material possesses the desired C* phase over a broad temperature range, as indicated by the phase sequence shown in Figure 1.[11]

Our approach for probing functional group orientation in low molar mass FLCs is to measure the sign and magnitude of the ferroelectric polarization in an aligned thin film between conducting glass plates.[10,12] This is done by switching the ferroelectric with an applied voltage step and measuring the current response of the cell. By a novel combination of interaction with a rubbed polymer alignment layer on the surface of the electrodes and shear, it proved possible with compound **1** to achieve excellent alignment, affording a monodomain of ordered polymer film 3 μm thick, with an electrode area of 1.17 cm^2.[11]

Switching in the standard geometry[12] was relatively slow (3 ms at 85 °C, 15 V/μm driving field) but easily allowed measurement of P for the material. In fact, neat compound **1** showed a polarization of +65 nC/cm^2 (85 °C). The sign and magnitude of P for the (*S*,*S*)-epoxide-containing polymer are consistent with the model presented earlier for the low molar mass mesogen itself (+45 nC/cm^2), where polar orientation of the epoxide dipole is the major contributor to the macroscopic polarization.[9] Previously reported FLCPs showed polarizations (measured in unaligned samples) on the order of 6 nC/cm^2.[6,7]

Small-angle neutron diffraction studies of achiral, deuterium labeled smectic A polymethylsiloxane side chain LCPs similar to **1** indicate that the backbone orients as a random coil between the layers of mesogen molecules (i.e., in the smectic layers), with the mesogenic units oriented relative to the layers much as they would be in a low molar mass A phase.[13] The reasonable extrapolation of this result to smectic C phases, in combination with the observed polarization of polymer **1**, suggests that the polar orientation of molecular dipoles in **1** is similar to that obtained in the analogous low molar mass material.

It is thus expected that when bound in the "crystal" lattice of a low molar mass C* host, the mesogenic units of the FLCP should orient in the bent cylinder binding site according to our model for the molecular origins of P,[1,9,12] and the observed polarization of host–guest mixtures (complexes) should be a linear function of concentration of the polar component (the FLCP in this case), since the presence of the backbone in the smectic layers is not expected to affect the shape of the binding site. Indeed, polymer **1** is miscible in all proportions with the standard C* host 4-[(*S*)-(+)-(4-methylhexyl)oxy]phenyl 4-(decyloxy)benzoate,[14] and the observed polarization for aligned samples of mixtures possessing 20% and 50% by weight of polymer **1** in the host (+11 nC/cm^2 and +33 nC/cm^2, respectively) are linear with concentration, as indicated by the plot shown in Figure 1. In total, the data presented here provides good evidence that the molecular recognition model for functional group orientation in low molar mass materials may be extended to the FLCP films of the present study.

In conclusion, an organic polymer ferroelectric thin film showing good global functional group orientation in a large-area monodomain has been created. Evidence is presented for a molecular-level interpretation of dipole orientation occurring in the FLCP phase which is similar to that for the analogous low molar mass material, with the slight modification that the polymer backbone is now present in the smectic layers. While by our interpretation the polymeric nature of the FLCP does not dramatically affect functional group orientation, obvious advantages with respect to processibility in some applications accrue from achieving this orientation in a polymer film relative to the low molar mass materials.

Acknowledgment. This work was supported in part by the Office of Naval Research, by the NSF Engineering Research Center program (Optoelectronic Computing Systems Center, Grant No. CDR-8622236), and by the National Science Foundation (Grant No. DMR-8611192).

