Cross-Polymerization of Hard Blocks in Segmented Copoly(ether urea)s

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ABSTRACT: Diacetylene-containing segmented copoly(ether urea) **1** was prepared via a polycondensation of 1,10-diisocyanato-deca-4,6-diyne with bis(3-aminopropyl)poly(tetrahydrofuran) ($M_n \approx 2300$ g/mol). The reactive diacetylene spacer, which resides within the hard domains of the segmented elastomer, was cross-polymerized topochemically by means of UV radiation, without disrupting the flexible nature of the material, resulting in an intensely blue insoluble material. The extent of cross-polymerization was determined using solid-state ^{13}C NMR and was found to be ∼10%. The optical properties of the cross-polymerized material could be modified mechanically and thermally as well as by changing the solvent. A study into the mechanochromic behavior—a color change from blue to yellow upon elongation—showed that the color changes are irreversible at strain levels greater than 80%. Polarized UV spectroscopy indicated that upon deformation the polydiacetylene chains orient parallel to the deformation axis. Thermochromic and solvatochromic behavior of **1** was completely irreversible.

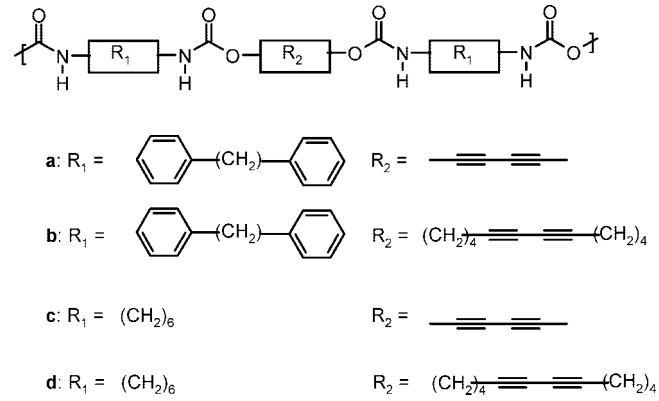
Introduction

Since the appearance of the seminal publication of G. Wegner,[1] in which the solid-state reactivity of certain substituted diacetylenes was explained in terms of a polymerization reaction, polydiacetylene (PDA) research has evolved to a multidisciplinary field with many active developments. Polydiacetylenes have been studied as bulk crystals and in monolayers. More recently, they have also been applied in multilayer films,[2] in vesicles,[3] and as nanocomposite components integrated into inorganic host matrices.[4]

A unique feature of polydiacetylenes is that the photopolymerization occurs via a topochemical polymerization from a well-ordered solid state, leading to extremely linear, aligned polymerized domains. A prerequisite for the polymerization to occur is highly ordered packing of the monomers. The polymerization successfully proceeds because the monomer spacing, imposed by the van der Waals forces between the pendant alkyl chains, is close or close enough to the spacing required for the diacetylene backbone to form.[5]

The most intensively studied properties of PDAs are the changes in color they undergo upon heating, applying force, or chemical interactions.[6] The color of PDAs is due to a $\pi \rightarrow \pi^*$ transition of the linear π-conjugated polymer backbone. Unpolymerized diacetylenes do not exhibit absorption in the visible region, but upon polymerization a blue color appears from an absorption band with a maximum around 640 nm. Color changes of PDAs involve a shift of this absorption band to a band around 540 nm, resulting in a transformation of the material from blue to red. Sandman has studied the mechanism behind the chromatic transitions.[7] These studies showed that the key to the transition consists of the interplay between the conformation of the pendant side groups and the backbone. Furthermore, the absorption properties of the backbone depend on strain. Rotation about the C−C bond of the polymer backbone is critical in this respect since it changes the planarity of the backbone. Theoretical calculations indicate that a rotation of only a few degrees around this bond drastically changes the π-orbital overlap, causing a significant blue shift of the absorption spectrum.[8]

Scheme 1. Hard Segment Structures of Polyurethane−Diacetylene Segmented Copolymers Prepared by Rubner et al.[10,a]



[a] Soft segments (not shown) consist of pTHF.

Polymers exhibiting the optical properties of polydiacetylenes and the mechanical behavior of a tough and highly extensible elastomer are highly desirable materials. As has been previously demonstrated, the reactive diacetylene group can be easily incorporated into many different polymeric structures.[9−13] In this way it is possible to modify the optical and mechanical properties of these materials by the controlled solid-state cross-polymerization of the diacetylene groups. The ability to couple the optical and mechanical behavior of a thermoplastic elastomer (TPE) presents a world of opportunities, ranging from optically anisotropic materials to mechano-optic sensors. Self-assembled polydiacetylene supramolecules in the form of Langmuir−Schaeffer films, Langmuir−Blodgett films, or vesicles[3] have already proven themselves as chemosensors monitoring ligand−receptor interactions involving viruses,[14] toxins,[15] and ionic interactions,[16] even though they function in an irreversible fashion. Recently however, Ahn and co-workers have studied the effect of enhanced hydrogen bonding in polydiacetylene Langmuir−Schaefer films, resulting in reversible color changes, which could be potentially useful for designing reversible calorimetric sensors based on polydiacetylenes.[17]

In the late 1980s and early 1990s, Rubner and co-workers have incorporated diacetylenes in polyurethane segmented

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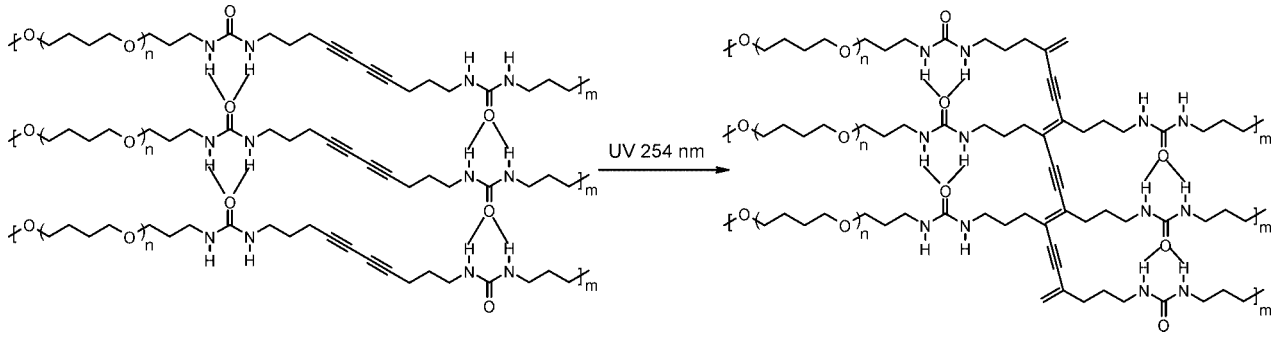
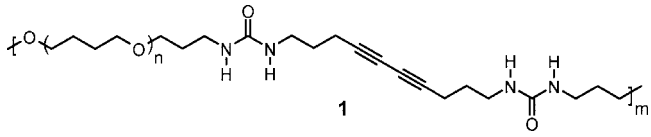


Figure 1. Cross-polymerization of diacetylene segmented copoly(ether urea)s, initiated with UV radiation.

copolymers (Scheme 1).[10,11,18,19] In these materials, the optical properties of diacetylenes were linked with the mechanical properties of thermoplastic elastomers. In the copolyurethane−diacetylene copolymers a polydiacetylene network is produced in the hard domains on irradiation in the solid state. The resulting cross-polymerized polyurethanes undergo color changes that are coupled to elastomeric strain (mechanochromism) as well as temperature changes (thermochromism). Stanford and coworkers have used urethane−diacetylene segmented block copolymers to study hard segment deformation with Raman spectroscopy.[20]

Recently, a new class of TPEs containing urea groups was developed in our laboratory.[21] They consist of a uniform bisurea hard block in which the urea groups are separated by a precisely defined number of carbon atoms. These hard blocks are embedded in a soft amorphous pTHF matrix. Association of the hard segment domains via hydrogen bonding results in the formation of reversible cross-links embedded in a soft, rubbery, amorphous pTHF matrix. These copoly(ether)ureas exhibit promising thermal and mechanical properties.[22]



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Nonpolymeric peptide and bisurea diacetylenes have been used in polymerizable organogels with thermochromic and solvatochromic properties.[23] In the present work, a bisurea-based thermoplastic elastomer with cross-polymerizable diacetylene hard blocks (**1**) is described. A reactive diacetylene spacer was incorporated between the two urea groups in the hard segment domains of the elastomer. In such an arrangement the diacetylene units may be cross-polymerized by means of heat or UV radiation without disrupting the flexible nature of the elastomeric phase (Figure 1).

