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# Articles

## Synthesis and Optical Properties of Chiral Polydiacetylenes

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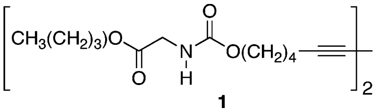
ABSTRACT: Chiral diacetylenes featuring ester and urethane groups are readily prepared from amino acids and diynediols. The ability of the butadiyne moiety to undergo topotactic polymerization is dependent on both the length of the chain to the urethane group and the size of the amino acid. In some cases, the polymerization proceeds as well as the well-studied achiral parent compound, 4BCMU. The polymers form yellow solutions in good solvents where the chains adopt a random-coil configuration. Addition of a nonsolvent changes the solution color to red as the chains adopt a helical conformation.

### Introduction

Most of the critical macromolecules in the biological world are built from chiral components.[1] The asymmetry of the repeating unit is critical to both the structures and functions of these polymers. Synthetic polymers possessing chirality are less common, but they are of interest in applications ranging from chiral separations to biomimetic materials to optical devices.[2] The macromolecular chirality may be a result of stereocenters along the polymer backbone or on pendant groups or by the formation of chiral secondary structures such as helicies. Helical structures may result from a regular array of stereocenters but may also be induced by steric requirements or by the addition of chiral additives.[3] Much current research in this area concerns efforts to control the chiroptical properties of helical polymers through various external stimuli with an eye toward the development of optical, magnetic, and electronic devices.[4]

Polymers containing $\pi$-conjugated backbones are a class of materials that feature many important physical, electronic, and optical properties. Several examples of helical polymers of this type have been reported, including polyacetylenes,[5] polyarylenes, and poly(areneethynylene)s.[4] We are interested in preparing helical polymers containing a polydiacetylene (pDA) backbone.

Achiral pDAs display a variety of interesting chromatic behaviors in both the solution and solid states, including solvatochromism, thermochromism, mechanochromism, and others.[6] The dramatic chromatic changes seen in solution, particularly in the *n*-butoxycarbonylmethylurethane family, have provided fertile ground for investigations over many years.[7] Particularly well studied is the 4BCMU derivative, **1**. This material readily reacts to give a high molecular weight (ca. 1000 repeat units), soluble material in excellent yield. The 4BCMU moiety has even been called a “polymerogenic” group, useful for engineering of asymmetric DAs having a “head group” of interest on one side of the DA and a 4BCMU “tail” to ensure the proper crystalline packing needed for topotactic polymerization.[8]



**1**

There are few examples of chiral pDAs known, and virtually no investigations of pDA chiroptical properties have been reported.[9] There are probably two principal reasons for this. Polymerization of DAs usually (though not always) involves a topotactic reaction with rather strict geometrical requirements, as shown in Figure 1.[10] This organization can be achieved in the solid state,[10] thin films,[11] liposomes,[6] and self-assembled monolayers,[12] but the polymerization reaction is highly sensitive to the substituents on the 1,3-butadiyene monomers. In addition, many pDAs are infusible and insoluble, limiting the candidates suitable for analysis.

Despite these challenges, some soluble, chiral pDAs have been prepared. Early work focused on the polymerization behavior of a handful of pDAs having terminal phenylurethane groups.[13] More recently, DA-containing lipids that feature pendant chiral headgroups have been prepared for use in liposome biosensors[6a] and gelators.[14] Amino acids have proven to be a versatile source of chirality in such systems. For example, amino acid-terminated DA−lipids have been prepared that spontaneously form helical ribbons. These structures are sensitive to both pH and temperature, with higher temperatures or pH causing fraying of the ribbons, a blue to red color change, and changes in the CD spectrum.[15] Related lipids have been incorporated into liposomes to prepare colorometric sensors for a variety of biomolecules.[6a]

Here we report the preparation of seven chiral DAs related to the BCMU family that incorporate the amino acids alanine and phenylalanine.

