# The Effects of Thermal History and Degree of Cross-Polymerization on the Thermochromic Behavior of Diacetylene-Containing Polyesters

By

Kelly Stengel

Submitted to the Department of Materials Science and Engineering in Partial
Fulfillment of the Requirements for the Degree of

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## ABSTRACT

10,12-docosadiyne-1,22 malonate polyester and 10,12-docosadiyne-1,22 glutarate polyester were synthesized for study of thermochromic behavior, with the goal of discovering a means of controlling onset and reversibility of thermochromic transitions. The study samples were chemically similar, differing only by the number of methylene group spacers between the diol and diacid components, with both exhibiting thermochromic transitions at or near room temperature. The thermochromic properties of the glutarate polyester were particularly sensitive to changes in thermal history, while those of the malonate polyester responded to changes in degree of cross-polymerization.

Annealing spin coated glutarate samples at a temperature within the melting temperature of the polyester consolidated thermal behavior, allowing onset of the irreversible thermochromic behavior to be pushed up to the annealing temperature with completion of transition occurring over a narrow temperature range. Glutarate samples quenched from melt in liquid nitrogen showed a thermochromic transition at a lower temperature than spin coated samples, which could change color reversibly in response to body contact. The reversibility and acuteness of the transition lessened over time, due to prolonged exposure to room temperature and/or repeated exposure to body surface temperature. Varying the degree of cross-polymerization in the malonates was achieved by controlling time of exposure to UV radiation. This had the effect of pushing up the onset temperature of the irreversible thermochromic behavior, while broadening the range of temperature for completion of the transition.

Thesis Supervisor: Dr. Michael F. Rubner

Title: Professor of Materials Science

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# 1. Background

## 1.1. Polydiacetylene macromonomers

Diacetylene monomers have long been a focus of study as they can be polymerized in the solid state by a variety of methods without generating a by-product. A single diacetylene unit is composed of two acetylenic groups connected by a single bond. These monomer units may be polymerized to form polydiacetylene chains. Additionally, diacetylenes may be cross-polymerized while incorporated into polymer chains to form a three-dimensional network.

Diacetylene cross-polymerization is a diffusionless and lattice-controlled process in which reactivity requires specific rotations of the monomer units and their subsequent 1,4 additions.[1] Reactivity depends primarily on the stacking sequence of the diacetylene units and the mobility of the side groups. Since the reactants do not migrate, specific packing geometries are required having optimal distance between monomers of ~5 Angstroms and optimal angle of ~45° as shown in Figure 1. The diacetylene and the side group must be separated by at least one methylene group which acts as a mobile spacer.[2] Reactions like this one which have distinct geometric constraints are referred to as topochemical reactions.

Since polydiacetylene cross-polymerization is topochemical in nature and yields no products, it incurs only minor morphological changes. Consequently, diacetylenes may be processed by a wide variety of methods and then cross-polymerized in their final form without significantly changing the resulting shape and morphology. The diacetylene functionality is highly reactive in the solid state and may be polymerized by a number of methods. Electron beam irradiation offers good bulk polymerization, while UV irradiation is sufficient for thin films and is more convenient. Since heat and pressure can also produce polymerization under the proper conditions, it is important to limit exposure to these energy sources.

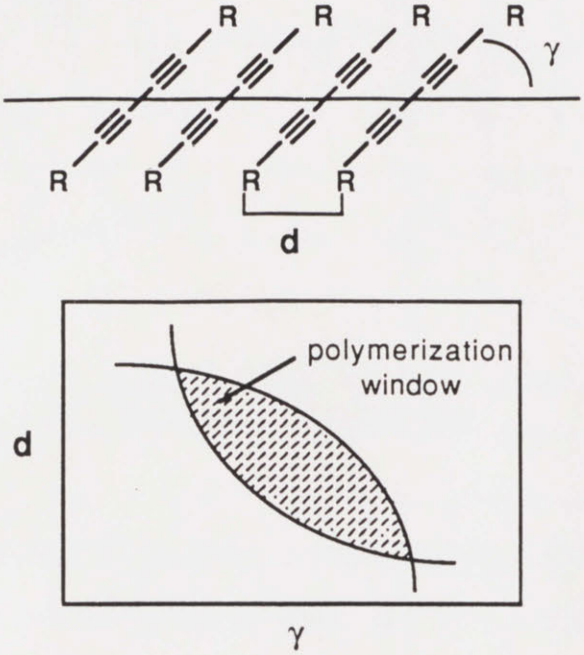


**Figure 1:** Geometric constraints for diacetylene cross-polymerization.

Polydiacetylene macromonomers form highly conjugated cross-polymerized networks, consisting of chains both normal and parallel to the original chain direction[3], with alternating single, double and triple bonds as shown in Figure 2.[4] Since polydiacetylenes are fully conjugated, π electrons are free to delocalize along the length of the ordered chain produced. These delocalized electrons appear in electron-hole pairs, called excitons, which have a lower excitation energy than the band gap associated with polydiacetylene.[5] These excitons exhibit a distinct absorption in the visible region. Since the unreacted monomer is colorless, the polymerization reaction is always accompanied by the appearance of color.

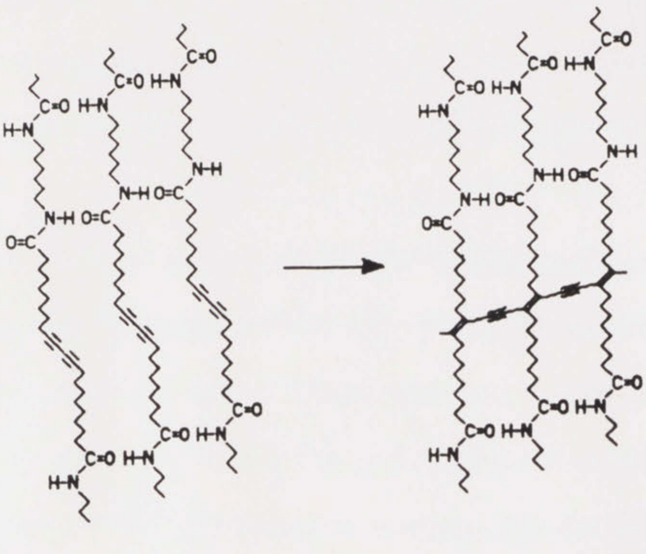


Figure 2: Schematic representation of the cross-polymerization of poly(hexamethylene-10,12-docosadiyne-1,22-diamide).

The shape and position of the absorption spectrum of the polydiacetylene is strongly dependent on the conjugation length, defined as the length over which the electrons may delocalize without interference. For polydiacetylenes, this is related to the length over which planarity is maintained in the polymer backbone.[6] Longer conjugation lengths have lower energies associated with them and will absorb longer wavelengths. Several factors can produce changes in the conjugation length of a polydiacetylene, such as thermal disruption, crystallographic transitions, order-disorder transitions, liquid crystalline transitions, mechanical stress and degree of cross-polymerization, all of which affect chromic behavior.[7] Changes in the conjugation length due to thermal disruption are the cause of thermochromism.

