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MULTIPLE ENVIRONMENT POLYDIACETYLENE CONTAINING SEGMENTED BLOCK COPOLYMERS

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INTRODUCTION

The solid-state polymerization of diacetylene groups incorporated within the repeat structure of a suitable host polymer provides a novel means to crosslink a polymer via the introduction of conjugated polydiacetylene chains [1-4]. In addition to the dramatic changes in mechanical properties that take place, the host polymer also develops unique optical properties, such as thermochromism and mechanochromism [1,3]. These chromic effects are directly associated with the strong coupling that exists between the electronic states of the polydiacetylene chains and the local molecular organization of the segments of the host polymer nearest to the conjugated backbone. Dramatic color changes, both reversible and irreversible, for example, can be observed with these materials when the molecular segments of the host matrix undergo thermally or mechanically driven phase transitions. A wide variety of phase transitions including order-disorder melting transitions [1], crystal-crystal phase transitions [1], and liquid crystalline phase transitions [5] have been found to trigger these interesting color changes (typically from blue-to-red or blue-to-yellow). Since the optical properties of the polydiacetylene chains are highly sensitive to their local molecular environment, it is possible to create materials with tailored optical responses via variations in the structure and organization of the host polymer. A particularly intriguing example of this approach is the use of segmented block copolymers in which the diacetylene groups reside in phase separated microdomains [1,3]. In this case, the phase transitions of the diacetylene containing microdomains determine the chromic behavior of the polymer.

In this work, we show that it is possible to incorporate polymerizable diacetylene groups within both the hard and soft segments of polyurethane/polyester-based segmented copolymers. The resultant microphase separated polymers are comprised of soft and hard segment domains that are both capable of supporting the solid-state polymerization of the diacetylene groups. Cross-polymerization of the diacetylene groups therefore creates polydiacetylene chains within two distinctly different microenvironments, each with its own thermal and mechanical behavior. As a result of this, these new multiple environment polydiacetylene containing block copolymers exhibit complex chromic behavior that is directly associated with the phase transitions of both the soft and hard segment domains.

EXPERIMENTAL

10,12-docosadiyne-1,22-diol was synthesized by oxidative coupling of 10-undecyne-1-ol as described by Hay [6]. The polyesters and polyester macrodiols were synthesized by a modified version of the method as described by Korshak and Vinogradova [7]. The desired stoichiometry of diol and diacid (1:1 for high molecular weight polymers) was added along with 2.0% by weight p-toluene sulfonic acid and toluene into a three necked

flask to make a 15% polymer solution. A soxhlet extractor system with sodium metal (to remove the water) placed in the thimble was attached to the middle neck. Chunks of glass were placed in the thimble along with the sodium to adjust the volume, so that the polymer concentration never exceeded 25%. The entire reaction was refluxed and stirred for 24 hours under a blanket of dry nitrogen. At the termination of the reaction, the entire mixture was precipitated in a beaker of methanol, and recovered in a buchner funnel. The recovered polyester was washed repeatedly with methanol to remove any remaining catalyst or monomers. The polymer was then dried under high vacuum overnight. The segmented polyurethane/polyesters were synthesized using a procedure similar to that described in a previous paper [1].

Thin films for optical studies were cross-polymerized using a low pressure mercury arc lamp emitting 254 nm radiation. Films for mechanical studies were cross-polymerized by electron beam radiation, as this process penetrates the full thickness of the polymer film. Differential scanning calorimetry (DSC) was done with a Perkin Elmer DSC7. Dynamic mechanical analysis (DMA) was performed using a Seiko DMS 200. Optical absorption data were obtained using an Oriel InstaSpec™ II.

RESULTS AND DISCUSSION

Segmented polyurethanes are typically synthesized by chain extending diisocyanate endcapped polyether or polyester macrodiols with small molecule diols or diamines. The incorporation of diacetylene groups into the hard segments of these materials has previously been accomplished via the use of diacetylene diols as chain extenders [1]. In order to incorporate diacetylene groups into the soft segments, we have synthesized a number of diacetylene containing polyester macrodiols. These materials exhibit thermal transitions at much lower temperatures than the diacetylene containing hard segment materials, thereby producing segmented copolymers with chromic transitions that are triggered at distinguishably different temperatures.

Examples of some of the polyester materials synthesized to date are shown in Table 1. High molecular weight polymers were initially synthesized in order to properly determine their basic structure/property relationships. As indicated in this table, the melting transitions of these polyester host polymers are quite low; in the range of 20-55 °C. This means that it is actually possible to drive the thermochromic transitions of many of these polymers with body heat [8].