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UV Photoisomerization of *N*-Methylacetamide and Resonance Raman Enhancement of a New Conformation-Sensitive Amide Mode

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Ultraviolet resonance Raman (UVRR) spectroscopy is being developed as a structure probe for proteins.[1,2] Near resonance with the first allowed electronic transition (ca. 190 nm) of the peptide bond, strong enhancement is seen for amide modes, particularly amide II (~1560 cm^{-1}), whose intensity is sensitive to the α-helix content in polypeptides and proteins.[3] Song et al.[4] have recently called attention to another peptide UVRR band, near 1390 cm^{-1}, which disappears in D_2O and may be a conformation marker. For the peptide model compound, *N*-methylacetamide (NMA), they identified this band at a much higher frequency, 1496 cm^{-1}, and assigned it to the overtone of the out-of-plane NH bend, amide V. A previous suggestion[2] that the 1496-cm^{-1} band arises from photoisomerized *cis*-NMA was rejected by Song et al.[4]

In Figure 1 we demonstrate, however, that the 1496-cm^{-1} band is indeed photoinduced. At low laser power incident on a flowing sample of aqueous NMA this band is *absent* in the 200-nm-excited RR spectrum (D), but it grows in when the power is increased (C) and particularly when the sample is stationary (B) even at low power. Its frequency is the same as the IR band assigned to amide II of *cis*-NMA prepared by matrix quenching from a high-temperature nozzle[5] and is the same as that of the intense amide II band in the 200-nm-excited RR spectrum of aqueous caprolactam (Figure 1A), a secondary amide for which the cis isomer is enforced by its cyclic structure. The 1496-cm^{-1} band can therefore be assigned with confidence to *cis*-NMA produced by photoisomerization from the stable trans form. Supporting this inference is the observation of intensity loss in the amide II and III bands of the trans isomer.

Importantly, photoisomerization is also observable in D_2O and is especially evident when the *N*-methyl group is replaced by CD_3 (Figure 2). For this isotopomer H/D exchange collapses the amide II and III bands of the trans isomer, arising from coupled C–N stretching and N–H bending coordinates,[6] into a single strong band at 1496 cm^{-1} which is essentially pure C–N stretching (amide II′). At high laser power levels, a new band grows in at 1471 cm^{-1},

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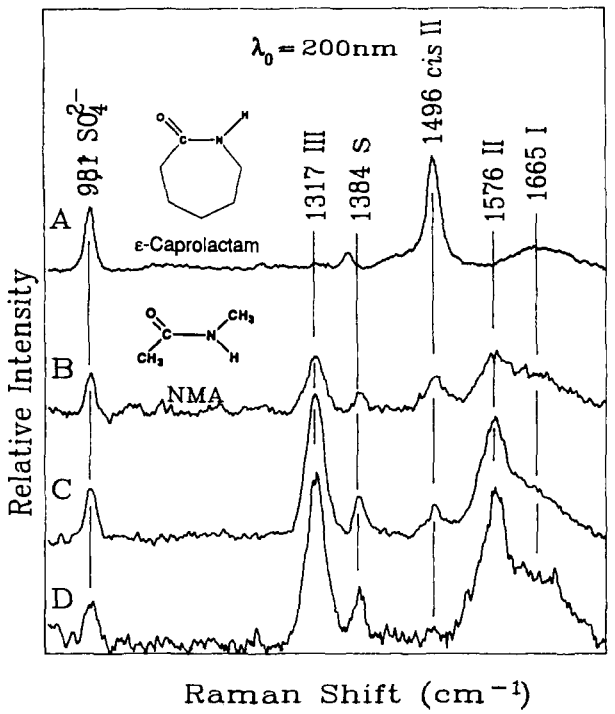

Figure 1. 200-nm-excited RR spectra of (A) aqueous caprolactam (3 mM, with 0.3 M Na_2SO_4) and (B–D) aqueous *N*-methylacetamide (10 mM, with 0.3 M Na_2SO_4). Spectrum B was obtained with a stationary sample (cuvette), while spectra C and D were obtained with a flowing sample[16] at high and low laser power levels, estimated to be 40 and 800 MW/cm²/pulse, respectively. The H_2-Raman-shifted YAG laser spectrometer is described in ref 16; an intensified diode array detector (Princeton Instruments) was employed. The peak assignments for the amide modes are indicated.