The order-disorder transition produced by heating to the melting temperature has associated with it a change in the conjugation length of the material. The melting temperature range will determine the temperature range of the thermochromic transition, so the temperature range of thermochromism can be specified by the selection of a macromonomer with an appropriate melting temperature. Consequently, incorporating diacetylene groups into the backbone of polymer chains affords some control over the temperature range of the thermochromic transitions.

Several polydiacetylene-containing polyesters have recently been found to exhibit thermochromism (change in color with a change in temperature) at the melting temperature of the polyesters.[7] These melting temperatures, in this case thermochromic in nature, can be varied by several means to create chromic transitions at the desired temperatures. Of particular interest are those polyesters that can be tailored by chemical constituents and processing conditions to exhibit thermal transitions at or near room temperature. Many of these materials may be activated by body contact to change color. Since body surface temperature varies with activity and individual, different people cause different color responses, yielding novelty "mood" polymers.

The research has a larger context, however, that must be considered to understand the usefulness of polydiacetylene-containing polyesters. Research has been under way for several years into the properties of diacetylenes incorporated into the hard segments of segmented polyurethanes.[8] These diacetylene-polyurethanes are synthesized by using diacetylene-containing diols as the chain extender. They exhibit thermochromism at the melting temperatures of the hard segments in which they reside, between 90°C and 120°C.

The next phase of the research will involve using diacetylene-containing polyesters as the soft segment component in these segmented polyurethanes. The resulting polymer will have diacetylenes in two separate environments— the hard and the soft segments— and will subsequently have two separate thermochromic transitions associated with the two environments. Upon stretching, these materials exhibit similar mechanochromic behavior as well, so they have potential applications in toys, novelty items and the packaging industry as materials which exhibit multiple chromic responses to heat and stress. Diacetylenes can also be used as a molecular probe for research purposes; shifts in the absorbance of the diacetylene-containing polymer can be used to detect and characterize changes in stress, temperature, pressure and crystal structure, giving insight into morphology and mechanical behavior.

The focus of this thesis is to understand the thermochromic properties of the individual diacetylene-containing polyesters as a step toward their application as the soft segment component in segmented polyurethanes and as body-heat activated thermochromic materials. Experimentation will be performed on two materials with slightly different chemistry which exhibit thermochromism at or near room temperature. Degree of polymerization and thermal history will be varied to observe the effects on the temperature range and reversibility of thermochromic transitions.

## 1.2. Polyesters

Several polydiacetylene-containing polyesters have already been synthesized with melting temperatures at or near room temperature (30°C-70°C).[7] These materials are ideal for study of the potential of diacetylene-containing polymers as body-heat activated thermochromic materials and as soft segments in polyurethanes. Small changes in the chemistry of polyester can have a tremendous effect on the thermal properties of the material. It has been shown that increasing the number of methylene spacers in the acid component of a polyester raises the melting temperature.[9] Polyesters having an odd number of methylene spacers will have lower packing efficiencies of the crystalline lattice relative to those having an even number of spacers, so these materials will tend to have lower melting temperatures. In combination with increasing order, this gives rise to an overall odd-even melting temperature disparity, which is most evident in polyesters with a small number of methylene spacers, as shown in Figure 3[10].

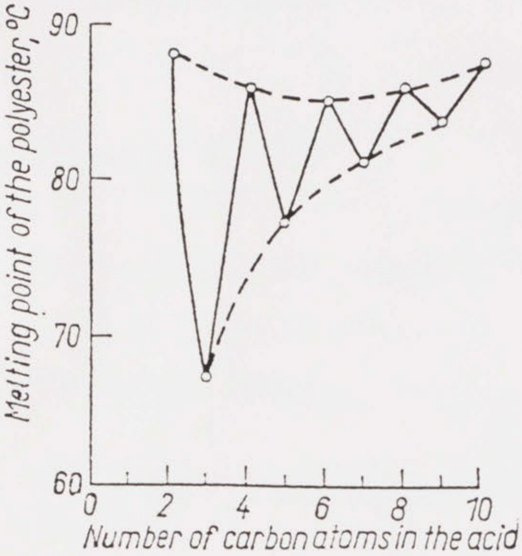
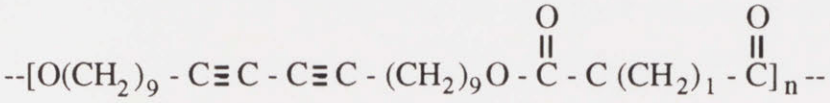


**Figure 3:** Odd-even melting temperature disparity in diacetylene containing polyesters as a function of the number of methylene group spacers (Korshak, 238).

Since the temperature of the thermochromic transition is highly dependent on macromonomer melting temperature, macromonomer chemistry can be used to specify the desired temperature range of thermochromic transitions. Of course, the sensitivity of the diacetylene cross-polymerization process to macromonomer-sensitive factors like packing geometries means that not all chemistries will yield thermochromic behavior.

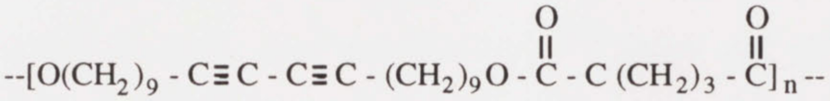
The series examined in this work consisted of 10,12-docosadiyne-1,22 malonate and 10,12-docosadiyne-1,22 glutarate (Figure 4). With one and three methylene spacers respectively, these polyesters have already shown melting temperatures at 34°C and 50°C.[7] Since packing geometry is so rigidly prescribed, changes in processing which affect the ability of the material to order itself can cause large variations in thermal behavior. The location and shape of the absorption spectra can give insight into the morphology of the polyester, since the diacetylenes will mimic the structure of their host backbone.

a) 10,1-docosadiyne-1,22 malonate



$$--[O(CH_2)_9 - C\equiv C - C\equiv C - (CH_2)_9O - \overset{\overset{O}{\|}}{C} - C\,(CH_2)_1 - \overset{\overset{O}{\|}}{C}]_n --$$

b) 10,12-docosadiyne-1,22 glutarate



$$--[O(CH_2)_9 - C\equiv C - C\equiv C - (CH_2)_9O - \overset{\overset{O}{\|}}{C} - C\,(CH_2)_3 - \overset{\overset{O}{\|}}{C}]_n --$$

**Figure 4:** The series to be examined for thermochromic properties, having a) one and b) three methylene group spacers respectively.