### Experimental Section

**Materials and Methods.** All chemicals and solvents were purchased from commercial houses. Unless otherwise noted, solvents were purified before use either over a solid-phase purifier or by distillation from appropriate drying agent. All reactions were

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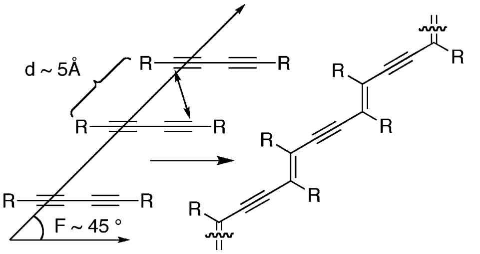

**Figure 1.** Geometrical requirements for DA polymerization.

carried out under dry nitrogen. $^1$H NMR and $^{13}$C NMR nuclear magnetic resonance (NMR) spectra were acquired using a Varian INOVA 500 spectrometer at room temperature. In all cases, deuterated chloroform ($CDCl_3$) was used as the solvent. Fourier transform infrared (FTIR) measurements were performed with a Nicolet Magna-IR 750 spectrometer. Raman data were collected on a Nicolet 6700 FTIR equipped with a NXR Raman module with an excitation frequency of 1064 nm. UV−vis spectra were recorded with a Varian Cary 100 Bio spectrophotometer. Thermal properties of monomers and polymers were analyzed by Perkin-Elmer DSC 7 and TGA 7 instruments. A 5 °C/min heating/cooling rate was used, and a nitrogen purge was maintained over the samples at all times. Circular dichroism (CD) spectra were obtained using a Jasco J-710 spectropolarimeter. GPC data were collected on chloroform solutions of polymers on a Waters 2690 GPC and compared to polystyrene standards.

**Monomer Synthesis.** *General Method for Preparation of Esters.* This method is similar to the previously reported route to methyl and isopropyl esters of amino acids.[16] Anhydrous alcohol (either butanol or methanol, 100 mL) was saturated with dry HCl at 0 °C. The amino acid (1 g) was added to this solution at the same temperature, and the resulting solution was then heated to reflux. The progress of the reaction was monitored by TLC. After the completion of the reaction, excess alcohol was removed under reduced pressure. The solid residue was dissolved in water and neutralized with cold solution of $NaHCO_3$ (5%). The resulting aqueous solution was extracted with $CH_2Cl_2$ ($2 \times 50$ mL). The organic layers were combined and dried over anhydrous $Na_2SO_4$, the solvent was removed, and the products were purified by column chromatography.

*5,7-Dodecadiyn-1,12-bis(chloroformate).* To a stirring solution of trichloromethyl chloroformate (1 mL, 8.2 mmol) in $CH_2Cl_2$ (50 mL) was added activated charcoal (0.5 g). After 1 h, the suspension was cooled to −10 °C, and a solution of 5,7-dodecadiyn-1,12-diol (1 g, 5.1 mmol) in $CH_2Cl_2$ (30 mL) was added dropwise over 15 min. The resulting mixture was allowed to warm up to room temperature and was stirred overnight. The mixture was filtered through a thin pad of celite and evaporated under vacuum, giving a yellow oil (1.5 g, 91%) which was pure enough for further reactions. IR (neat): 1770, 1138 cm$^{-1}$. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 1.60 (m, 4H, $2 \times CH_2$), 1.82 (m, 4H, $2 \times CH_2$), 2.30 (t, $J = 7$ Hz, 4H, $2 \times CH_2$), 4.31 (t, $J = 6.5$ Hz, 4H, $2 \times CH_2$). $^{13}$C NMR ($CDCl_3$): $\delta$ 18.6, 24.2, 27.3, 65.8, 71.4, 76.4, 150.4.

*3,5-Octadiyn-1,8-bis(chloroformate).* This compound was prepared by the same method as was 5,7-dodecadiyn-1,12-bis(chloroformate) and used without further purification.

*General Method for Preparation of Diacetylenes.* To a stirred solution of either 5,7-dodecadiyn-1,12-bis(chloroformate) or 3,5-octadiyn-1,8-bis(chloroformate) (2.4 mmol) in $CH_2Cl_2$ (10 mL) at −10 °C a solution of either the methyl or butyl esters of an L-amino acid (4.3 mmol) and pyridine (4.8 mmol) in $CH_2Cl_2$ (5 mL) was added dropwise over 10 min. The progress of reaction was monitored with TLC. The reaction mixture was then washed with $NaHCO_3$ (5%), dried over anhydrous $Na_2SO_4$, and evaporated under vacuum, and the product was purified by column chromatography.