Additional hydrogen bonding in **1** results in a well-defined geometry of the hard domains and excellent phase separation.[21,22] It is of interest to see whether the diacetylene groups satisfy the requirements for topochemical polymerization to the same extent as those in the polyurethane diacetylene segmented copolymers reported by Rubner et al.

The mechanical properties as well as the orientation of the different chromophores under tensile conditions were studied with polarized IR and polarized UV measurements. Furthermore, the thermo- and solvatochromic behavior of the remarkable material are discussed.

Experimental Section

General Methods and Instrumentation. NMR spectra were recorded on a Varian Inova 500 MHz spectrometer, a Bruker 500 MHz spectrometer, and a Varian Gemini 300 MHz spectrometer at 20 °C unless otherwise noted. Infrared sprectra were measured on a Perkin-Elmer 1600 FT-IR.

Materials. Di-*tert*-butyl tricarbonate was prepared according to a literature procedure.[24] All further reagents and solvents were purchased from commercial sources and used without further purification unless otherwise noted. THF was distilled over potassium and sodium. Chloroform was dried over molecular sieves. All reactions were carried out under a dry argon atmosphere.

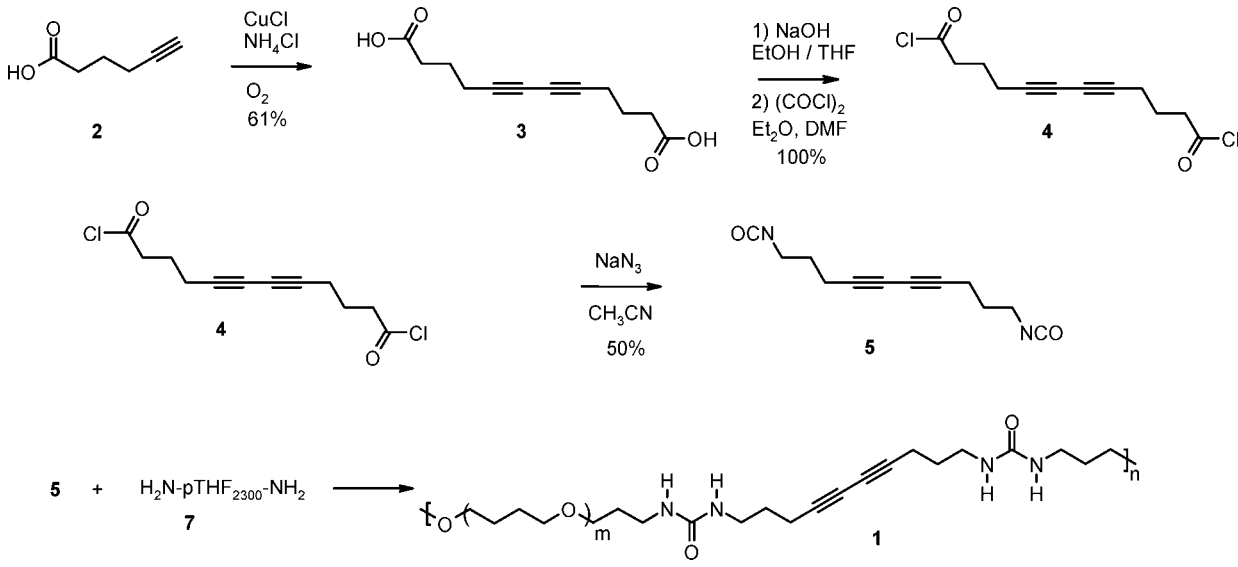
5,7-Dodecadiynedioic Acid (3).[25] A suspension of copper(I) chloride (7.9 g, 80.1 mmol) and ammonium chloride (14.34 g, 0.27 mol) in 40 mL water was added to a solution of 5-hexynoic acid (**2**; 3 g, 26.7 mmol) in 40 mL of water. The green reaction mixture was heated to 60 °C, and air was bubbled through the solution while stirring vigorously for 2 h. The reaction mixture was quenched with 46 mL of concentrated hydrochloric acid, and the resulting precipitate was collected by suction filtration, washed with a 1/1 mixture of hydrochloric acid/water, and recrystallized from a water/methanol mixture (2/8), resulting in white crystals (1.8 g, 61%). ^{1}H NMR (CD_3OD): δ: 2.43 (t, 4H, C═OCH_2), 2.35 (t, 4H, CH_2−C), 1.81 (m, 4H, CH_2−CH_2−CH_2). ^{13}C NMR (CD_3OD): δ: 174.3 (*C*═O), 77.9 (CH_2−*C*), 66.0 (*C*−*C*), 32.9 (C═O−*C*H_2), 23.7 (CH_2−*C*H_2−CH_2), 18.2 (*C*H_2−C). ^{13}C NMR (DMSO): 174.3, 77.9, 66.0, 32.9, 23.7, 18.2.

5,7-Dodecadiynedioic Acid Dichloride (4).[26] 5,7-Dodecadiynedioic acid (**3**; 0.8 g, 3.6 mmol) was dissolved in an ethanol/tetrahydrofuran (5 mL/5 mL) mixture. To this solution was added an ethanolic NaOH solution (7.2 mmol, 5 mL) at room temperature. After stirring for 5 min the solvent was evaporated, and the residue was dried under vacuum for 5 h. The residue was dissolved in 10 mL of ether and 1 drop of DMF and was cooled to 0 °C. At this temperature oxalyl chloride (2.8 mL, 32 mmol) was added, and the solution was stirred for 2 h. The resulting suspension was filtered, and the filtrate was evaporated to dryness, resulting in 0.85 g of **4**, which was used in the next step without purification. ^{1}H NMR ($CDCl_3$): δ: 3.07 (t, 4H, O═CCH_2), 2.40(t, 4H, CH_2−C), 1.94 (m, 4H, CH_2C*H*$_2$$CH_2$).

1,10-Diisocyanatodeca-4,6-diyne (5).[27] To 5,7-dodecadiynedioic acid dichloride (**4**; 1.8 g, 6.98 mmol) in dry acetonitrile (25 mL) was added sodium azide (1.0 g, 15.3 mmol) with stirring under an argon atmosphere. The reaction mixture was heated to 65 °C. N_2 started to evolve. After the nitrogen evolution had become negligible (1 h), a white solid was filtered off, and the filtrate was purified by distillation. The diisocyanate was collected as a colorless oil (0.75 g, 50%). ^{1}H NMR ($CDCl_3$): δ: 3.45 (t, 4H, O═C═N−CH_2), 2.39(t, 4H, CH_2−C), 1.80 (m, 4H, CH_2C*H*$_2$$CH_2$). ^{13}C NMR: δ 122.4 (O═*C*═N), 79.4 (CH_2−*C*), 65.9 (*C*−*C*), 42.2 (N−*C*H_2), 31.8 (CH_2−*C*H_2−CH_2), 13.7 (C−*C*H_2). IR ν: 2249.5 cm^{-1} (−N═C═O stretch).

