from 180 and 200 °C, the liquid crystalline phase absorption bands are completely quenched in, and it is possible to see details in the cooled sample that were not visible at the actual mesophase temperatures due to the broadening effects of molecular thermal vibrations. The presence of multiple bands suggests the possible presence of more than one type of ordering. The new peaks were not present in the original, unheated state, and they coexist with the original 570 nm peak at 130 °C in the heated state, and in the cooled state quenched from 150 °C. These facts indicate that the thermochromic behavior of 10,12-DHDP/TC corresponds to a first-order phase transition at approximately 110−120 °C, which is the melting point of the polyester.



10, 12 DHDP Polydiacetylene



10, 12 DHDP/TC Cross-polymerized polyester

Figure 11. Schematic of the polydiacetylene backbone in the 10,12-DHDP monomer and the 10,12-DHDP/TC polyester.

Discussion

It is apparent that the thermochromic behavior of 5,7-DODBA corresponds directly to the thermal transitions of 5,7-DODBA. The shapes of the original absorption band and the spectrum in the liquid crystalline state suggest that a well-ordered, stable liquid crystalline phase is formed. These findings confirm earlier observations made of the 5,7 diacid. Infrared spectroscopy proved to be a good complementary technique to visible spectroscopy, and it was established that hydrogen bonding is maintained upon melting to the liquid crystalline state and remains intact up to the clearing point. This observation supports the idea that the diacid dimerizes in the melt, forming a layered smectic A phase.

The 10,12-DHDP monomer, and its corresponding polyester, 10,12-DHDP/TC, exhibit nearly identical optical behavior when polymerized or cross-polymerized, corresponding to order−disorder and liquid crystalline transitions. To fully explain the similarities between the diacetylene monomer and the polyester, a schematic of the two materials after polymerization of the diacetylene groups is shown in Figure 11. Wide angle X-ray diffraction results published previously reveal that upon solid state polymerization, the long range ordering of 10,12-DHDP is greatly improved.[2] The result is an improved registry of the DHDP repeat units with neighboring molecules; the hydrogen bonding between units, though not as strong as that in 5,7-DODBA, no doubt plays some role in attaining this highly regular ordering. With the added degree of ordering, and the associative effects of hydrogen bonding, the 10,12-DHDP in its polymerized form appears very much like the cross-polymerized polyester, with weaker associative interactions of the hydrogen bonds in place of the covalent polyester linkage. The rigid mesogenic portion of the semiflexible polyester consists of three covalently bonded aromatic rings. The corresponding rigid portion of the small monomeric side chain is made of a phenoxy group, hydrogen bonded to a neighboring phenoxy as part of a crystalline lattice. The crystalline structures of the DHDP monomer and polyester have similar spacings,[2,3] each exhibiting two major diffraction peaks at approximately 4.5 and 3.8 Å.

The spectral changes that each material undergoes are therefore similar because the host environments of the polydiacetylene chains are nearly identical. In both cases, their thermochromic transitions are driven by conformational changes in the nine methylene spacer sequence positioned on either side of the polydiacetylene chain. The low-temperature thermochromic behavior involving the 640 nm peak appears to be the result of an order−disorder transition characteristic of conformational changes in the methylene sequences, due to increased rotational freedom. NMR observations of thermochromic transitions involving the same nine methylene sequence in a poly(amide-diacetylene) indicated that the thermochromic transition was an order−disorder transition induced by gauche to trans conformational changes in the alkyl spacer.[13] Conversely, the decreased absorption of the primary peak originally at 570−580 nm is characteristic of a first-order transition. In both cases, a melting transition brings about the appearance of a second absorption band with its own excitonic transition; this is evidence of a first-order transition, rather than an order−disorder process.

In general, the shape of the mesogenic phase absorption band appears to be highly dependent on the degree of order present in the mesophase. 10,12-DHDP yields a much cleaner optical transition than the broad, ill-defined transitions of the polyester mesophase. In turn, the 5,7-DODBA absorption spectra taken in the liquid crystalline state are the most well-defined. The different shapes of the absorption curves obtained upon heating reflect differences in the degree of order between the well-aligned smectic phase of a diacid monomer, a side chain polydiacetylene mesophase, and the less ordered smectic state of the main chain polyester. These differences are confirmed in WAXD studies discussed in previous papers.[2,3] The visible absorption spectra of the polydiacetylene chain in all three cases discussed here are highly sensitive to the original solid state morphology and the final liquid crystalline state.

Conclusions

For the first time, thermochromic transitions were successfully induced in new aromatic, mesogenic diacetylene-containing monomers and polymers at each of their mesogenic transitions, illustrating that thermochromic transitions actually can be designed into liquid crystalline diacetylenes. This study illustrates two ways in which the diacetylene backbone can be induced to undergo chromic changes at specific points. One can begin with a liquid crystalline monomer that, when cross-polymerized at low levels, produces polydiacetylene chains immersed in a monomeric crystalline lattice. An alternative approach is to choose a monomer that forms a mesogenic liquid crystalline polydiacetylene with transitions in the temperature range of interest and allow the thermochromic transitions to be driven by the liquid crystalline nature of the polydiacetylene itself. The use of a main chain liquid crystalline polymer with the diacetylene incorporated in the backbone is actually a combination of these two approaches. The polyester is a host to the polydiacetylene chain, as in the first case; however, it is also covalently bonded to the backbone as a macromonomer side chain. The polyester is much more reversible than the monomers, which were irreversible immediately upon reaching the melting point. This may be due to the constraints imposed on the system by the cross-polymerized polydiacetylene network, as well as the reversible nature of the polyester's thermal transitions.

In summary, the design of optical transitions in liquid crystalline diacetylenes is a viable means of manipulating the unique chromic behavior of these materials for new engineering applications. Future directions for this study might include an examination of polyesters with a shorter methylene spacer group to introduce a broader range of melting points. Other chemical structural changes might increase or depress the melting points of these materials. It is possible, for example, to create a material that undergoes mesogenic phase transitions near room temperature. Finally, further investigations of diacetylenic monomers would be worthwhile, considering the optical results from 5,7-DODBA. A liquid crystalline material that undergoes sharper transitions, or more than one transition, would prove especially interesting. An important factor to consider is the reversibility of the thermochromic transitions, and therefore, of the mesogenic transitions, themselves. The thermochromic transitions of cross-polymerized macromonomers are more reversible than those of polymerized monomer.

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