*2MCAU*, ***2***. Yield: 58%; mp 67−8 °C. IR (neat): 3343, 2954, 1742, 1692, 1527, 1256, 1209, 1079 cm$^{-1}$. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ (ppm) 1.42 (d, $J = 6.5$ Hz, 3H, $CH_3$), 2.59 (t, $J = 7.0$ Hz, 2H, $CH_2CH_2$), 3.76 (s, 3H, $CH_3$), 4.16 (t, 2H, $OCH_2CH_2$), 4.36 (m, 1H, CH), 5.31 (d, H, NH). $^{13}$C NMR ($CDCl_3$): $\delta$ (ppm) 19.24, 20.78, 50.33, 53.30, 63.20, 67.15, 74.40, 156.22, 174.19.

*2MCPU*, ***3***. Yield: 68%; mp 91−2 °C. IR (neat): 3325, 2956, 1738, 1696, 1538, 1262, 1217, 701 cm$^{-1}$. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ (ppm) 2.54 (t, $J = 6.5$ Hz, 2H, $CH_2$), 3.09 (m, $J = 6.0$ Hz, 2H, $CH_2Ph$), 3.70 (s, 3H, $CH_3$), 4.11 (m, 2H, $OCH_2CH_2$), 4.60 (t, $J = 6.0$ Hz, 1H, CH), 5.17 (d, 1H, NH), 7.09 (d, $J = 6.5$ Hz, 2H, $2 \times$ H arom), 7.28 (m, 3H, $3 \times$ H arom). $^{13}$C NMR ($CDCl_3$): $\delta$ (ppm) 20.81, 39.01, 53.08, 55.52, 63.21, 67.24, 74.37, 127.97, 129.32, 130.18, 136.57, 155.99, 172.71.

*2BCAU*, ***4***. Yield: 72%; mp 61−2 °C. IR (neat): 3334, 2960, 2874, 1745, 1695, 1532, 1258, 1208, 1179, 1082 cm$^{-1}$. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ (ppm) 0.92 (t, $J = 7.5$ Hz, 3H, $CH_3$), 1.37 (m, $J = 7.5$ Hz, 2H, $CH_2CH_3$, $J = 7.5$ Hz, 3H, $CHCH_3$), 1.63 (m, 2H, $CH_2CH_2CH_2CH_3$), 2.57 (t, $J = 6.5$ Hz, 2H, $CH_2CH_2$), 4.14 (m, 2H, $OCH_2CH_2$; 2H, $OCH_2CH_2CH_2CH_3$), 4.32 (t, $J = 7.5$ Hz,-1H, CH), 5.28 (d, H, NH). $^{13}$C NMR ($CDCl_3$): $\delta$ (ppm) 14.31, 19.23, 19.67, 20.95, 31.27, 50.44, 63.21, 66.16, 67.15, 74.52, 156.10, 173.79.

*2BCPU*, ***5***. Yield: 59%; mp 35−6 °C. IR (neat): 3342, 2959, 1736, 1692, 1529, 1256, 1194, 1072, 700 cm$^{-1}$. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ (ppm) 0.92 (t, $J = 7.5$ Hz, 3H, $CH_3$), 1.33 (m, 2H, $CH_2CH_3$), 1.58 (m, 2H, $CH_2CH_2CH_2CH_3$), 2.57 (t, $J = 6.5$ Hz, 2H, $CH_2CH_2$), 3.11 (m, 2H, $CH_2Ph$), 4.12 (m, 2H, $CH_2CH_2O$; 2H, $OCH_2CH_2CH_2CH_3$), 4.61 (m,1H, CH), 5.21 (d, H, NH). $^{13}$C NMR ($CDCl_3$): $\delta$ (ppm) 14.33, 19.73, 20.79, 31.18, 39.27, 55.70, 63.40, 66.22, 67.25, 74.43, 127.81, 129.28, 130.02, 136.54, 156.04, 172.21.