Bis(2-cyanoethyl)poly(tetrahydrofuran) (6). Poly(tetrahydrofuran)diol, M_n = 2000 g/mol, (60.00 g, 30.0 mmol) and 15-crown-5 (132 mg, 0.6 mmol) were dissolved in acrylonitrile (120 mL) and cooled in an ice bath. Sodium hydride (24 mg 60% dispersion in mineral oil, 0.6 mmol) was added to the solution, and the reaction mixture was stirred at 0 °C for about 15 min, after which the reaction mixture turned slightly yellow. At this point, the reaction

Scheme 2. Synthesis of Diacetylene-Containing Segmented Copoly(ether urea) 1



was quenched by addition of a few drops of concentrated hydrochloric acid. The solution was concentrated, and the residue was taken up in dichloromethane (100 mL) and centrifuged at 4500 rpm. The mixture was decanted, filtered, and concentrated in vacuo. The product was obtained as a slightly yellow viscous liquid that slowly crystallized (58.57 g, 93%). ^{1}H NMR ($CDCl_3$): δ 3.62 (t, 4H, OCH_2CH$_2$CN), 3.51 (t, 4H, CH_2OCH$_2$CH$_2$CN), 3.40 (br. t, 106H, OCH_2CH$_2$CH$_2$CH_2O main chain), 2.59 (t, 4H, CH_2CN), 1.60 (br m, 110H, OCH$_2$CH_2CH_2CH$_2$O main chain). ^{13}C NMR ($CDCl_3$): δ 117.7 (*C*N), 71.0 (*C*H$_2$OCH$_2$CH$_2$CN), 70.4 (OCH$_2$CH$_2$CH$_2$*C*H$_2$O main chain), 65.1 (OCH$_2$CH$_2$CN), 26.3 (OCH$_2$*C*H$_2$*C*H$_2$CH$_2$O main chain), 18.7 (*C*H$_2$CN). FT-IR (ATR): ν 2939, 2855, 2161 (w, C≡N stretching), 1367, 1103 (C−O stretching) cm^{-1}.

Bis(3-aminopropyl)poly(tetrahydrofuran) (7). To a solution of borane−tetrahydrofuran complex (250 mL, 1 M in THF, 250 mmol) in dry THF (240 mL) was added slowly bis(2-cyanoethyl)poly(tetrahydrofuran) (**6**; 58.57 g, 27.9 mmol) dissolved in dry THF (250 mL) at 0 °C. The solution was stirred for 30 min at 0 °C, after which it was heated to reflux for 2.5 h. The reaction mixture was cooled to 0 °C, and methanol (80 mL) was added dropwise. Hydrochloric acid (10 mL, 37% in water) was added slowly, and the reaction mixture was stirred for 30 min and subsequently evaporated to dryness under reduced pressure. Trimethyl borate was removed by three coevaporations with methanol (3 × 150 mL). To the viscous liquid was added sodium hydroxide solution (150 mL, 1 M in water), and this mixture was extracted with diethyl ether (2 × 500 mL). The combined organic layers were dried with sodium sulfate and filtered, and the solvent was evaporated on a rotary evaporator without the use of a water bath. During solvent evaporation, the polymer precipitated from the cold solution and was obtained as a white powder (54.30 g, 93%). ^{1}H NMR ($CDCl_3$): δ 3.49 (t, 4H, OCH_2CH$_2$CH$_2$NH$_2$), 3.41 (br t, 138H, OCH_2CH$_2$CH$_2$CH_2O main chain), 2.79 (t, 4H, CH_2NH$_2$), 1.71 (t, 4H, OCH$_2$CH_2CH$_2$NH$_2$), 1.62 (br m, 142H, OCH$_2$CH_2CH_2CH$_2$O main chain), 1.1 (br s, 4H, NH_2). ^{13}C NMR ($CDCl_3$): δ 70.5 (OCH$_2$CH$_2$CH$_2$*C*H$_2$O main chain), 68.8 (OCH$_2$CH$_2$CH$_2$NH$_2$), 39.7 (*C*H$_2$NH$_2$), 33.6 (OCH$_2$*C*H$_2$CH$_2$NH$_2$), 26.4 (OCH$_2$*C*H$_2$CH$_2$CH$_2$O main chain). FT-IR (ATR): ν 3564, 3539, 2941, 2862, 1492, 1372, 1107, 996 cm^{-1}.

Diacetylene Segmented Copolyether Urea (1). Bis(3-aminopropyl)poly(tetrahydrofuran),[21] $M_n \approx$ 2300 g/mol (**7**; 6.3 g, 2.77 mmol), was dissolved in dry chloroform (60 mL), and a solution of 1,10-diisocyanatodeca-4,6-diyne (**5**; 0.6 g; 2.77 mmol) in dry chloroform (15 mL) was slowly added. The reaction was followed with IR, and addition of the diisocyanate was stopped once a isocyanate peak at 2249 cm^{-1} appeared. The solution was partly evaporated, and methanol (5 mL) was added. The product was precipitated in hexane (400 mL), filtered, and dried in vacuo. It was obtained as white, fluffy, elastic fibers (6.1 g) and was stored in the dark and at −10 °C to prevent cross-polymerization. ^{1}H NMR ($CDCl_3$): 4.8−4.6 (4H, NH), 3.45 (4H O−CH_2CH$_2$CH$_2$N), 3.42 (96 H CH_2−O), 3.25 (8H, NCH_2), 2.30 (4H, CCH_2), 1.77 (8H, OCH$_2$CH_2CH$_2$N, CCH$_2$CH_2), 1.61 (96H, OCH$_2$CH$_2$CH$_2$CH_2O). FT-IR (ATR): ν 3327 (N−H stretching), 2940, 2855, 1615 (C═O stretching), 1581, 1369, 1103 (C−O stretching) cm^{-1}. SEC (NMP, rel to PS): M_n: 56 × 10^3 g/mol.

Film Preparation. Diacetylene segmented copolyether urea **1** was dissolved in chloroform/methanol mixtures (9/1). The solution was poured into silylated Petri dishes or Teflon molds, and films were obtained by slow evaporation of the solvents in the dark to prevent cross-polymerization. All films were dried further under reduced pressure at room temperature before analysis.

Tensile Testing. Dumbbell-shaped tensile bars with a parallel length of 22 mm and a width of 5.0 mm were cut from solution-cast films with a thickness of ∼0.3 mm. Tensile tests were performed on a Zwick Z010 Universal Tensile Tester at an elongation rate of 100%/min, using a minimum of eight samples for each material.

Polarized UV Measurements. UV−vis spectra were recorded on a Perkin-Elmer Lambda 900 spectrometer equipped with a polarizer accessory. Films of **1** were elongated and clamped, and spectra were recorded at 0° and 90° polarization angle with respect to the deformation axis.

Infrared Linear Dichroism and Raman Spectroscopy. Infrared (IR) spectra were recorded by means of a Biorad UMA 500 microscope, coupled to an FTS6000 FT-IR spectrometer. Tensile bars were elongated and clamped. Infrared spectra were recorded in transmission at 0° and 90° polarization angle with respect to the deformation axis. Raman scattering experiments were performed in Dilor Labram Raman spectrometer at room temperature with an incident radiation of 632.81 nm using a HeNe laser.

Solid-State ^{13}C NMR. Solid-state ^{13}C NMR spectra were recorded on a Bruker DMX500 spectrometer operating at a ^{1}H and ^{13}C NMR frequency of 500 and 125 MHz, respectively. The spectra were obtained by use of cross-polarization (CP) in combination with magic angle spinning (MAS). Thin slices of the polyurea−diacetylenes or polyurea−polydiacetylenes were packed in a 4 mm rotor and rotated at 8 kHz. A cross-polarization contact time of 3 ms was used in combination with a 10 s recycle time.