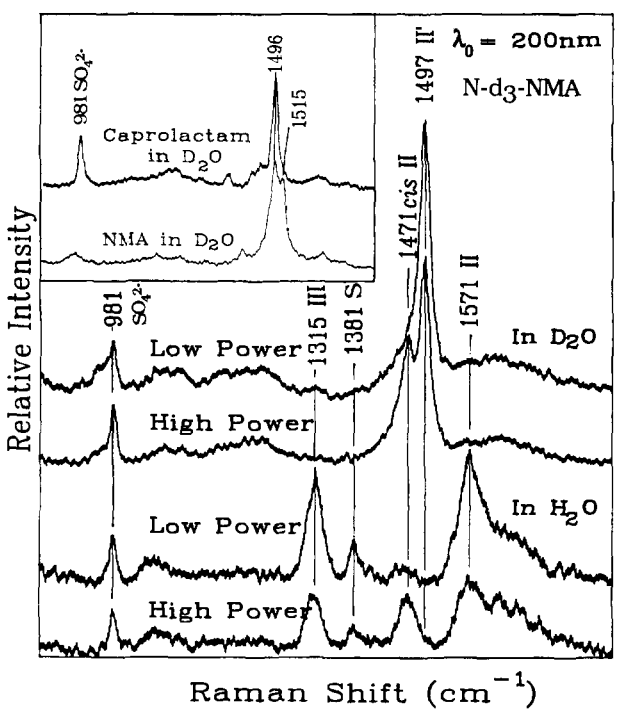

Figure 2. 200-nm-excited RR spectra of *N*-methylacetamide-d_3 (10 mM, with 0.3 M Na_2SO_4) in H_2O and D_2O, contained in a stirred cuvette, at low and high power levels (as in Figure 1), showing the photoinduced 1471-cm^{-1} band, assigned to the cis isomer.

close to the frequency in H_2O, and is assigned to the amide II′ mode of *cis*-NMA. (For the CH_3 isotopomer, this phenomenon is obscured by a strong doublet band at 1496/1515 cm^{-1}, which we attribute to a Fermi resonance between the trans amide II′ mode and a CH_3 asymmetric deformation mode.[7])

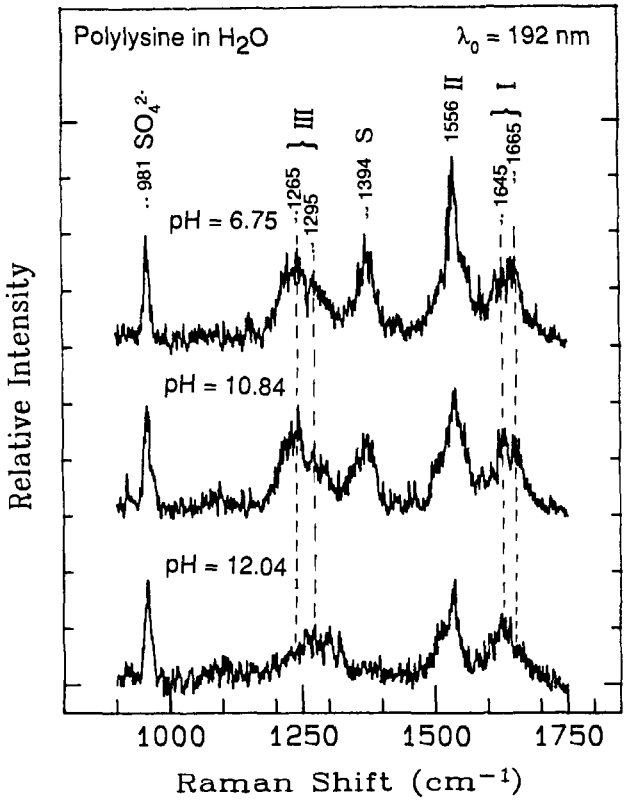

Figure 3. 192-nm-excited RR spectra of aqueous poly-L-lysine (2 mg/mL with 0.3 M Na_2SO_4) showing spectral changes due to increasing α-helical content with increasing pH. The sample was dialyzed against NaCl to remove bromide ions, which causes photocoloration.