Table 1
Polyester Structures and Properties

Polyester Structures	DSC T _m Peak (°C)
$-\left[O(CH_2)_9-C\equiv C-C\equiv C-(CH_2)_9O-\overset{O}{\parallel}C-(CH_2)_1-\overset{O}{\parallel}C\right]_n-$	33
$-\left[O(CH_2)_9-C\equiv C-C\equiv C-(CH_2)_9O-\overset{O}{\parallel}C-(CH_2)_2-\overset{O}{\parallel}C\right]_n-$	54

$-\left[\text{O}(\text{CH}_2)_9 - \text{C}\equiv\text{C} - \text{C}\equiv\text{C} - (\text{CH}_2)_9 \text{O} - \overset{\text{O}}{\parallel}{\text{C}} - (\text{CH}_2)_3 - \overset{\text{O}}{\parallel}{\text{C}} \right]_n -$	44
$-\left[\text{O}(\text{CH}_2)_9 - \text{C}\equiv\text{C} - \text{C}\equiv\text{C} - (\text{CH}_2)_9 \text{O} - \overset{\text{O}}{\parallel}{\text{C}} - (\text{CH}_2)_4 - \overset{\text{O}}{\parallel}{\text{C}} \right]_n -$	47
$-\left[\text{O}(\text{CH}_2)_9 - \text{C}\equiv\text{C} - \text{C}\equiv\text{C} - (\text{CH}_2)_9 \text{O} - \overset{\text{O}}{\parallel}{\text{C}} - \text{CH}_2 - \text{CH}_2 - \overset{\text{CH}_3}{\underset{ }{\text{C}}} - \text{H} - \overset{\text{O}}{\parallel}{\text{C}} - \text{CH}_2 - \overset{\text{O}}{\parallel}{\text{C}} \right]_n -$	22
$-\left[\begin{array}{l} 50\% \text{ O}(\text{CH}_2)_8 \text{O} \\ 50\% \text{ O}(\text{CH}_2)_9 - \text{C}\equiv\text{C} - \text{C}\equiv\text{C} - (\text{CH}_2)_9 \text{O} \end{array} \right] \overset{\text{O}}{\parallel}{\text{C}} - (\text{CH}_2)_4 - \overset{\text{O}}{\parallel}{\text{C}} \right]_n -$	31

All of the diacetylene containing polyesters were found to be reactive to either UV or electron beam radiation. Cross-polymerization of the diacetylene groups in this manner converted colorless materials to materials that were either blue or red in color. Each of these cross-polymerized polyesters also exhibited thermochromic behavior. An example of the thermochromic behavior of a cross-polymerized diacetylene functionalized polyester is displayed in Figure 1. This figure illustrates the general behavior observed for all of the cross-polymerized polyesters, namely a dramatic thermochromic transition occurring at the melting temperature of the original host polymer. For this particular polymer, the thermochromic transition involved an irreversible color change from blue-to-red.

Using suitable macrodiols of the above diacetylene containing polyesters (M_n in the range of 2000-5000 g/mol), it was possible to synthesize a variety of different types of segmented copolymers with diacetylene groups in the soft segments only or in both the soft and hard segments. The structure of a typical segmented block copolymer created by chain extension of a diisocyanate endcapped diacetylene containing polyester macrodiol with a diacetylene diol is shown in Figure 2. In this case, the soft segment is poly(10,12-docosadiyne-1,22 malonate), the diisocyanate is hexamethylene diisocyanate, and the chain extender is 5,7-dodecadiyne-1,12-diol.

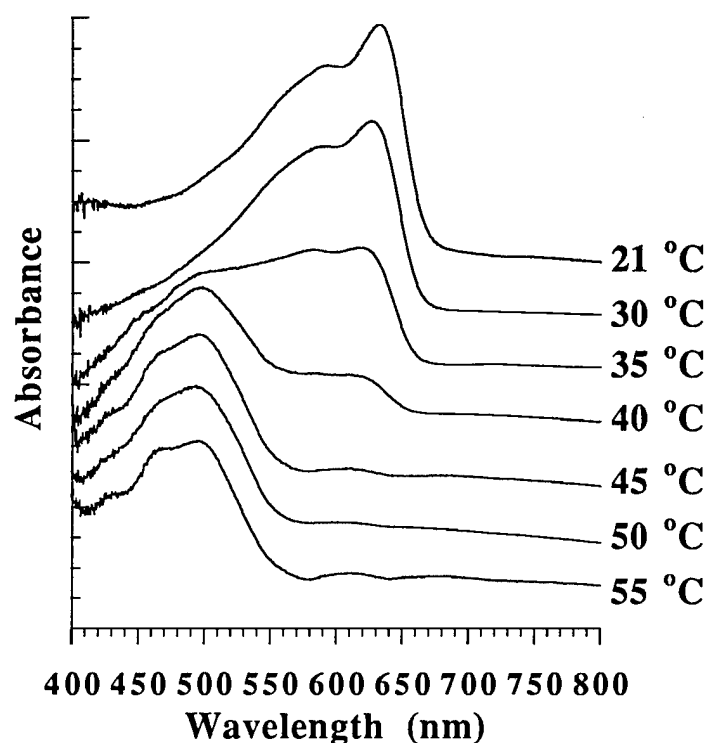


Figure 1. Visible absorption spectra as a function of increasing temperature. The sample is a thin spin coated film of poly(10,12-docosadiyne-1,22 malonate) polymerized by UV light.