Results and Discussion

Synthesis. The synthesis of diacetylene-segmented copolymer **1** is schematically depicted in Scheme 2. **1** was synthesized via

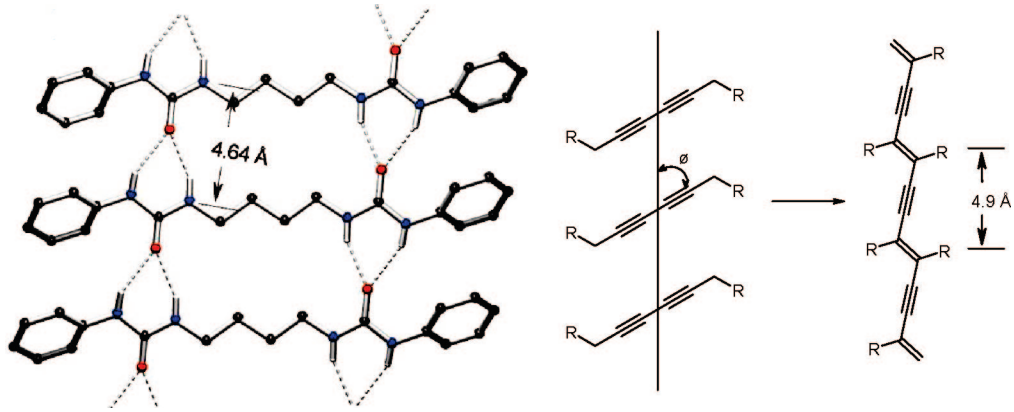


Figure 2. Matching between the repeat distance of bisurea groups as determined with single-crystal X-ray structure of a bisurea model compound[29] (left) and the requirements for the stacking distance for topochemical polymerizations of diacetylenes (right).[28]

the oxidative coupling of 5-hexynoic acid to 5,7-dodecadiynedioic acid with $CuCl_2$. The acid was converted to the 5,7-dodecadiynedioic acidchloride with oxalyl chloride. This was converted to the diisocyanate via a Curtius rearrangement. Compound **1** was finally obtained via a polycondensation of the diisocyanate with amine-terminated polyTHF prepolymer with a M_n of ~2300 g/mol. After precipitation of **1** in hexane, the polymer was obtained as white fluffy fibers. The molecular weight of **1** as determined with SEC was 56×10^3 g/mol.

Cross-Polymerization. As already mentioned in the Introduction, in topochemical polymerizations of diacetylenes the intermolecular spacing is critical. For polymerization to occur, the diacetylene monomers should be aligned at 4.9 Å, the repeat distance in the final polymer (Figure 2).[28] Since this distance is similar to the molecular repeat distance of bisurea model compounds[22,29] that were synthesized to gain more insight into the way copoly(ether urea)s associate (Figure 2), the copoly(ether urea)s could in principle be used to position diacetylenes for topochemical polymerization. Besides the stacking distance, the monomer packing is also characterized by the angle Θ between the diacetylene rod and the stacking axis (Figure 2).

Clear colorless films of **1** were solution cast from chloroform/methanol mixtures. The films were cross-polymerized by means of 254 nm radiation. The conversion of the diacetylene functionality into polydiacetylenes (Figure 1) was followed with UV−vis spectroscopy. Since the electronic transition of the π-electrons of the backbone occurs in the wavelength region of the visible light, the material becomes intensely blue when the conjugated backbone is formed.

After exposure to UV radiation for 24 min, the copolymer had developed an intense absorption band with a maximum at about 665 nm (Figure 3). The relatively sharp absorption band at 665 nm can be attributed to exciton formation, shown to be delocalized over ~8 repeat units.[30] The presence of a second band has often been assigned as a vibrational sideband due to coupling of the valence electronic levels with the vibrations of the backbone double and triple bonds (phonon band),[31] but since at 616 nm it is separated from the main band by only 1200 cm^{-1} instead of 1443 cm^{-1} required by the Raman spectrum (vide infra), assignment as a band of a "purple form", intermediate in order between the blue phase and the red phase,[3] is probably more appropriate. The position and width of the third, broader band at about 530 nm make it more likely that this should be assigned to polydiacetylene groups in a less ordered environment, in a so-called "red phase".[6]

Topochemical cross-polymerization of diacetylenes generally occurs without disrupting the packing and order of the polymer chains. To study this, the extent of hydrogen bonding of the urea groups before and after cross-polymerization of the

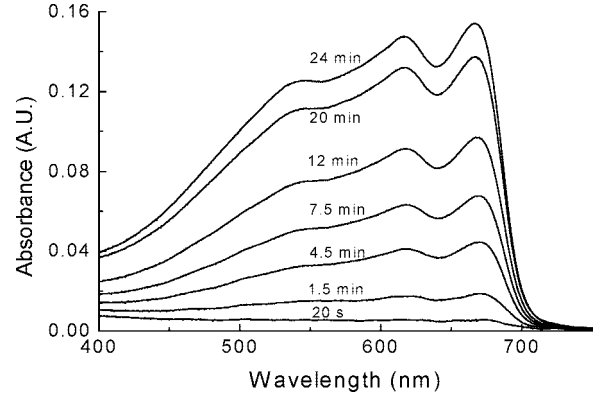


Figure 3. Visible absorption spectra of a thin film of **1** recorded after exposure to 254 nm UV radiation for times of 20 s to 24 min.

diacetylenes was investigated with FT-IR. In the IR spectra of copolymer **1** before and after cross-polymerization, the urea C═O stretch vibration was found at 1615 cm^{-1} and the urea NH vibration at 3326 cm^{-1}. Coleman and Painter reported a temperature-dependent infrared study of a polyurea and model ureas. They concluded that the frequency of both the N−H and the C═O vibration depend strongly on the hydrogen-bonding nature of the urea groups.[32] If the hydrogen-bonding strength between urea groups increases, the frequency of both the N−H and C═O vibrations decreases (from 3350 to 3325 cm^{-1} and 1640 to 1615 cm^{-1}, respectively), in contrast to the amide II band (a combined N−H bending and C−N stretching vibration) at ~1575 cm^{-1}, which increases in frequency. The position of both bands in the unpolymerized and polymerized films thus indicates that strong hydrogen bonds persist after cross-polymerization and that cross-polymerization does not disturb the organization of the hard domains of the copolymer, which is favorable for the mechanical properties of the material. Furthermore, the absence of bands of non-hydrogen-bonded N−H and C═O groups indicate that a similar high degree of phase separation between soft and hard blocks exists as in the pTHF−bisurea segmented copolymers described earlier by us.