Several conditions will be placed on synthesis of the diacetylene-containing polyesters which reflect constraints imposed by the requirements of the polyesters for use as soft segments in polyurethanes. The polyester must have a molecular weight of 600-3000g/mol, depending upon the intended application. The end groups must be functionalized almost entirely by hydroxyl groups to produce higher molecular weight polyurethanes. It is necessary to control the degree of crystallinity for mechanochromic applications lest the polyurethane tear under mechanical stress instead of elongating, limiting its usefulness as an elastomer. Simultaneously, crystal structure must be relatively ordered so that the diacetylene will be able to cross-polymerize to form polydiacetylene chains.

## 2. Experimental Procedure

### 2.1. Synthesis

Both polyester macromonomers were made with 10,12-docosadiyne-1,22 diol as the diol.[7] The diol was synthesized by oxidative coupling of 10-undecyne-1-ol as described by Hay.[11] Polyesters were synthesized by a modified version of the method described by Korshak and Vinogradova[10]. To form a material with one methylene spacer, malonic acid was used as the diacid component to form 10,12-docosadiyne-1,22 malonate. To form a material with three methylene spacers, glutaric acid was used as the diacid component to form 10,12-docosadiyne-1,22 glutarate. These materials will be referred to here as malonate and glutarate polyesters, respectively.

### 2.2. Sample Preparation

All samples were spin coated from solution in THF at a rate of 1500 rpm prior to cross-polymerization unless otherwise indicated. Samples for thermal analysis were encapsulated with a minimum of crushing after scraping from spin coat substrate.

### 2.3. Cross-polymerization

Cross-polymerization was performed by exposure of thin films in air to UV radiation using a low pressure mercury arc lamp emitting 254nm radiation.

### 2.4. Thermal Processing

Samples to be annealed for spectral analysis were maintained at temperature for an hour in air using a beaker sealed in a hot water bath prior to cross-polymerization.

### 2.5. Thermal Characterization

Thermal characterization was performed using a Perkin-Elmer subambient DSC7 at ramping rates of 5°C/min and quenching rates of 200°C/min.

### 2.6. Spectral Analysis

Optical absorption data were taken using an Oriel Instaspec 250. For scans at varying temperatures, spectra were taken on samples secured in a hot cell with a temperature range of room temperature to 200°C. Each sample was held at temperature for five minutes prior to optical scan.

## 3. Results and Discussion

Since the purpose of the experimentation was to investigate thermochromic behavior with the goal of controlling the temperature range and reversibility of the color change, material processing was varied according to the likeliness of controlling thermochromic properties. Preliminary examination showed that the glutarate is responsive to annealing and that the malonate shows varying thermochromism with varying degree of cross-polymerization. Thermal history studies were therefore performed primarily on the glutarate polyester and effects of degree of cross-polymerization were investigated primarily on the malonate polyester.

## 3.1. Effects of Thermal History

Glutarate samples as spin coated were characterized thermally and compared to the samples as melted in the DSC and quenched. As shown in Figure 5, there was sufficient similarity between the thermal behavior of the quenched DSC samples and the spin coated samples to warrant use of the DSC-quenched samples as characterizations of spin coated glutarate behavior. To determine reversibility of thermochromism, individual samples were exposed to a cycle of heating and cooling during which optical data were taken. Comparison of scans of cycled samples with scans performed on samples which were heated directly to temperature showed that there was no hysteresis behavior.

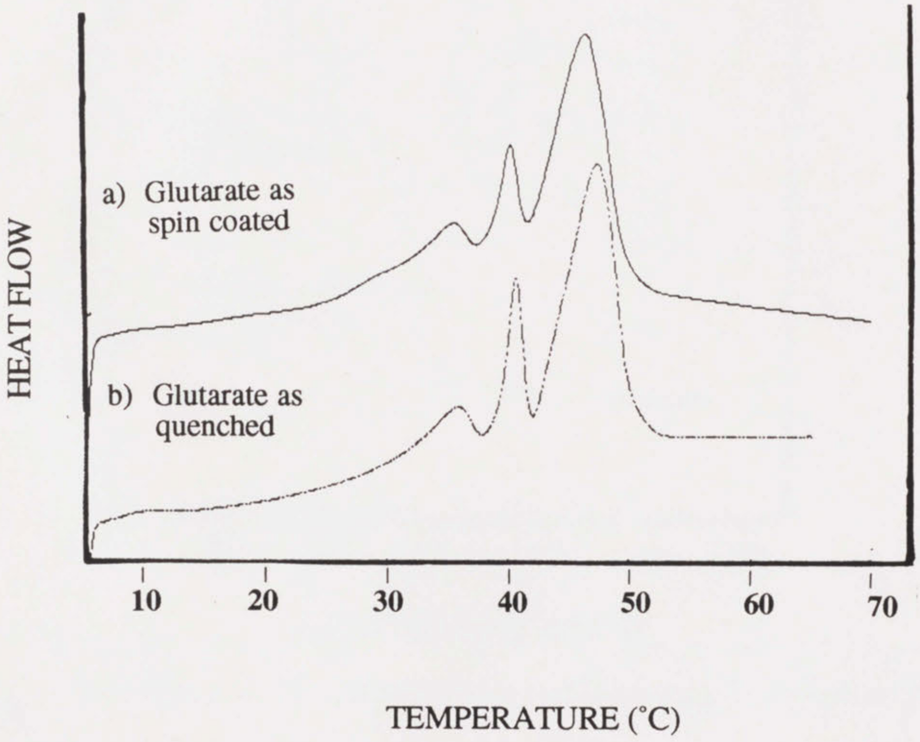


**Figure 5**: Comparison of thermal behavior of glutarate samples a) as spin coated and b) as quenched from melt

To eliminate the effects of varying degrees of cross-polymerization, all glutarate samples were exposed to UV radiation for a constant time of ten minutes. The effect of cross-polymerization on thermal behavior can be seen in Figure 6. At ten minutes exposure, all visible endotherms have almost completely disappeared. Since diacetylene cross-polymerization binds the structure of the diacetylene-containing polyester, the amount of disorder induced by increased temperature is not sufficient to cause an endotherm to appear on the DSC thermal analysis. Changes in order still occur at the melting temperature, however, as the polyester segments continue to have a partial disordering response when the melting temperature is reached. Thermochromic behavior therefore occurs in the range of the unpolymerized sample melting temperature, despite the lack of any visible endotherm, as will be shown.