*4MCAU*, ***6***. Yield: 64%; mp 74−5 °C. IR (neat): 3320, 2958, 1733, 1687, 1535, 1275, 1229, 1070 cm$^{-1}$. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ (ppm) 1.41 (d, $J = 7.0$ Hz, 3H, $CH_3$), 1.60 (m, 2H, $CH_2CH_2CH_2CH_2$), 1.74 (m, 2H, $CH_2CH_2CH_2CH_2$), 2.30 (t, 2H, $CH_2C$), 3.76 (s, 3H, $CH_3$), 4.09 (t, 2H, $J = 6.5$ Hz, 2H, $CH_2O$), 4.37 (m,1H, CH), 5.17 (d, H, NH). $^{13}$C NMR ($CDCl_3$): $\delta$ (ppm) 19.39, 19.56, 25.43, 28.90, 50.31, 53.24, 65.27, 66.44, 77.60, 156.78, 174.09.

*4MCPU*, ***7***. Yield: 61%; mp 52−3 °C. IR (neat): 3336, 2952, 1742, 1685, 1525, 1213, 1038, 700 cm$^{-1}$. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ (ppm) 1.55 (m, $J = 7.0$ Hz, 2H, $CH_2$), 1.68 (m, 2H, $CH_2$), 2.26 (t, 2H, $J = 7.0$ Hz, $CH_2$), 3.07 (m, 2H, $CH_2Ph$), 3.70 (s, 3H, $CH_3$), 4.04 (t, $J = 6.0$ Hz, 2H, $OCH_2CH_2CH_2CH_2$), 4.61 (d, H, CH), 5.07 (d, H, NH), 7.09 (d, $J = 7.0$ Hz, 2H, $2 \times$ H arom), 7.28 (m, 3H, $3 \times$ H arom). $^{13}$C NMR ($CDCl_3$): $\delta$ (ppm) 19.56, 25.39, 28.98, 39.07, 53.11, 55.57, 65.41, 66.65, 127.94, 129.31, 130.16, 136.56, 156.74, 172.99.

*4BCAU*, ***8***. Yield: 69%. This compound has been previously reported.[17]

*Polymerization.* For UV polymerization experiments, each diacetylene monomer was exposed to irradiation from a high-intensity UV (254 nm) lamp while on a cold plate set to 5 °C. For bulk polymerization, the monomers were sealed under $N_2$ in glass ampules and were exposed to $\gamma$-irradiation (50 mrad) from a $^{60}$Co source. The resulting material was thoroughly extracted with benzene to remove residual monomer and small oligomers.

## Results and Discussion

**Monomer Synthesis and Polymerization.** The preparation of the bis(urethane)diacetylene monomers **2**−**8** was straightforward, as shown in Figure 2. The commercially available acetylene alcohols were dimerized by a copper-catalyzed Glaser coupling, followed by conversion to the corresponding chloroformate. Treatment with esters of either alanine or phenylalanine gave the products in good yields (58−72%). NMR experiments with a chiral lanthanide shift reagent (europium(III) 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedionate, Eu(fod)$_3$) demonstrate that the stereocenters are unaffected by the reaction conditions, giving products with an enantiopurity >98% in all cases.[18] The compounds are named using a modification of the designations commonly used for the *n*BCMU family. The

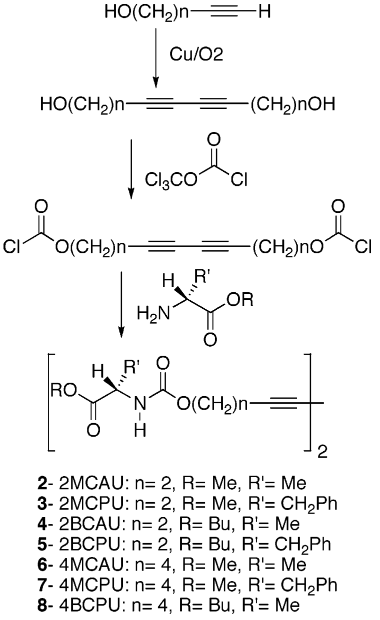

**Figure 2.** Synthesis and structure of new DAs **2**−**8**.

**Table 1. Solid-State Polymerization Behavior of DA Monomers**

| derivative | UV | $\gamma$ | yield | $M_N$ |
|---|---|---|---|---|
| 4BCMU (**1**) | blue | blue | 48 | $1.8 \times 10^5$ |
| 2MCAU (**2**) | orange | purple | 35 | $1.1 \times 10^5$ |
| 2MCPU (**3**) | pink | purple | 64 | $2.6 \times 10^6$ |
| 2BCAU (**4**) | yellow | pink | 0 | N/A |
| 2BCPU (**5**) | orange | purple | 0 | N/A |
| 4MCAU (**6**) | purple | blue | 41 | $2.8 \times 10^6$ |
| 4MCPU (**7**) | red | red | 19 | N/A |
| 4BCAU (**8**) | red | purple | 64 | $2.7 \times 10^6$ |