In order to understand how cross-polymerization chemistry influences the final properties of the material, knowledge of the extent of cross-polymerization is of critical importance. Cross-polymerized samples of **1** are completely insoluble. Therefore, solid-state NMR was used to estimate the fraction of cross-polymerized diacetylene groups.[13,33] The diacetylene signals decrease upon polymerization. Since the urea carbonyl carbon has no signal overlap with other resonances in the ^{13}C NMR spectrum, it served as an internal reference, against which the diacetylene peak area was followed. In general, cross-polariza-

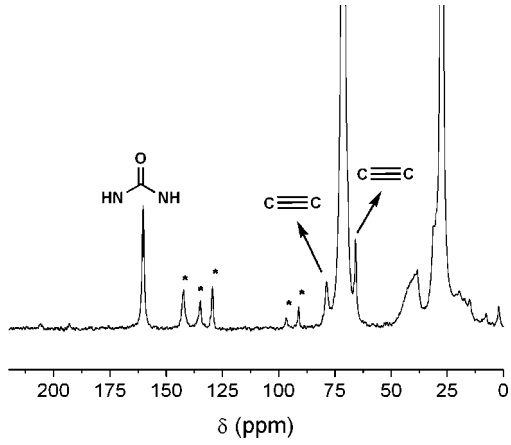


Figure 4. CPMAS ^{13}C NMR spectrum of cross-polymerized diacetylene segmented copoly(ether urea) **1**. The spectrum was obtained with a contact time of 3 ms and a recycle time of 10 s (16 K scans). Spinning sidebands are marked with a star (*).

tion (CP) is not a quantitative NMR technique. In this case, however, the relative intensity ratio between the carbonyl and the diacetylene signals was found to be independent of the CP contact time, which makes the intensity ratio amenable to quantitative analysis. In the CPMAS ^{13}C NMR spectra (Figure 4), the peaks at 30 and 70 ppm were assigned to the ether carbons of the pTHF soft block and the peak at 160 ppm to the carbonyl carbon, while the acetylenic carbons appear at 65 and 78 ppm, with the interior carbon resonating at higher field due to additional shielding provided by the π-electrons. Figure 4 also shows spinning sidebands (SSB) at 142, 134, 129, 96, and 94 ppm, which are respectively associated with the centerbands at 78, 70, 65, 160, and 30 ppm (8 kHz = 64 ppm). The particularly big chemical shift anisotropy of sp-hybridized carbon nuclei explains the large relative intensities of the SSBs of the acetylenic carbon compared to the ether carbons.[34]

Strong overlap between the signals of the ether carbon and the two acetylenic carbons hampers the determination of the extent of cross-polymerization. However, after deconvolution an extent of solid-state cross-polymerization of 10% (±3%) after exhaustive irradiation with 254 nm UV radiation for 8 h was determined from the intensity ratio between the carbonyl and the acetylenic signals. Upon formation of the polydiacetylene backbone, new resonances reflecting the sp- and sp^2-hybridized carbons of the conjugated backbone should appear around 130 and 110 ppm. These however were not observed. An explanation may be the large dispersion of chemical shifts observed for conjugated carbons chains of varying length. The resulting multitude of small signals may be hidden under the baseline noise. Chemical shift fluctuations were also observed for poly(1,11-dodecadiyne) before and after cross-polymerization.[33] In order to confirm the formation of cross-polymerized material from the irradiation of diacetyelene segmented copoly(ether urea) **1**, the Raman spectra of the cross-polymerized material was recorded (excitation wavelength: 631.8 nm). The observed Raman bands at 1443 and 2090 cm^{-1} correspond to characteristic carbon−carbon double bond and triple bond (Figure 5). These values also give an indication on the extent of delocalization on the conjugated backbones since a greater amount of delocalization led to lower bond stretching force constants, thus lowering the frequency of vibration.[10,35a]

Mechanical Properties of 1. The mechanical properties of the diacetylene-segmented copolymer can be modified by cross-polymerization and were determined by tensile testing. The resulting stress−strain curves are displayed in Figure 6 for an unpolymerized sample and a sample that was cross-polymerized for 30 min with 254 nm UV radiation. After this irradiation

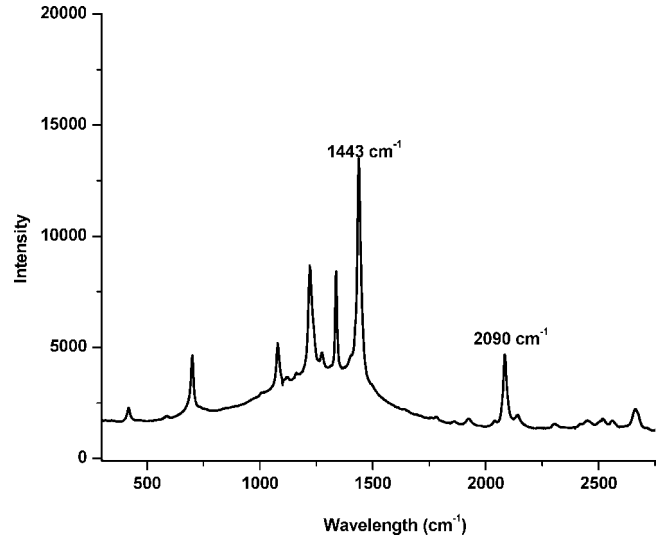


Figure 5. Raman spectrum of cross-polymerized diacetylene segmented copoly(ether urea) **1**. The peaks at 1443 and 2090 cm^{-1} correspond to carbon−carbon double and triple bond in the cross-polymerized material.

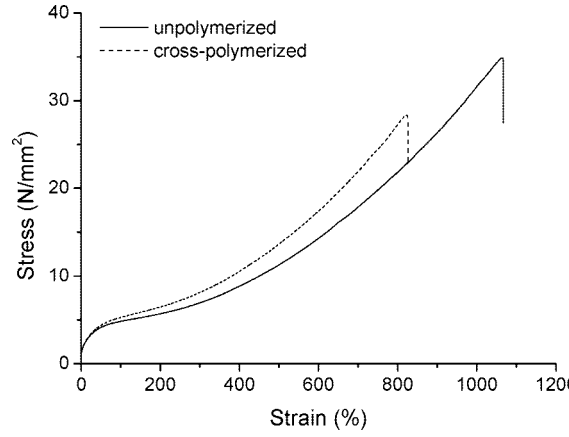


Figure 6. Stress−strain curves of **1** before (—) and after (•••) cross-polymerization for 30 min with 254 nm UV radiation.

time the extent of cross-polymerization is believed to be just slightly higher than after 24 min.

The ultimate strain at break of the cross-polymerized copolymer compared to the nonpolymerized copolymer decreases from 1060 to 820% because the permanent cross-links within the hard domains limit plastic deformation of the sample. Furthermore, the modulus at high strains is higher for the cross-polymerized polymer, indicating stiffening.[18] Because the hard domains do not form an interconnected network, the increase in modulus upon cross-polymerization must be ascribed to increasing hard domain modulus. Xue-Hai and co-workers also reported an increase in Young's modulus upon increasing the rigidity of the hard domains via increases in crystallinity or ionic aggregation in PDMS−polyurethane elastomers.[35b]

Chromic Behavior of 1. Upon elongating the cross-polymerized sample of **1**, a color change from blue to red to yellow was observed. This is a result of transfer of strain to the hard domains of the material: Polydiacetylenes are known to be highly susceptible to the molecular environment of their polymeric backbone. Changes in the molecular environment result in significant changes in the position and shape of the absorption bands since the electronic states of polydiacetylenes are strongly linked to the conformation of the conjugated backbone. It is therefore possible to use the polydiacetylene

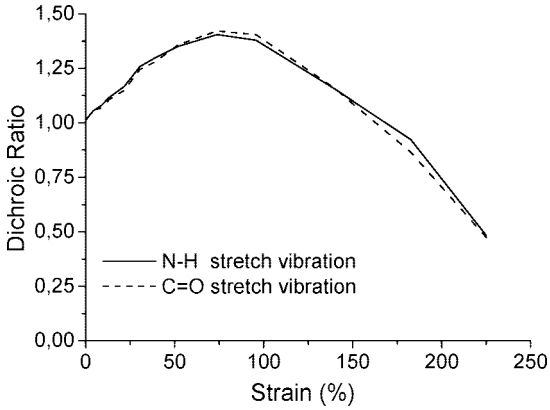


Figure 7. Dichroic ratio as a function of the elongation for the NH (—) and C═O (---) vibrations of **1** that was cross-polymerized for 30 min.

chains as visible monitors of changes that take place within the polymer matrix. Not only can these chromic transitions be induced by mechanical stress, they are also known to be temperature and solvent dependent. The mechanochromic as well as thermo- and solvatochromic behavior of **1** is described in detail in the remainder of this paper.