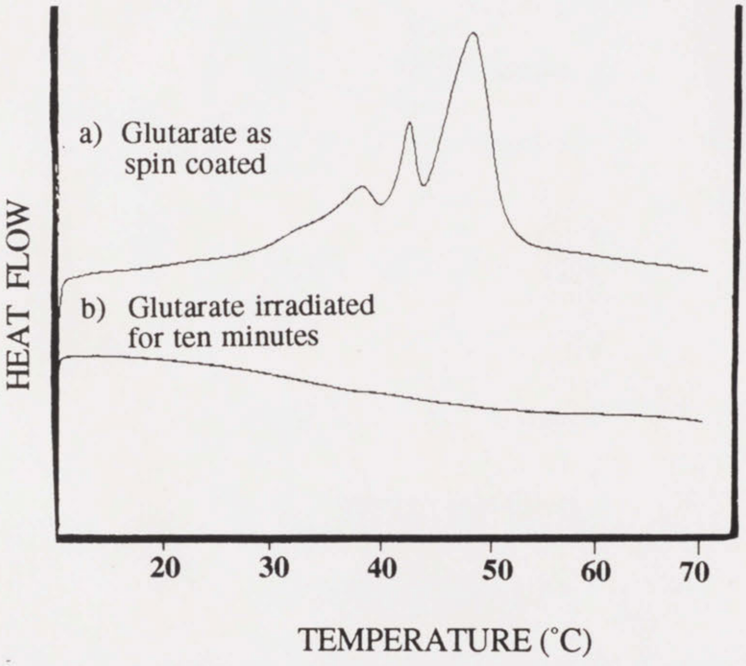


**Figure 6**: The effect of cross-polymerization on the thermal behavior of glutarate polyesters

Thermal characterization of the glutarate polyester showed polymorphism in samples which were spin coated from solution, with endotherms at 38°C, 43°C and 48°C. The polymorphic nature of the materials indicates that the glutarate backbones did not have sufficient time to order themselves, resulting in multiple phases and/or varying degrees of order. Figure 7 shows thermal data for glutarate samples as spun and as annealed at increasing temperatures. Annealing allows the onset of melting behavior to be pushed up to the annealing temperature as the disordered phases are provided enough time and energy to gain a greater degree of order. Endotherms above the anneal temperature are also elevated slightly in temperature upon anneal, presumably as these phases become slightly more ordered than in the quenched material. The glutarate reaches a maximum melting temperature at 50°C.

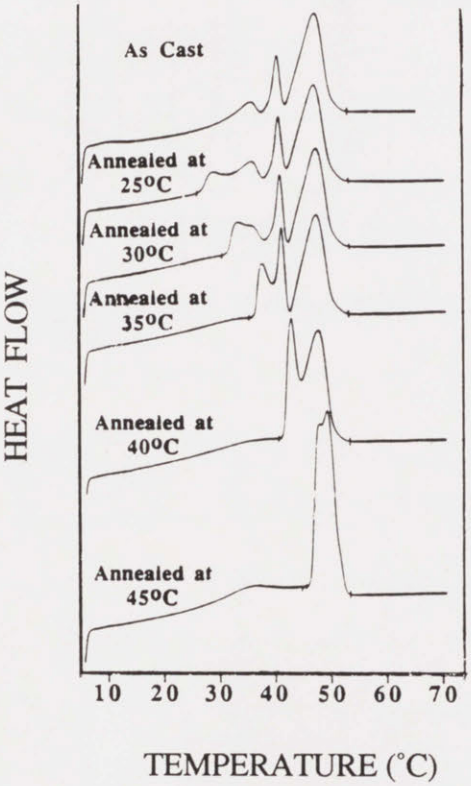


**Figure 7:** The effect of annealing on the thermal behavior of glutarate polyester.

Optical absorption spectra for the glutarate as spin coated and for the glutarate annealed at 45°C are shown in Figure 8 and Figure 9, respectively. Both samples turned purple in color upon cross-polymerization. Heating produced an irreversible color change to yellow. The anneal primarily affected the temperature