number “*n*” refers to the number of methylene units between the butadiyne moiety and the carbamate oxygen (Figure 2). The first letter describes the terminal ester (either butyl, B, or methyl, M). The second letter is always C, for “carbonyl”, while the third letter indicates the amino acid used (either alanine, A, or phenylalanine, P). The last letter is always U, for urethane.

A series of seven pDAs were prepared for this study in which the groups R and R′, as well as the length of the linker chain, were systematically varied. An eighth compound, 4BCPU, was also prepared but could only be isolated as a viscous oil.[16] As prepared, the DAs are a light yellow color, but several of them quickly begin to change under ambient light. Exposure to UV light caused a deepening of the color change in most cases, to a red or blue color. This is typical of DAs undergoing topotactic polymerization, as shown in Figure 2. As is also typical, the polymerization only occurs on the surface of the solids, since the high absorption cross section of the polymer prevents penetration of the light into the bulk solid. Therefore, the samples were sealed in glass ampules under nitrogen and exposed to $\gamma$-irradiation. The results of these experiments are shown in Table 1. The columns labeled “UV” and “$\gamma$” list the color of the crude product after exposure to radiation. The “yield” column gives the percent yield after extracting out residual monomer and small oligomers, while the column $M_N$ gives the number-averaged molecular weight of the high molecular weight fraction. This value was obtained versus a polystyrene standard. No attempts were made to optimize the polymerization conditions. For comparison, the well-studied 4BCMU was irradiated under identical conditions (Table 1, first entry).

All of the new diacetylenes show sensitivity to ambient light, with the exception of compound **3**. Upon exposure to $\gamma$-irradiation, all showed color changes consistent with the 1,4-topotactic polymerization reaction that is seen with other members of the BCMU family. As has been observed in previous studies, a four-carbon linker between the butadiyne moiety and the urethane group generally results in better polymerization than a two-carbon linker (for example, DAs **4** and **5** give only oligomers).[19] Here, all three examples containing the longer linker give isolatable quantities of high molecular weight materials. The most dramatic example is the case of the *n*BCAU monomers, which forms a negligible quantity of polymeric material in the case of a two-carbon linker (**4**), but 64% polymerization is observed in the case of the four-carbon linker (**8**). Surprisingly, DA **3**, 2MCPU, gave good yields of polymer, while its four-methylene linker analogue **7** showed only a low production of high molecular weight materials. The high molecular weight fraction of this latter product mixture was also extremely polydispersed, preventing any meaningful measurement of molecular weight.

**Table 2. Raman Scattering (nm) for Acetylene Stretching in DAs 1−8 and Their Corresponding Polymers**

| derivative | monomer | polymer |
|---|---|---|
| 4BCMU (**1**) | 2258 (2084) | 2098 |
| 2MCAU (**2**) | 2261 | 2096 |
| 2MCPU (**3**) | 2262 (2118) | 2118 |
| 2BCAU (**4**) | 2262 | N/A |
| 2BCPU (**5**) | 2262 | 2125 |
| 4MCAU (**6**) | 2257 (2111) | 2108, 2060 (br) |
| 4MCPU (**7**) | 2255 (2113) | 2117, 2076, 2060, 2042 |
| BCAU (**8**) | 2256 | 2078 (br) |

The influence of the other two parameters, the nature of R and R′, is less clear-cut. Very good results could be achieved with both the very small alanine and the much larger phenylalanine derivatives, but nonpolymerizable examples were also seen. All of the methyl esters gave at least some polymer, but the butyl esters also performed very well in some cases. It is likely that this latter parameter is of little significance.