The mechanochromic behavior was studied using polarized UV spectroscopy and infrared linear dichroism spectroscopy, a technique that has often been used to study the orientation of functional groups within polymers.[36] Infrared linear dichroism spectroscopy was used to investigate mechanical orientation of urea blocks of polymers **1** that was cross-polymerized for 30 min. Using this technique, strain-induced orientation of hard segments in polyether urethane ureas has been shown to be perpendicular to the deformation axis at strains beyond the yield point.[37] Similar trends were observed for copoly(ether urea)s.[22]

In cross-polymerized films of **1**, the dichroic ratio of absorption bands due to stretch vibrations was measured with polarized infrared light parallel and perpendicular to the deformation axis. Upon elongation of 10 μm thin tensile bars, the difference in absorption of linearly polarized infrared light was measured on the N−H stretch vibration at 3326 cm^{-1} and the C═O stretch vibration at 1615 cm^{-1}. Figure 7 shows the dichroic ratio (absorption parallel/perpendicular with respect to the deformation axis) for the two bands as a function of elongation. At low strains, below the yield point (80% strain), the carbonyl and N−H bonds orient parallel to the orientation axis. Above the yield point, however, the hard blocks break up, and the carbonyl and amine orient perpendicular to the deformation axis. This can of course only occur for urea groups that are separated by diacetylene chains instead of polydiacetylenes. As a reminder, only ∼10% of all diacetylene functionalities were cross-polymerized.

The orientation of the polydiacetylenes blocks was studied in further detail with polarized UV spectroscopy. The results are depicted in Figure 8 and strongly resemble the results obtained for Rubner's polyurethane−diacetylene segmented copolymer **d** (**d** in Scheme 1).[19a] In the spectra recorded with vertically polarized light (Figure 8a) a continuous shift of the absorption band to higher energies was observed. Furthermore, the band broadened and became poorly defined as a function of increasing strain. Even at a strain of 20% there already is a blue shift indicating that stress is transmitted to the hard domain resulting in a change in the molecular environment of the polydiacetylene backbone. Above 240% strain only a very broad featureless absorption band with a maximum around 490 nm was observed, suggesting that the hard domains become highly disordered.

In the spectra recorded with a horizontal polarizer (perpendicular to the stretch direction) (Figure 8b) the shift of the excitonic peak was less dramatic. However, the intensity of the overall absorption band decreased significantly relative to the band observed for vertically polarized light, indicating that the polydiacetylene chains are oriented along the stretch direction as a function of elongation. The blue shift for the excitonic peak was less dramatic and retained its shape to higher strains for horizontally polarized light. This indicates that the polydiacetylene chains remaining perpendicular to the elongation direction experience less stress than the chains that align parallel to the stretch direction.

To get a better understanding of residual hard block orientation and the reversibility of the deformation process, visible absorption spectra were recorded of **1** after relaxation from different increasing strain levels with a vertical polarizer (parallel to deformation axis) and a horizontal polarizer (perpendicular to deformation axis). The results are depicted in Figure 9. The shape of the original absorption band was more or less recovered after relaxing from strains up to 80%. Only a small decrease in intensity of the excitonic peak as well as the appearance of a very small higher energy band was observed. As the material was subjected to higher strain levels, the intensity of the excitonic peak decreased significantly, and furthermore the intensity of the higher energy absorption band increased strongly and became more intense than the excitonic peak. Apparently, the hard domains remained structurally intact up to ∼80% strain. Above 80% strain, a deformation mechanism set in, resulting in stress being transmitted to the hard domains of the material. Those results are in agreement with the infrared dichroism results: up to the yield point (80% strain) the urea groups orient parallel to the deformation axis.

This orientation process is reversible. Above the yield point, however, the hard blocks break up and the carbonyl and N−H bonds become oriented perpendicular to the deformation axis. As a result of this mechanism, stress is being transmitted to the polydiacetylene blocks permanently.

As mentioned before, the conjugated backbone is sensitive to changes in side-group organization. One way to achieve this is with temperature. Therefore, it should be possible to further modify the optical properties of the polydiacetylenes by changes in temperature. UV measurements were performed on a thin film of cross-polymerized elastomer of **1**, which was heated to different temperatures and then cooled back to room temperature. An irreversible shift of the absorption band to higher energies was observed during temperature cycling (Figure 10).

Even after heating to 40 °C a significant increase of the higher energy absorption band at 530 nm was observed. A featureless absorption band was observed when the sample was heated to 120 °C. This high-energy absorption band is similar to that exhibited by a soluble polydiacetylene when it is dissolved in a thermodynamically good solvent.[38] Therefore, it can be concluded that this is an example of a thermally induced disordering process in which the polydiacetylene chains are completely disordered upon heating similar to the solution state.[39] In contrast to the mechanochromic behavior of **1**, which resembled Rubner's polyurethane−diacetylene segmented copolymer **d** (**d** in Scheme 1), the irreversible thermochromic behavior of **1** resembles the results obtained for Rubner's polyurethane−diacetylene segmented copolymer **a** (**a** in Scheme 1). Whereas cross-polymerized **1** and Rubners material **a** show spectral changes during heating that are the result of a disordering process, the spectral changes that are observed during the heating of Rubner's material **d** take place without incurring a significant amount of disorder in the system. Therefore, this system shows reversibility up to 130 °C but becomes permanently irreversible beyond this point. As a

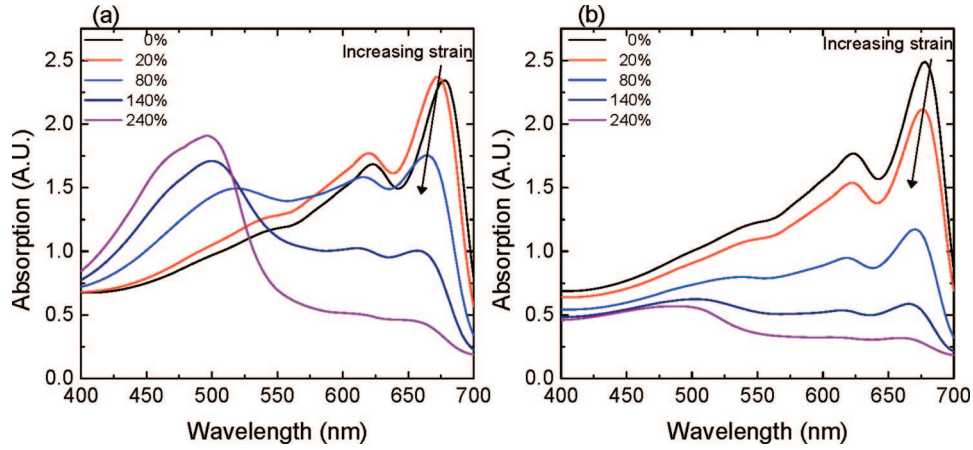


Figure 8. Visible absorption spectra of **1** as a function of increasing strain with (a) vertically polarized light (parallel to deformation axis) and (b) horizontally polarized light (perpendicular to deformation axis). For clarity reasons, not all spectra are shown.