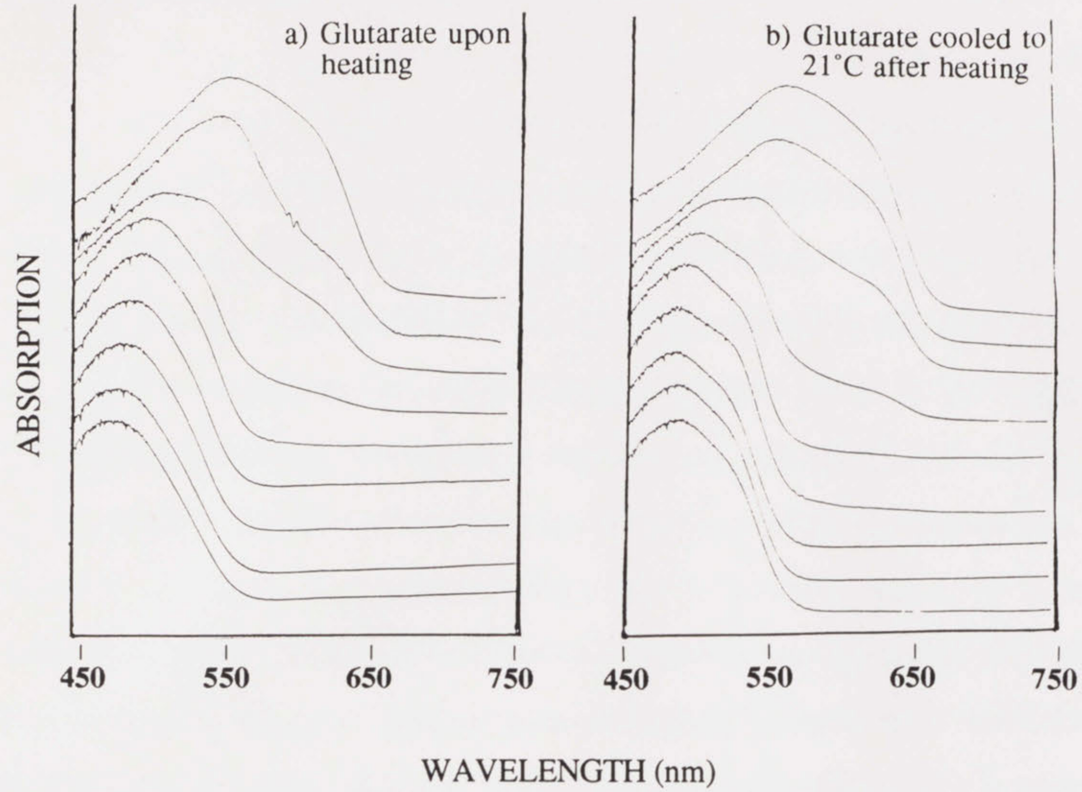


**Figure 8**: Optical absorption spectra of the as spin coated glutarate a) upon heating and b) upon subsequent cooling.

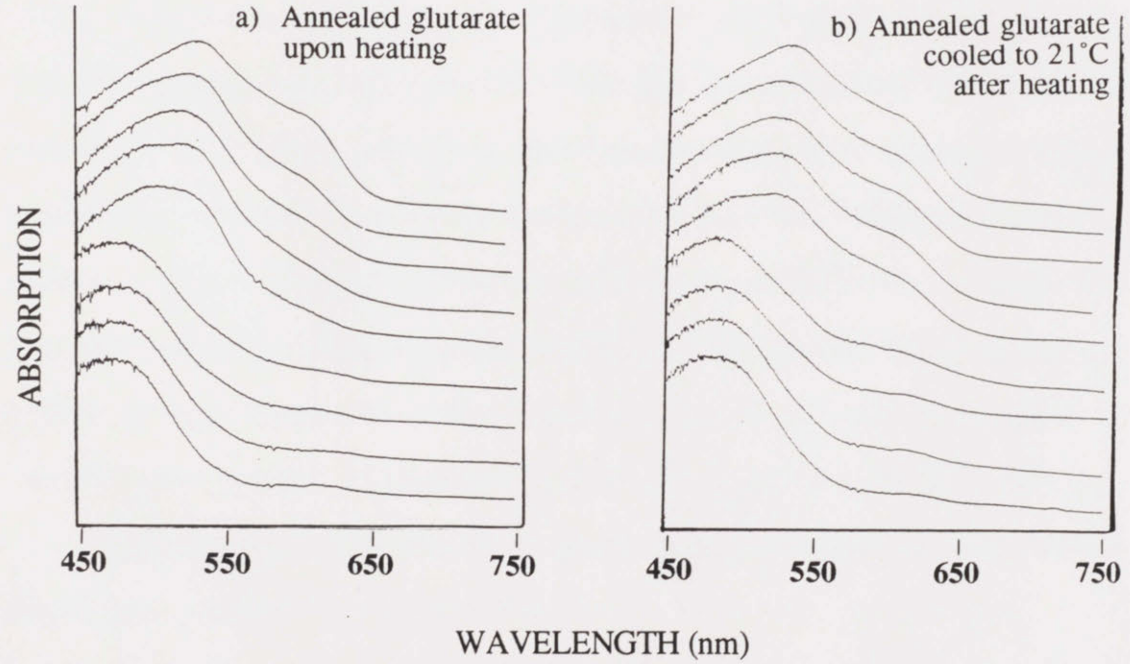


**Figure 9**: Optical absorption spectra of the glutarate annealed at 45°C a) upon heating and b) upon subsequent cooling.

range associated with thermochromism.

The thermochromic transition from purple to yellow takes place over a temperature range from room temperature to 45°C. The room temperature scan of the as spun glutarate showed a major absorption peak at 560nm, absorbing in the blue region, and a less distinct peak at 615nm, absorbing in the red region, corresponding to phases having different degrees of order [Figure 8(a)]. Since thermal analysis shows three endotherms, we might have expected three absorption peaks. The peaks are not very distinct, however, indicating a broad range of conjugation lengths, so broad in fact that a third peak may very well be masked entirely by its two neighboring peaks. The two peaks which are visible, and any other peaks which may be hidden, can be expected to respond somewhat differently to increased temperature, since different morphologies will vary in their response to increases in thermal energy.

The 615nm peak decreases in magnitude with increased thermal activity, until it disappears completely at 45°C. This peak shows an easily visible partial reversibility when heated to 30°C, as can be seen in Figure 8(b). Heating to higher temperatures, however, destroys nearly all reversibility. The 560nm peak does not disappear, but rather shifts into the blue region until at 55°C it lies at 490nm. At 35°C, this peak resolves into two peaks at 510nm and 540nm. The lower wavelength peak is the larger of the two, so this behavior cannot be attributed to the effect of intramolecular vibration. The behavior is confined between 30°C and 40°C. The two peaks reappear upon cooling from temperatures as high as 55°C, past which only a single peak remains at 490nm.

This could mean that the original peak is actually two overlapping peaks which undergo blue-shifting at different rates, or that the two peaks emerge from the first as a result of an incomplete transformation to a less ordered phase. In the latter case, further heating causes transformation of the entire phase to one disordered phase. Alternately, this behavior could indicate that both the vanishing phase associated with the peak absorbing in the red region, or the red peak, and the phase associated with the peak absorbing in the blue region, or the blue peak, transform to the same disordered phase. The presence of three distinct endotherms in the thermal analysis supports the idea that there are actually three separate peaks present, which respond differently to the application of thermal energy.

The initial optical absorption scan of the glutarate annealed at 45°C revealed behavior similar to the unannealed sample, showing peaks at 550nm and 625nm, as shown in Figure 9(a). The peaks are more distinct after annealing at 45°C than in the as spin coated sample. Since wavelength of absorption is associated with conjugation length, broader absorption peaks indicate a wider variety of conjugation lengths. Since anneal has sharpened absorption peaks, this indicates that anneal has allowed the time for the sample to assume one of the favored morphologies at the anneal temperature. Thermal analysis of the sample annealed at 45°C showed two peaks, one main peak just at the anneal temperature and a very small one below temperature that seems to have survived the anneal. In accordance with this two phase behavior, we see virtually none of the three peak behavior in the absorption spectra which we saw in the as spin coated sample.

The 625nm peak decreases upon heating until it disappears into the bottom of the 550nm peak. Upon completion of the melt, a small amount of this peak reappears to remain unaffected by thermal disruption. The 550nm peak shows nearly none of the hidden peak behavior of the unannealed glutarate. Upon cooling, a barely discernible separation of peaks occurs after heating to 40°C and 45°C. The shifting of the blue peak was dramatically affected by the anneal, occurring completely in the 45°C-50°C range, whereas for the unannealed sample the most dramatic blue-shift occurred across the 35°C-40°C temperature range. The anneal caused the largest effect on the least-ordered phase associated with the blue peak. The red peak, which was almost completely destroyed by thermal disruption in the unannealed sample, remains clearly discernible at high temperature after annealing. It would seem that the anneal is promoting the more ordered phase associated with the red peak.

Since the red peak exhibits distinct reversibility, this should increase the reversibility of the glutarate. Unfortunately, the red peak is so much smaller than the blue peak that this behavior does not produce clearly visible changes in the color of the material. Furthermore, the as spin coated glutarate cannot be body heat activated since its temperature range is in excess of the human surface body temperature. Internal body temperature is 37°C, with surface temperatures lower by 5°C-10°C, varying with the individual and the circumstances. Annealing the material to promote order after the initial processing of spin coating tends to raise the melting temperature further out of the range of body temperature. A quench procedure which limits the order more completely than the spin coating process could lower the melting temperature to a range which is body-heat activated.

Quenching the glutarate from melt in liquid nitrogen before cross-polymerization does indeed produce a less ordered material as shown in Figure 10. The endotherm at 33°C has disappeared, while a distinct melting endotherm at 25°C and a barely discernible endotherm at 30°C have emerged. The more ordered phases at about 43°C and 50°C are still present, with very little of the most ordered phase being able to form and a much larger 43°C endotherm.