**Thermal and Vibrational Analysis.** The thermal behaviors of all new monomers were unsurprising and consistent with the achiral parent family. Each of the new compounds melts between 50 and 95 °C without polymerizing. None of them showed evidence of thermal polymerization in either the solid or the melt. Likewise, the new polymers behave much like poly(4-BCMU). Differential scanning calorimetry of the high molecular weight fractions showed no evidence of a glass transition or any other thermal event below 300 °C. Thermal gravimetric analysis of the polymers showed that all of them began to degrade between 280 and 350 °C.

Raman spectroscopy has proven to be a valuable tool for probing the structures of DAs and their polymers.[20] The most distinctive scattering comes from the acetylene stretching at ca. 2250 nm in the monomer and 2100 nm in the polymer. Table 2 shows the Raman data for the seven compounds under discussion and their polymers.

The acetylene stretching in the monomers is only affected by the length of the methylene chains attached to the butadiyne moiety, with the vibration in the four-carbon-linked compounds red-shifted by about 6 nm. In the cases of **3**, **6**, and **7** traces of polymer, due to brief exposure to ambient light during handling, were observed. This was evidence by the appearance of a reddish tinge and the appearance of an additional acetylene stretching vibration in the Raman spectra. The vibrational modes due to the polymer contamination of the monomer are shown in parentheses (Table 2).

After exposure to $\gamma$-irradiation, vibrations due to the acetylenes in the conjugated backbone were observed, except in the case of **4**, which did not undergo reaction to a large enough extent. While **5** also did not form high molecular weight materials, the appearance of a signal at 2125 nm confirms that small quantities of conjugated oligomers were formed. The polymer products from **2**, **3**, and **8** each gave only a single scattering peak (though the latter was quite broad). In the case of **4**, the frequency of the scattering from the $\gamma$-irradiated material was identical to that of polymer formed under ambient light. In contrast to this, the product from irradiation of **6** gave two distinct peaks, one similar to that of the product from ambient light and a second broad and much more intense peak at 2060 nm. The product mixture from irradiation of monomer **7** also retains a peak consistent with that formed by visible light, but at least three other smaller, but distinct, peaks are observed.

It is well-known that pDAs can exist in two principal geometric forms. In some systems, these can be reversibly transformed from one to the other, while in others the change is irreversible. The blue form is planar and has often been considered to be the more stable and ordered form, while the red form was originally thought to have a twisted backbone that effectively shortened the conjugation length. However, Schott (and others) have strongly argued that both forms can be highly ordered, that the color is unrelated to effective conjugation, and that the lowest energy conformation depends upon the side groups.[21] Here, it appears that the two forms are being generated simultaneously, with the red form more prominent when the reaction is initiated by visible light, while the blue form becomes more important upon $\gamma$-irradiation. In the case of 4MCPU, the relatively poor conversion to a highly polydispersed product and the variety of peaks in the Raman spectrum indicate a marginal system for polymerization.

In contrast to our systems, 4BCMU, **1**, appears to preferentially generate the blue form under all conditions. We note also that the width of the scattering from acetylene vibration is significantly narrower when polymerized under identical conditions than any of our materials.

**Chiroptical Properties.** There has been considerable debate as to the origin of the solvoatochromism of pDAs.[7] In good solvents, the polymers are yellow, with a broad absorbance centered at 475 nm (Figure 3a). Upon addition of a poor solvent, the solutions become either red or blue and begin to aggregate. It is now generally agreed that the chains in the yellow solutions are random coils, while the red solutions contain extended chains, with relatively planar backbones.

We have examined the electronic spectrum of the five pDAs in chloroform and in chloroform/hexane mixtures. Not surprisingly, these data are very similar to each other and to that of 4BCMU. In pure chloroform, only the yellow form is observed. In a 1/1 mixture, the red form can be observed, and complete conversion to the red form generally occurs at a ratio of between 1/2 or 1/3 chloroform to hexane, while very high hexane concentrations results in aggregation and precipitation, as evidenced by a loss of signal intensity and scattering of the light. The sole exception to this trend was poly**8**, which required a somewhat higher hexane concentration to undergo the chromatic transformation.