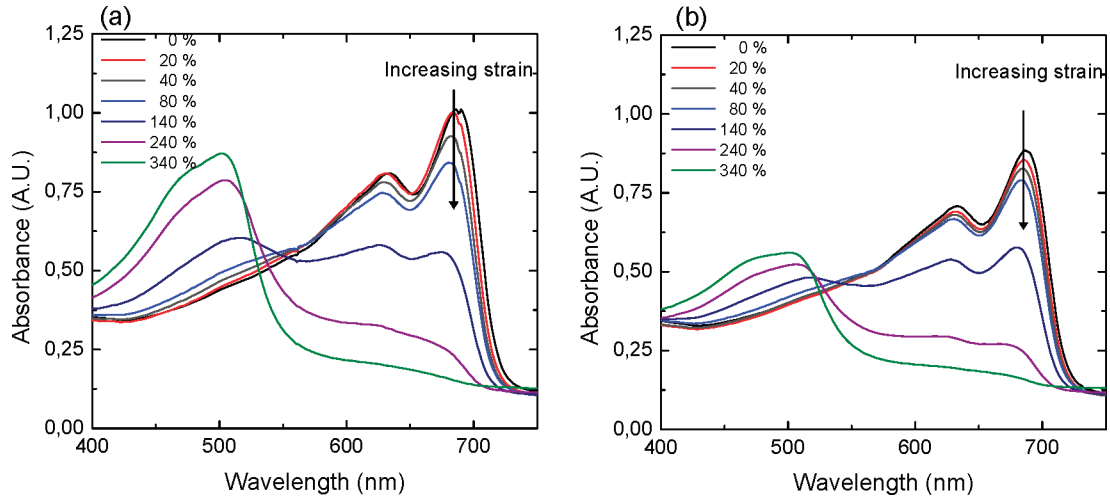


Figure 9. Visible absorption spectra of **1** recorded after relaxation from the indicated strain levels with (a) vertically polarized light (parallel to deformation axis) and (b) horizontally polarized light (perpendicular to deformation axis).

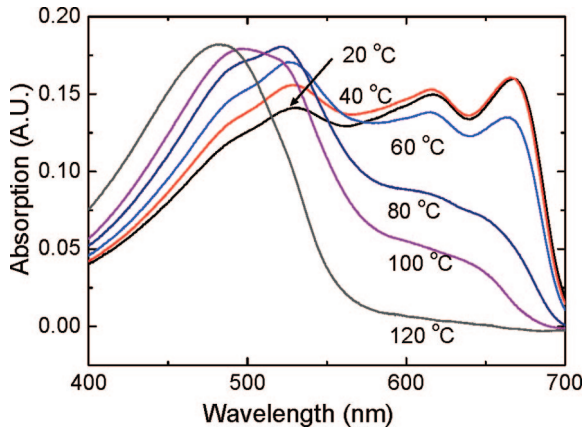


Figure 10. Visible absorption spectra of thin films of **1** that were cross-polymerized for 30 min with 254 nm UV radiation recorded at 20 °C after being heated to the indicated temperatures for 5 min.

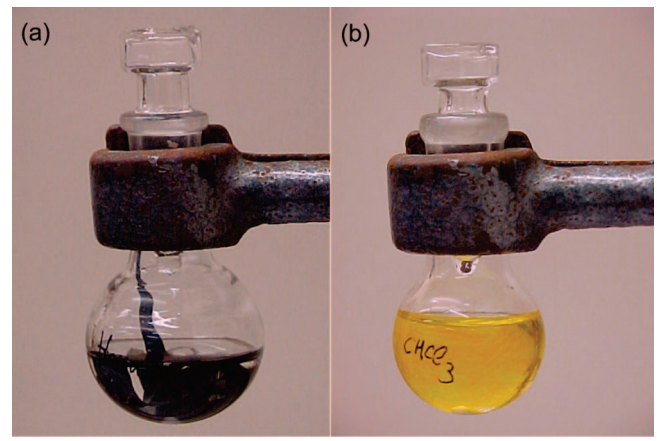


Figure 11. Solvatochromic behavior of **1** in (a) hexane and (b) chloroform.

comparison, cross-polymerized **1** only shows reversible behavior up to 40 °C.[11]

A similar irreversible color change was also observed when the material was swollen in different solvents (Figure 11). In hexane, a thermodynamically bad solvent, the material did not swell at all and the material remained blue, indicating that there were no conformational changes of the hard domains and consequently of the conjugated backbone (Figure 11a).

However, in chloroform, a thermodynamically good solvent, the material swelled due to dissolution of the pTHF soft block (Figure 11b). Because of the changes in the molecular environment of the polydiacetylene, they became more disordered, the primary excitonic peak broadened, and the higher energy bands became obscured by a broad absorption. As a result of this, the color of the material changed from blue to yellow. Once in the disordered state, it was not possible to go back to the ordered

state by replacing the chloroform with hexane. Even upon removal of the solvent, the material remained yellow.

Conclusions

A diacetylene segmented copoly(ether urea) has been prepared, with a reactive diacetylene functionality residing in the hard segment domains of the elastomer. The diacetylene groups provide a means to topochemically cross-link TPE **1** in the solid state using UV radiation. With the development of a diacetylene segmented copoly(ether urea), the study of this class of thermoplastic elastomers has been expanded to include mechano-optical and chromic properties and the mechanical properties of the copoly(ether urea) could be altered, without altering its hard block morphology. The cross-polymerization reaction yielded highly ordered polydiacetylenes, as is evident from a maximum absorption in the product 665 nm. A similar high wavelength maximum was observed upon photopolymerization of a bisurea organogel with the same propylene spacer between the diacetylene and the urea unit as in **1**,[23b] while in organogels obtained from sterically hindered bisureas[23b] or peptide amphiphiles[23a] the maximum absorption is found at a lower wavelength. The yield of the topochemical cross-polymerization was ~10% (±3%), which is relatively low. Photopolymerization of the analogous bisurea organogel was reported to enable the formation of highly conjugated fibers, but the conversion was not given.[23b]

The orientation of the polydiacetylenes blocks was studied in detail with polarized UV spectroscopy. Even at low strains a relatively large blue shift of the absorption maximum was observed, indicating that stress is transmitted to the hard domain resulting in a change in the molecular environment of the polydiacetylene backbone. The decrease in intensity of the overall absorption band observed for horizontally polarized light relative to the band observed for vertically polarized light indicates that the polydiacetylene chains orient along the stretch direction as a function of elongation. Infrared linear dichroism spectroscopy was used to study the molecular orientation of the bisurea groups of the cross-polymerized material during tensile testing. A deformation process similar to copoly(ether urea)s was observed: Below the yield point (80% strain), the hard domains tilt in a direction parallel to the deformation axis. Above the yield point, however, fragmentation and irreversible reorganization of the hard domains occur, resulting in perpendicular orientation. As a result of this reorganization process, an irreversible mechanochromic transition was observed at strains larger than 80%. As a comparison, Rubner's diacetylene segmented polyurethane **d** was found to be reversible up to 350% strain. This large difference is a consequence of the fact that in polyurethane **d** disruption of hard domain ordering occurs at much higher strains than in polymer **1** (above 300%). The optical properties of the diacetylene-segmented copolymer were further modified by temperature. An irreversible shift of the absorption band to higher energies was observed during temperature cycling, with a resultant featureless absorption band, indicative of an order−disorder transition.

The mechanochromic and thermochromic behavior of **1** make these materials highly useful for the design of optical sensors for respectively stress and temperature. A drawback of this system is the irreversible nature of the transitions at higher strains. Improved molecular design of diacetylene-segmented system might result in the ability to control the optical and mechanical properties. This may be accomplished by further functionalization of copoly(ether urea)s and a systematic variation of the chemical structure of both hard and soft blocks to achieve the desired range of chromic response.