As pointed out by Song et al.[4] UVRR enhancement of the amide V overtone would in fact be expected if the resonant excited state is twisted, by analogy with ethylene, for which strong enhancement of the twisting mode overtone is seen in resonance with the first allowed excited state.[8] The observation of trans–cis photoisomerism supports the view that the amide excited state is twisted. Although the 1496-cm^{-1} band is not the amide V overtone, there is another candidate at 1384 cm^{-1} (Figure 1). This band is not photoinduced and is eliminated in D_2O (Figure 2) and therefore involves the NH group. The problem with an amide V overtone assignment is that 1384 cm^{-1} is much lower than twice the fundamental frequency, which was assigned at 725 cm^{-1} in neat NMA in an early IR study by Miyazawa et al.[9] and which was reported by Song et al.[4] to shift up to 748 cm^{-1} in aqueous solution; this was the basis of their 1496-cm^{-1} overtone assignment. However the recent study of Fillaux and Barron[10] implicates a barrier in the NH bending potential in line with structural evidence for appreciable pyramidalization of the peptide N atom.[11,12] If there is a barrier, then the overtone levels for NH bending will of course display large anharmonicities. Because of this complexity it seems advisable to reserve judgement on the 1384-cm^{-1} band assignment and to give it a noncommittal label, amide S.

The frequency of amide S is close to that of the conformation-sensitive band near 1390-cm^{-1} in polypeptides and proteins.[4,13] Figure 3 shows 192-nm-excited RR spectra of polylysine, which is converted from random coil to α-helical structure at high pH,[14]

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as can be seen from the amide I and III frequency shifts.[15] The diminished amide II and III resonance enhancement, due to transition dipole alignment in α-helices, has already been noted.[3] At the same time the amide S band vanishes completely in the α-helical form. While hypochromism can account for some of the intensity loss, the reason for its disappearance is uncertain; possibly the NH out-of-plane force constant is unaltered in the excited state for α-helix, in contrast to unordered peptide. In any event the marked intensity dependence makes amide S a promising marker for α-helical content in proteins. We note that there is no evidence for *cis*-amide links in the polylysine spectra nor in published protein spectra,[3] but the possibility of photoinduced isomerization in UVRR studies of proteins or peptides should be kept in mind.

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Mechanism of Organocuprate Conjugate Addition: Observation of Cuprate–Olefin Complexes and Li-Coordinated Intermediates in the Reaction of Lithium Dimethylcuprate(I) with 10-Methyl-$\Delta^{1,9}$-2-octalone[1a]

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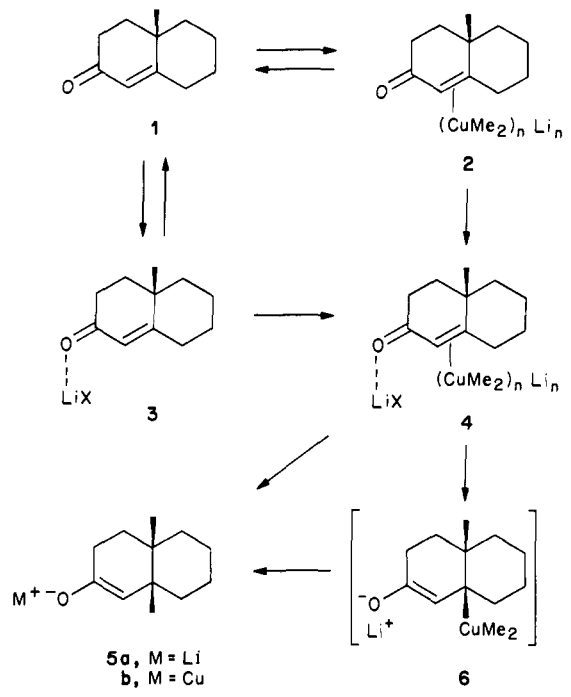
Organocuprates react with α,β-unsaturated ketones to yield the enolates of the corresponding β-alkylated ketones.[2] Paradoxically, this reaction is both one of the most useful of those mediated by transition-metal reagents and yet one of the least understood. We have discovered that treatment of 10-methyl-$\Delta^{1,9}$-2-octalone (**1**) with halide-free lithium dimethylcuprate(I), $(Me_2CuLi)_2$,[3] at low temperatures in diethyl ether-d_{10} allows the intermediates in the sequence from **1** via **2** and **4** to enolate **5** (Scheme I) to be observed by using ^{13}C NMR spectroscopy.