As expected, the diacetylene groups contained within the hard and soft segment domains of these microphase separated copolymers could be cross-polymerized by exposure to UV or electron beam radiation. By varying the temperature of cross-polymerization, it is possible to exclusively polymerize the diacetylene groups within the hard domains or polymerize the diacetylene groups contained within both the hard and soft domains [8]. The crosslinking that occurs in the hard and soft domains has a dramatic effect on the mechanical properties of the copolymer. Figure 3 shows how cross-polymerization influences the thermal/mechanical properties of a segmented copolymer with diacetylene groups in the soft segments only. This particular polyurethane has a soft segment of poly(10,12-docosadiyne-1,22 adipate), with hexamethylene diisocyanate as the diisocyanate, and 1,8-octane diol as the chain extender.

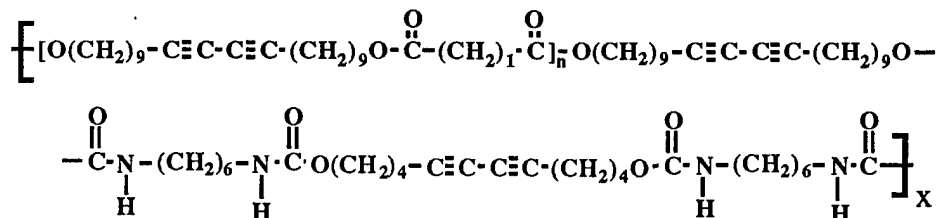


Figure 2. Chemical structure of a typical dual-environment diacetylene containing segmented polyurethane. The upper part of the structure represents the soft segments, while the lower part constitutes the hard segments.

In this case, cross-polymerization of the soft domains is seen to significantly increase and extend the plateau modulus of the polymer. Melting of the hard domains, however, limits the high temperature capability of the 50 Mrad material as indicated by the significant drop in modulus at about 140 °C. For segmented polyurethanes containing diacetylene groups in both the hard and soft domains, the plateau modulus is further extended to temperatures as high as 200 °C, as a result of the additional crosslinking that takes place in the hard domains (curves not shown).

As anticipated, the segmented polyurethanes with polydiacetylene chains supported in both the soft and hard segment domains exhibit a wide range of interesting and complex mechano- and thermochromic properties. Details of the optical properties of these materials will be presented in a separate paper.

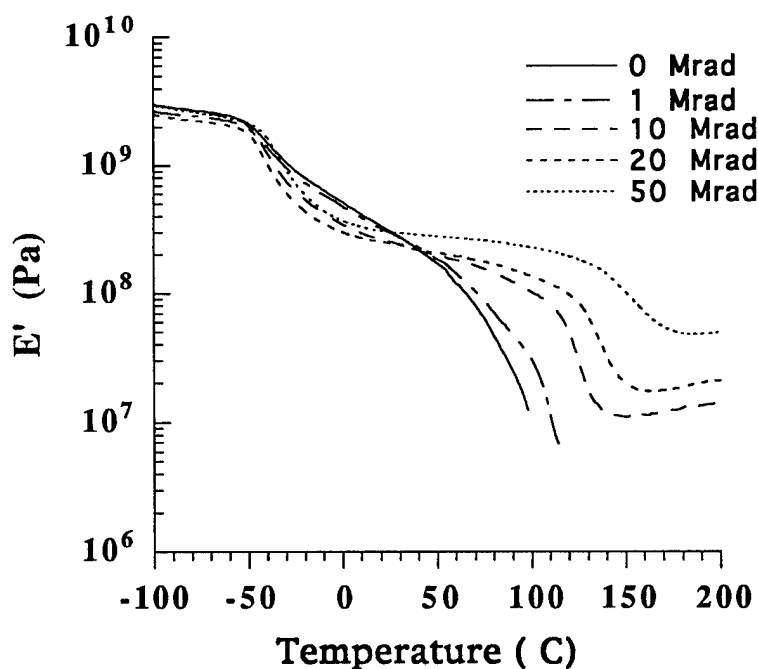


Figure 3. DMA scans of a segmented polyurethane with diacetylene groups in the soft domains. Radiation dosage in Mrads is indicated in the legend.

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