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References and Notes

(1) Wegner, G. *Z. Naturforsch.* **1969**, *24b*, 824–832.
(2) (a) Spevak, W.; Nagy, J. O.; Charych, D. H. *Adv. Mater.* **1995**, *7*, 85. (b) Sasaki, D. Y.; Carpick, R. W.; Burns, A. R. *J. Colloid Interface Sci.* **2000**, *229*, 490.
(3) Okada, S.; Peng, S.; Spevak, W.; Charych, D. *Acc. Chem. Res.* **1998**, *31*, 229–239.
(4) Lu, Y.; Yang, Y.; Sellinger, A.; Lu, M.; Huang, J.; Fan, H.; Haddad, R.; Lopez, G.; Burns, A. R.; Sasaki, D. Y.; Shelnutt, J.; Brinker, C. J. *Nature (London)* **2001**, *410*, 913–917.
(5) Bloor, D.; Chance, R. R. *Polydiacetylenes: Synthesis, Structure, and Electronic Properties*; Martinus Nijhoff: Dordrecht, The Netherlands, 1985.
(6) Carpick, R. W.; Sasaki, D. Y.; Marcus, M. S.; Eriksson, M. A.; Burns, A. R. *J. Phys.: Condens. Matter* **2004**, *16*, R679–R697.
(7) (a) Lee, D.; Sahoo, S.; Cholli, A.; Sandman, D. *Macromolecules* **2002**, *35*, 4347–4355. (b) Sandman, D. J. *Trends Polym. Sci.* **1994**, *2*, 44–55.
(8) (a) Orchard, B. J.; Tripathy, S. K. *Macromolecules* **1986**, *19*, 1844–1850. (b) Eckhardt, H.; Boudreaux, D. S.; Chance, R. R. *J. Chem. Phys.* **1986**, *85*, 4116–4119.
(9) Thakur, M.; Lando, J. B. *Macromolecules* **1983**, *16*, 143–146.
(10) Rubner, M. F. *Macromolecules* **1986**, *19*, 2114–2128.
(11) Rubner, M. F. *Macromolecules* **1986**, *19*, 2129–2138.
(12) (a) Liang, R. C.; Lai, W. Y. F.; Reiser, A. *Macromolecules* **1986**, *19*, 1685–1689. (b) Liang, R. C.; Reiser, A. *J. Polym. Sci., Part A: Polym. Chem.* **1987**, *25*, 451–465.
(13) Beckham, H. W.; Rubner, M. F. *Macromolecules* **1989**, *22*, 2130–2138.
(14) (a) Spevak, W.; Nagy, J. O.; Charych, D. H.; Schaefer, M. E.; Gilbert, J. H.; Bednarski, M. D. *J. Am. Chem. Soc.* **1993**, *115*, 1146–1147. (b) Charych, D. H.; Nagy, J. O.; Spevak, W.; Bednarski, M. D. *Science* **1993**, *261*, 585–588.
(15) Pan, J. J.; Charych, D. *Langmuir* **1997**, *13*, 1365–1367.
(16) Kolusheva, S.; Shahal, T.; Jelinek, R. *J. Am. Chem. Soc.* **2000**, *122*, 776–780.
(17) Ahn, D. J.; Chae, E.-H.; Lee, G. S.; Shim, H.-Y.; Chang, T.-E.; Ahn, K.-D.; Kim, J.-M. *J. Am. Chem. Soc.* **2003**, *125*, 8976–8977.
(18) (a) Nallicheri, R. A.; Rubner, M. F. *Macromolecules* **1990**, *23*, 1005–1016. (b) Nallicheri, R. A.; Rubner, M. F. *Macromolecules* **1990**, *23*, 1017–1025. (c) Hammond, P. T.; Nallicheri, R. A.; Rubner, M. F. *Mater. Sci. Eng., A* **1990**, *126*, 281–287.
(19) (a) Nallicheri, R. A.; Rubner, M. F. *Macromolecules* **1991**, *24*, 517–525. (b) Nallicheri, R. A.; Rubner, M. F. *Macromolecules* **1991**, *24*, 526–529.
(20) (a) Day, R. J.; Hu, X.; Stanford, J. L.; Young, R. J. *Polym. Bull.* **1991**, *27*, 353–359. (b) Stanford, J. L.; Young, R. J.; Day, R. J. *Polymer* **1991**, *32*, 1713–1725.
(21) Versteegen, R. M.; Sijbesma, R. P.; Meijer, E. W. *Macromolecules* **2005**, *38*, 3176–3184.
(22) Versteegen, R. M.; Kleppinger, R.; Sijbesma, R. P.; Meijer, E. W. *Macromolecules* **2006**, *39*, 772–783.
(23) (a) Hsu, L.; Cvetanovich, G. L.; Stupp, S. I. *J. Am. Chem. Soc.* **2008**, *130*, 3892–3899. (b) Dautel, O. J.; Robitzer, M.; Lere-Porte, J. P.; Serein-Spirau, F.; Moreau, J. J. E. *J. Am. Chem. Soc.* **2006**, *128*, 16213–16223.
(24) Dean, C. S.; Tarbell, D. S.; Friederang, A. W. *J. Org. Chem.* **1970**, *35*, 3393–3397.
(25) Seher, A. *Justus Liebigs Ann. Chem.* **1954**, *589*, 222–238.
(26) Masuda, M.; Hanada, T.; Okada, Y.; Yase, K.; Shimizu, T. *Macromolecules* **2000**, *33*, 9233–9238.
(27) Earl, R. A.; Vollhardt, K. P. C. *J. Org. Chem.* **1984**, *49*, 4786–4800.
(28) Enkelmann, V. In *Polydiacetylenes: Advances in Polymer Science*; Springer-Verlag: New York, 1984; Vol. 63.
(29) Koevoets, R. A.; Versteegen, R. M.; Kooijman, H.; Spek, A. L.; Sijbesma, R. P.; Meijer, E. W. *J. Am. Chem. Soc.* **2005**, *127*, 2999–3003.
(30) Kollmar, C.; Ruhle, W.; Frick, J.; Sixl, H.; Schutz, J. U. V. *J. Chem. Phys.* **1988**, *89*, 55–62.
(31) Batchelder, D. N.; Bloor, D. *J. Phys. C* **1982**, *15*, 3005–3018.
(32) Coleman, M. M.; Sobkowiak, M.; Pehlert, G. J.; Painter, P. C.; Iqbal, T. *Macromol. Chem. Phys.* **1997**, *198*, 117–136.
(33) Havens, J. R.; Thakur, M.; Lando, J. B.; Koenig, J. L. *Macromolecules* **1984**, *17*, 1071–1074.
(34) Leyerla, J. R. In *Polymers, Part A: Molecular Structure and Dynamics*; Academic Press: New York, 1980; Vol. 16,Chapter 4.
(35) (a) Shand, M. L.; Chance, R. R.; LePostollec, M.; Schott, M. *Phys. Rev. B* **1982**, *25*, 4431–4436. (b) Xue-Hai, Y.; Nagarajan, M. R.;

Grasel, T. G.; Gibson, P. E.; Cooper, S. L. *J. Polym. Sci., Part B: Polym. Phys.* **1986**, *24*, 2681–2702.
(36) (a) Lee, H. S.; Hsu, S. L. *J. Polym. Sci., Part B: Polym. Phys.* **1994**, *32*, 2085–2098. (b) Lee, H. S.; Ko, J. H.; Song, K. S.; Choi, K. H. *J. Polym. Sci., Part B: Polym. Phys.* **1997**, *35*, 1821–1832. (c) Kischel, M.; Kisters, D.; Strohe, G.; Veeman, W. S. *Eur. Polym. J.* **1998**, *34*, 1571–1577. (d) Van Asselen, O. L. J.; van Casteren, I. A.; Goossens, J. G. P.; Meijer, H. E. H. *Macromol. Symp.* **2004**, *205*, 85–94.
(37) Bonart, R. *J. Macromol. Sci., Part B* **1968**, *2*, 115–138.
(38) Patel, G. N.; Chance, R. R.; Witt, J. D. *J. Chem. Phys.* **1979**, *70*, 4387–4392.
(39) Wenz, G.; Müller, M. A.; Schmidt, M.; Wegner, G. *Macromolecules* **1984**, *17*, 837–850.

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