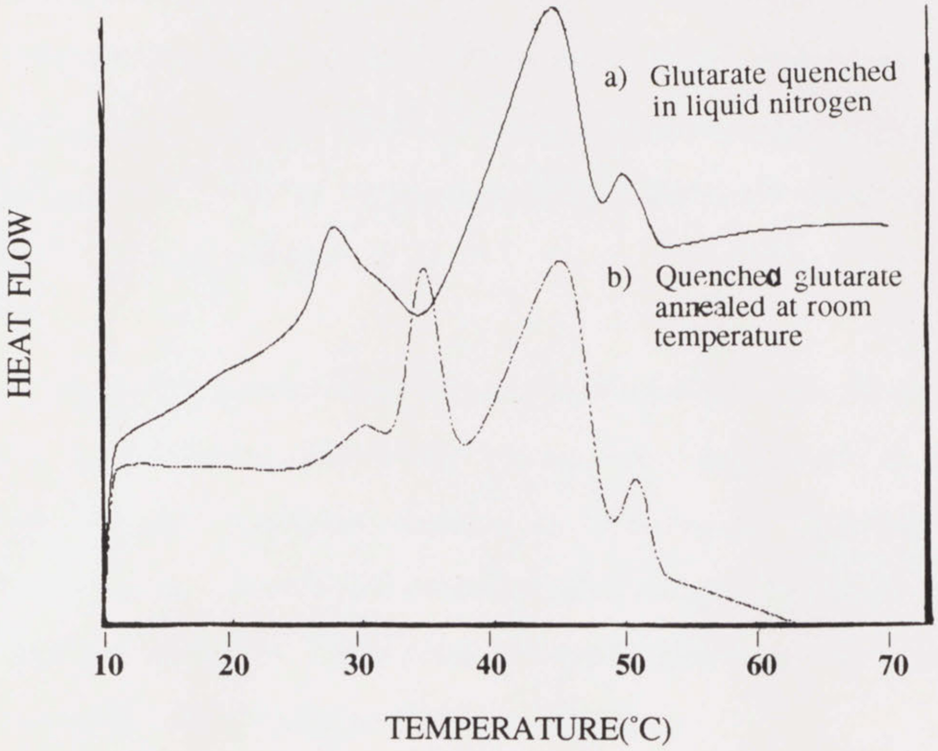


**Figure 10**: Thermal behavior of glutarate a) as quenched from melt in liquid nitrogen and b) subsequently annealed at room temperature.

Paper impregnated with the liquid nitrogen quenched glutarate changes from purple to red upon body contact and back to purple upon cooling. This reversibility suggests that body contact is not sufficient to cause melting in the material but induces a temporary heat-activated disorder, either because of insufficient time or temperature for thermal disruption. Over time, the chromic transition becomes less visually acute and the reversibility of the reaction less complete as the material begins to take on an orange tint. This indicates that the liquid nitrogen quenched glutarate impregnated paper sample is annealing, perhaps because of accumulated exposure to body temperature or from room temperature anneal.

Figure 10(b) shows that a solid piece of the glutarate which is quenched from melt in liquid nitrogen will anneal at room temperature. Just twelve hours after the first scan, the two lower endotherms have shifted to 30°C and 33°C respectively. The 33°C endotherm, presumably shifted from the small 30°C endotherm in the initial scan, has become much larger than the lower temperature endotherm, indicating that standing at room temperature will cause annealing of the liquid nitrogen quenched glutarate to a more ordered form.

Room temperature annealing seems to have little effect on the higher-temperature endotherms, presumably because room temperature is too low. However, even room temperature annealing has pushed up the highest two melting endotherms slightly. It would be interesting to investigate the effects of higher temperature annealing on the location and ratio between the 43°C and 50°C endotherms, but outside the scope of work done here.

Optical absorption spectra show that the thermochromic transition is complete and irreversible in the unannealed sample by 30°C as shown in Figure 11. The broadness of the absorption peak indicates a wide range of conjugation lengths. This is consistent with the thermal analysis which showed that quenching has the effect of freezing additional phases into the structure. Together, these data indicate a high variation in degree of order in the sample.

Since body surface temperature is upwards of 30°C, it seems likely that touching the sample for a few seconds produces small amounts of permanent disorder, like that associated with melting, which has the effect of irreversibly changing the color from purple to orange. Although one brief exposure to body temperature causes a reversible thermochromic transition, multiple exposures in combination with room temperature anneal can cause an irreversible thermochromic transition over time.

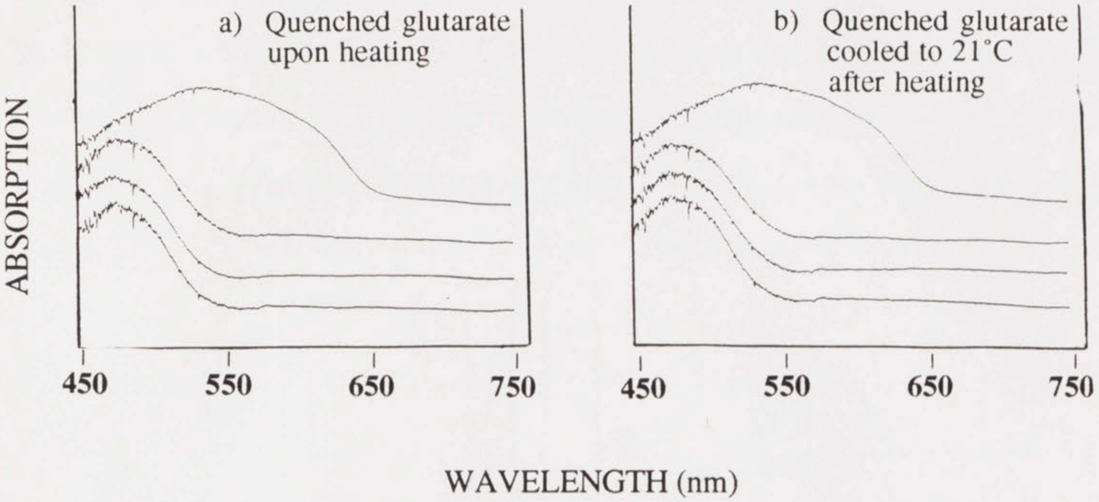


**Figure 11**: Optical absorption spectra of glutarate polyester as quenched from melt in liquid nitrogen a) upon heating and b) upon subsequent cooling.

## 3.2. Effects of Degree of Cross-Polymerization

Degree of cross-polymerization can have a profound effect on the temperature range of the thermochromic transition of diacetylene-containing polyesters. DSC thermal analysis of malonates as a function of polymerization shows that after five minutes of polymerization these materials have virtually no visible endotherms, much like the glutarate polyester (Figure 12). The cross-polymerized malonate no longer exhibits a distinct melting temperature, softening and melting over a broader range. The network produced by cross-polymerization locks the structure such that a greater temperature is required before disorder may be induced. Consequently, the thermochromic transitions can be expected to require a much broader range for completion with increased degree of cross-polymerization.