When 0.25 M $(Me_2CuLi)_2$ in diethyl ether-d_{10} at −78 °C is treated with 2 equiv of **1** (1 equiv of **1** vs Me_2CuLi as it is usually written), it assumes a deep orange color, and three sets of lines attributable to cuprate–olefin π-complexes of general structure **2** are observed by ^{13}C NMR (Figure 1b). With 1 equiv of **1**, a small amount of a fourth π-complex is also observed. We tentatively assign the four complexes **2** to exo and endo isomers of monomeric and dimeric cuprates (Scheme I, $n = 1, 2$). The major olefin complex (50%) is characterized by lines with chemical shifts of 191.0, 82.5 (J_{CH} = 149 Hz), and 80.9 ppm for the carbonyl C and the olefinic α-C and β-C, respectively.[4] The corresponding lines for (uncomplexed) **1** are at 196.9, 125.1 (J_{CH} = 159 Hz), and 168.1 ppm (Figure 1a). The relatively unperturbed carbonyl C and the dramatic upfield shifts (42.6 and 87.2 ppm, respectively) of the olefinic α-C and β-C atoms are precisely what is expected for the change in bonding upon transformation of **1** into a h^2-olefin

Scheme I



complex.[5] For comparison, the α and β olefinic C atoms of *tert*-butyl cinnamate are shifted upfield by 67.2 and 82.6 ppm, respectively, upon complexation by $Me_2CuLi{\cdot}LiI$.[6]

A significant amount of lithium–carbonyl complex **3** is also present: 15% with 1 equiv of **1** and 30% with 2 equiv at −78 °C (Figure 1b).[7] The ^{13}C lines characteristic of **3** are 204.2 ppm (carbonyl C), 124.8 ppm (J_{CH} = 162 Hz, olefin α-C), and 176.1 ppm (olefin β-C), in accord with the observed effects of adding Li salts to α,β-unsaturated ketones.[8] With 2 equiv of **1**, the proportion of **3** increases to 45% when the temperature is raised to −60 °C. When the sample is returned to −78 °C, the original ratio of **2**/**3** is restored. In their cuprate–cinnamate system Ullenius et al. also observed a lithium–carbonyl complex, which is "the major component when the ester is present in excess and also at higher temperatures...".[6a] In their system the lines due to the copper–olefin and lithium–carbonyl complexes coalesce before enolate appears. In our system exchange processes are apparently much slower, and we have been able to observe all the species **2**–**5** in a single spectrum (see Figure 2, Supplementary Material; see Figure 1d for **3**–**5** in a single spectrum).

With 1 equiv each of **1** and $(Me_2CuLi)_2$, three new species are present in addition to the complexes **2** and **3** discussed above (see Figure 1c). Two are proposed to be Li-coordinated copper–olefin complexes of general structure **4**, based on the downfield shifts of the olefinic resonances compared to those of **2**. One of these has broad signals at 188.3, 87.0, and 86.7 ppm, and the other has sharp lines at 188.0 (carbonyl C), 87.2 (J_{CH} = 148 Hz, olefinic α-C), and 87.4 ppm (olefinic β-C). Such lithium–carbonyl/copper–olefin complexes were proposed by Berlan to be the antepenultimate intermediate in the reaction of cuprates with enones.[9] The greater upfield shift of the β-C (>2× that of the α-C) indicates that the Cu–C_β bond is significantly stronger than the Cu–C_α interaction and suggests that conversion of **4** to the σ-allylcuprate(III) **6** is a plausible path to enolate **5**.

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