The CD spectra of the compounds were somewhat more complex. In all cases, no Cotton effect could be observed when only the yellow form was present, and there was no evidence of circular intensity differential scattering (CIDS).[9] This is consistent with highly solvated, random coil chains. Upon the addition of hexane, signals begin to appear in the 450−600 nm region of the spectrum. The dominant feature in all cases is a positive Cotton effect at approximately the same wavelength as the largest electronic absorption in the red form (Figure 3b). The magnitude of this feature is polymer dependent, with those of **6** and **7** being quite strong, while those of **1** and **3** are markedly weaker in solutions where the absorbance in the UV was approximately the same. In each of the spectra, a weaker feature with a negative Cotton effect could be seen at 450 nm. In some cases, additional fine features in the form of shoulders on the major peaks could be observed. Of course, the CD spectrum of the achiral polymer of **1** remained featureless throughout the yellow to red solvent-induced transition. Other solvent combinations also affected the yellow-to-red chromatic transition. For example the polymer of **6** gave a yellow solution in THF. Addition of hexane gave the color change and a signal in the CD. Conversely, addition of ethanol to the THF solution resulted in only a barely perceptible feature in the CD, though the yellow-to-red color change was still observed.

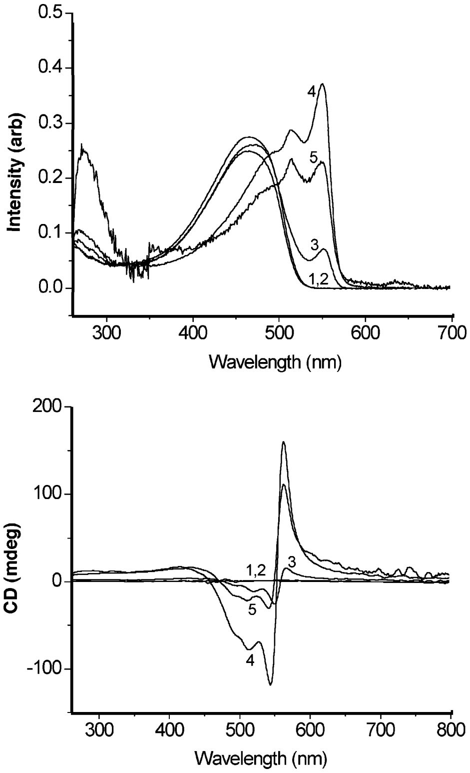

**Figure 3.** (a) UV spectra of poly(**6**) in CHCl$_3$/hexane solutions at ratios of (1) 1:0, (2) 2:1, (3) 1:1, (4) 1:2, and (5) 1:10. (b) CD spectra of the same solutions.

The observation of features in the 450−600 nm region of the CD spectrum indicates the adoption of a helical conformation of the conjugated polymer backbone. While related pDAs based on lipids have been shown to form helical ribbons and other structures (under very different conditions than those used here),[15] it is more likely that the features seen here are due to conformational changes of well-dissolved, individual chains. Aggregation and precipitation of the polymers are clearly present at very high nonsolvent concentrations, but the lack of CIDS around the onset of the color transition indicates that aggregates (at least on the order of the wavelength of the incident radiation) are not being formed.[9] The degree of helicity and possibly more subtle structural features may vary somewhat between polymers, but the spectral data are generally consistent across the series. Clearly though, not all “red” solutions of the polymer have identical chain structures as is suggested by the THF/ethanol experiment. It may be that ethanol disrupts hydrogen bonding between urethane groups along the chain and inhibits helix formation. Related behavior has been seen in chiral polyacetylenes, where solvent and pH-induced manipulation of helicity has been demonstrated.[5]

## Conclusions

Chiral derivatives of 4BCMU are readily prepared from alanine and phenylalanine, and the synthetic route described here should be readily adaptable to a variety of amino acids. As with other classes of diacetylenes, small structural changes can have a significant effect on the crystalline packing of the compound and therefore greatly affect the ability of the material to undergo topotactic polymerization. Despite this, the BCMU-like motif is robust, and it is likely that many related species will also undergo ready polymerization to high molecular weight materials. Like other pDAs, the polymers studied here display solvatochromism, but the structural transformation that extends the average conjugation length by straightening the pDA backbone may also organize the chain into a helix. We expect that it would be possible to fine-tune this helical structure through careful design of the starting monomers.

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