Malonate polyester cross-polymerized by exposure to UV radiation for thirty seconds has a thermochromic transition which is completed by 35°C (Figure

13). The initial scan of the malonate shows a peak at about 640nm with a long tail into the blue region. Since there are multiple endotherms in the thermal behavior, indicating several phases, the tail could be due to overlap of several peaks. Additionally, as with the glutarate quenched in liquid nitrogen, there is a wide distribution of conjugation lengths, causing peaks to be indistinct. After heating to

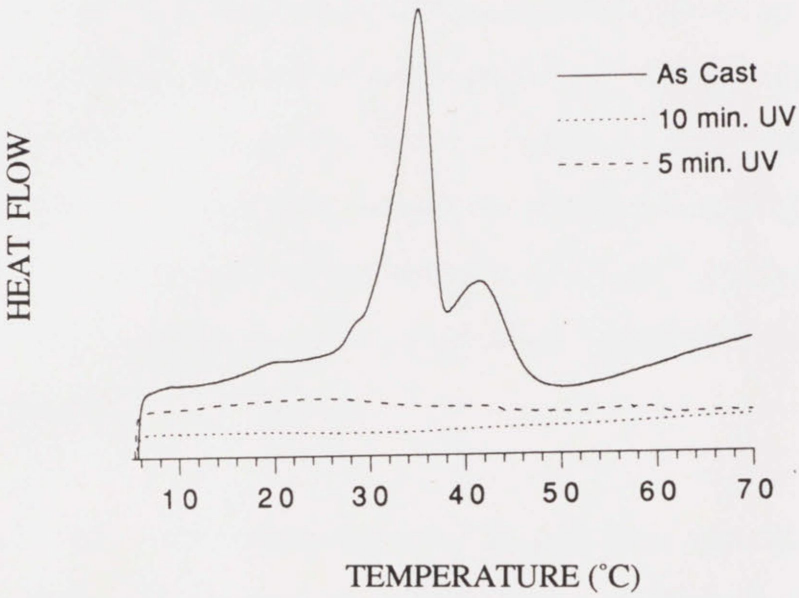


**Figure 12**: The effect of cross-polymerization on thermal behavior of malonate polyester.

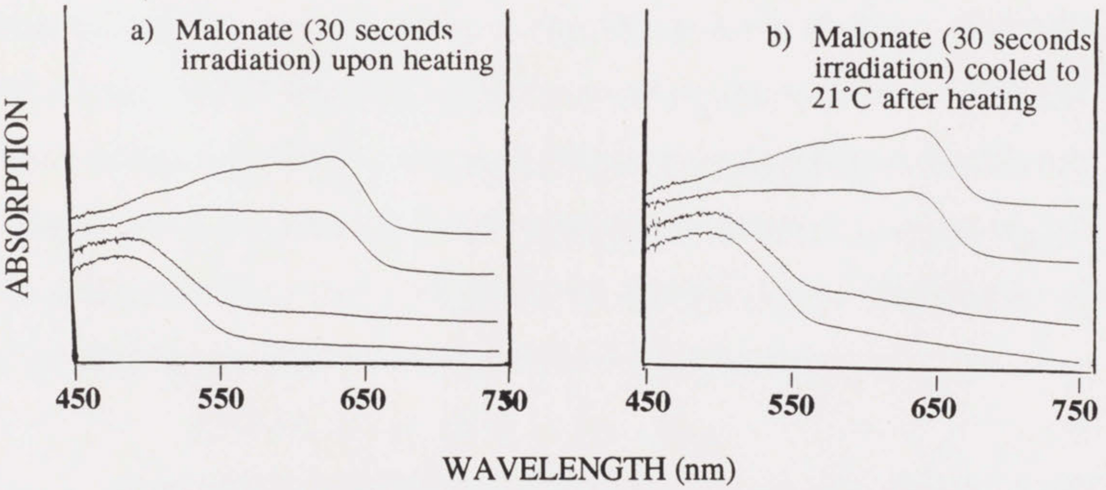


**Figure 13**: Optical absorption spectra of malonate polyester irradiated for thirty seconds a) upon heating and b) upon subsequent cooling.

35°C, the peak shifts to 500nm, and the malonate turns irreversibly from a light blue to yellow. Further heating produced no change in the optical absorption spectra and the spectra of cooled samples reveal no reversibility.

The behavior shown in Figure 13 seems much like that of the glutarate quenched in liquid nitrogen, which has a melting temperature and range for completion for thermochromic transition which is very close to body surface temperature and a large distribution of conjugation lengths indicating a high degree of disorder. One might predict that this sample would exhibit a reversible thermochromic transition upon body contact like the quenched glutarate. This is unfortunately not the case, perhaps because the low degree of polymerization allows the malonate to melt to a permanently disordered phase upon body contact more readily than the glutarate samples.

Further cross-polymerization, by five minutes of exposure to UV radiation, causes better resolution of the absorption peaks as shown in Figure 14. Here, the macromonomer has had sufficient exposure to radiation to more fully form a network structure. The absorption behavior begins to reflect the multiple distinct phase behavior evident in the thermal analysis. Endotherms appear at 640nm, 590nm and 560nm, though they still have a high degree of overlap as in the thirty second polymerized sample. The total area under the spectrum, proportional to the amount of energy absorbed, is much greater for the more irradiated sample, in accordance with the much higher levels of cross-polymerization. The sample is consequently a much deeper blue, with a thermochromic transition to a brighter yellow.

Upon heating the 640nm and 590nm peaks decrease and simultaneously blue-shift, so that the peaks become less distinguishable. The principle

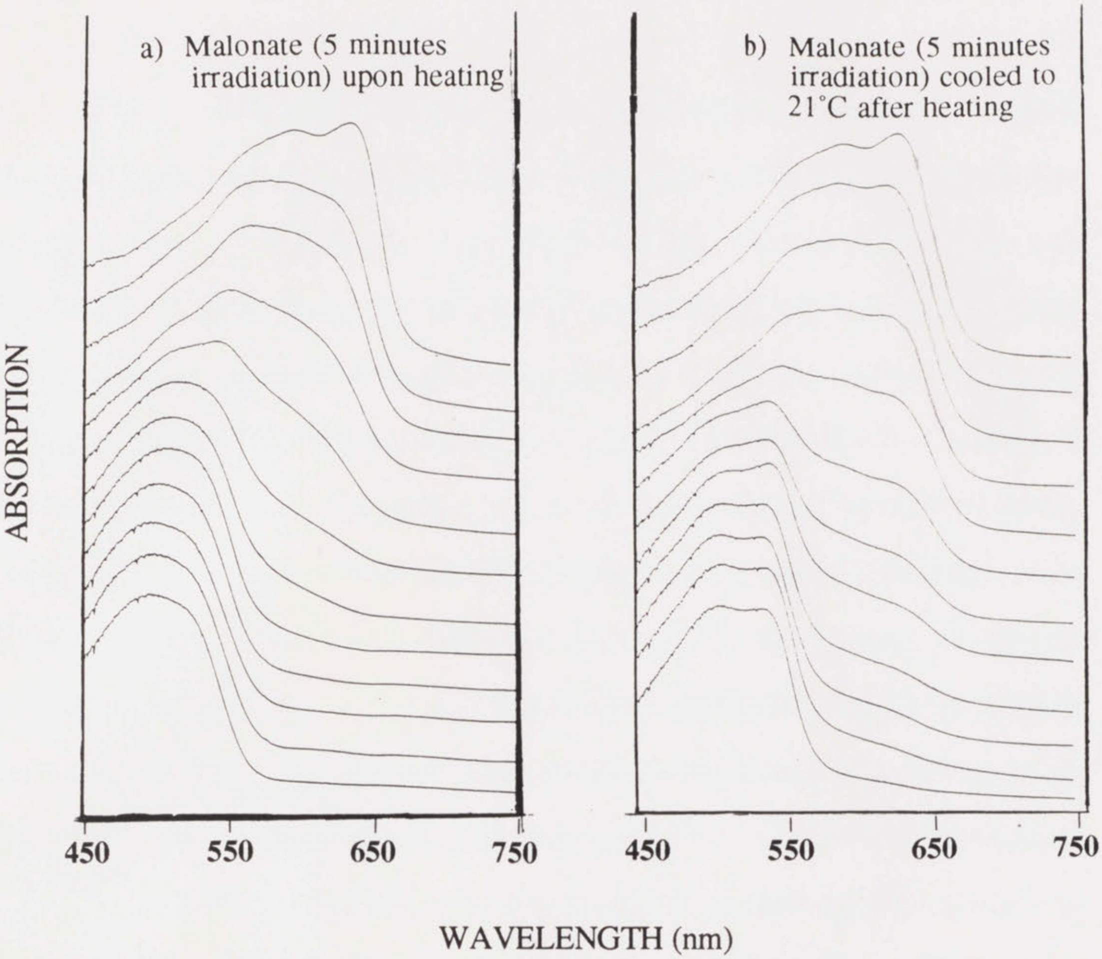


**Figure 14**: Optical absorption spectra of malonate polyester irradiated for five minutes a) upon heating and b) upon subsequent cooling.

thermochromic transition occurs from 35°C-50°C, where blue-shifting of all three peaks occurs. Reversibility in this material is increased relative to the sample irradiated for thirty seconds, so that the absorption spectra upon cooling look markedly different from the heated spectra (Figure 14). By 60°C all thermochromic change has occurred, resulting in a single peak at 500nm. After cooling from 60°C, however, all three peaks remain clearly visible. Eventually, even upon cooling the blue-shifted 640nm peak is annihilated, so that after cooling from 80°C, two final peaks remain at 500nm and 540nm. Unfortunately, cooled samples still appear yellow after transition as the partial reversibility is not sufficient for the eye to discern.

Further cross-polymerization by exposure to UV radiation for twenty minutes increased the trend of raising the onset and broadness of thermochromic transition. The bulk of the thermochromic transition occurred in the range from 45°C–75°C. The distinctness of the absorption peaks and the partial reversibility evident after five minutes of irradiation is virtually gone after twenty minutes of irradiation. Apparently, the structure is so completely locked in place by the extent of cross-polymerization that conjugation lengths remain unaffected by thermal energy prior to melt. Changes in conjugation length upon heating remain irreversible upon cooling. The peak broadening could be due to several factors. Perhaps stresses are produced upon excessive cross-polymerization which yield a mechanochromic effect, by causing changes in conjugation length locally, consequently broadening peaks. Alternately, the peak broadening may mean that the material is beginning to decompose under the excessive bombardment with UV radiation, counteracting the preference for certain conjugation lengths which is produced by cross-polymerization. Whatever the explanation, increasing time of exposure to UV radiation will promote reversibility and peak distinctness only to a point. It is important to choose a moderate time of exposure to UV radiation— too brief and the pale color will yield a thermochromic transition which is less than dramatic, too prolonged and the desired properties will begin to degrade.

## 4. Conclusion

The melting behavior of diacetylene-containing polyesters varies greatly with processing history, as they exhibit varying polymorphism in response to different stimuli. Materials which have been spin coated from solution exhibit multiple endotherms, characteristic of the presence of several crystal structures and/or varying degrees of perfection. Annealing these materials within the temperature range of the melting endotherms promotes order in the material. If the anneal is successful, this behavior manifests itself in a consolidation of the melting endotherms, indicating a preference for a particular lattice arrangement. Optically, this has the effect of elevating the temperature range of the most significant band of thermochromic change. These materials are not sensitive to body contact, however, and do not have visible reversibility.

Glutarate polyester which has been quenched from melt in liquid nitrogen exhibits a thermochromic transition upon body contact, that seems in the short term to provide the qualities we seek in a thermochromic material, that is, good chromic response and good reversibility. Over time, however, this material loses its reversibility, and whether this can be attributed to room temperature anneal or to an accumulation of partial melting caused by body contact, the effect remains undesirable.

A material which has already been annealed to push the melting temperature to just above room temperature would not show considerable room temperature annealing effects. Since annealing pushes up melting temperature, it would be useful to begin with a material which has a melting temperature slightly below room temperature and then to anneal the material such that its melting temperature is elevated. This would produce a material which has a small temperature range of thermochromic transition just above room temperature. Furthermore, reversibility produced by anneal is likely to remain more permanent over time and upon exposure to high temperatures than that produced by a less ordered quenched material.

Materials, such as malonate polyester, which are sensitive to degree of polymerization, offer a different sort of control over the temperature range of the thermochromic transition. Cross-polymerization of the malonate promotes survival upon heating of the slightly more ordered phase associated with the 540nm absorption peak. More importantly, the network structure caused by cross-polymerization impedes the melting process so that the onset for melting temperature increases and its range for completion becomes broader. While annealing pushes up onset and narrows the range of temperature for blue-shifting, increasing the degree of cross-polymerization pushes up onset and broadens the range for the transition. To produce a broad transition at or near room temperature, it would again be necessary to begin with a macromonomer which has a melting temperature below room temperature, since heavy cross-polymerization elevates the onset temperature of thermochromic transition. In order to produce a material with a visibly reversible thermochromic transition, it would be necessary to find a material in which reversibility can be promoted in a phase which dominates the absorption spectrum.

Unfortunately, the series of diacetylene-containing polyesters studied here have greater irreversibility than reversibility. Though the reversibility of the red peak is promoted by anneal and by moderate increases in the degree of cross-polymerization, this effect is masked by the much greater magnitude of absorption associated with the irreversibly blue-shifted peak. Variations in chemistry may perhaps produce a material in which proper processing promotes reversibility in a phase which dominates the absorption spectrum. Whether a material exists which can be processed such that it has a small thermochromic temperature range at or near room temperature and simultaneously has a large reversible absorption peak remains to be seen.

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