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Thermal effects on the optical spectra of a polydiacetylene: Poly{1,2-bis[4-(isopropylcarbamoyloxy)-*n*-butyl]-1-buten-3-ynylene}^{a)}

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The reflection spectra of single crystals of the polydiacetylene, IPUDO [$R=(CH_2)_4OCONHCH(CH_3)_2$], were measured between 25°C and 160°C. A nearly reversible thermochromic change is observed together with a variation of hysteresis upon cycling. The latter is attributed to annealing that permits the pendant groups to adopt a conformation which favors the butatriene-type configuration of the polymer at high temperatures. Intensities of the high and low temperature spectra obtained by Kramers-Kronig transforms are in excellent agreement with the spectral intensities of polydiacetylenes which are prototypes for the two configurations.

I. INTRODUCTION

The study of the influence on electronic spectra by variation of intensive quantities has often provided spectroscopists with powerful probes of the energetics of molecular systems. However, the interpretation of the spectra arising from these perturbations can lead to such complicated phenomena so as to render detailed understanding quite difficult. One perturbation which, although quite simple itself, can cause such difficulty is temperature. This may lead from such mild perturbations as hot bands to the appearance of entirely new absorptions due to creation of new chemical entities. It would be useful to study the nature of thermochromism in systems wherein the thermally induced spectral changes observed in the electronic spectra are sizeable but where the chemical change is minimal or, preferably, nonexistent.

In earlier papers,¹⁻³ it has been shown that variously substituted polydiacetylenes exhibit changes in their electronic spectra which may be induced by variation of temperature or pressure. The spectral changes are usually reversible in these systems and there are no large chemical changes in the polymer. Similar studies of the temperature dependent resonance Raman spectra of polydiacetylenes^{4,5} have shown large changes in the frequency and intensity of the active vibrations.

The changes observed in these spectra have been attributed to the conversion of the polydiacetylene from an acetylenic form (I of Fig. 1) to a butatriene (II) configuration. Thus, these two apparent resonance forms are believed actually to be valence tautomers. X-ray crystallography has allowed the correlation of spectra to the two forms. The prototype for form I is DCHD⁶ [R is $-CH_2N(C_6H_4)_2$] and for form II is TCDU⁷ [R is $-(CH_2)_4-OCONHC_6H_5$].

In the studies of resonance Raman spectra, the frequency and intensity of the $\nu(C\equiv C)$ and the $\nu(C=C)$ bands are found to vary with temperature thus lending support to the tautomer hypothesis. By comparison with the frequencies and band shapes of electronic spectra of crystals of polydiacetylenes which have been shown by x-ray crystallography^{6,7} to have one or other of the two tautomeric forms (Fig. 1), it was concluded¹ that the thermochromic change may be associated with a stabilization of one form over the other. In particular, the electronic bands associated with the I tautomeric form lie in the frequency region about 15 500 cm^{-1} and show some spectral congestion whereas those associated with the II tautomer are found at frequencies near 17 500 cm^{-1} with simpler band shapes. To further investigate the importance of lattice packing on the thermochromism of the polydiacetylenes, we have investigated the temperature dependence of the new polydiacetylene IPUDO where R is $-(CH_2)_4OCONHCH(CH_3)_2$. In particular, the change of the absorption cross section with temperature and the hysteresis of the crystal will be of interest.

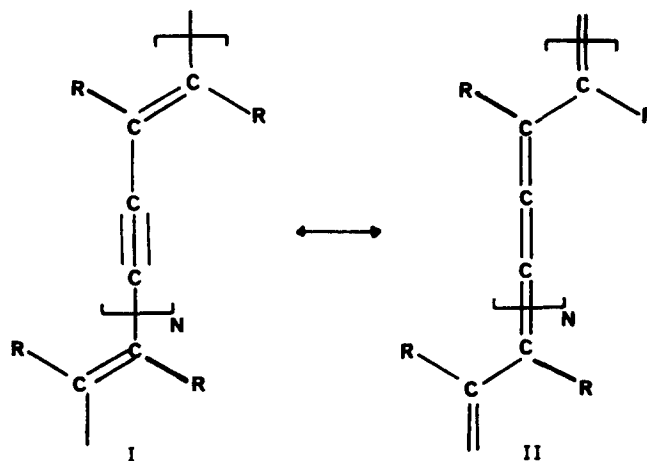


FIG. 1. Acetylenic (I) and butatrienelike (II) tautomers.

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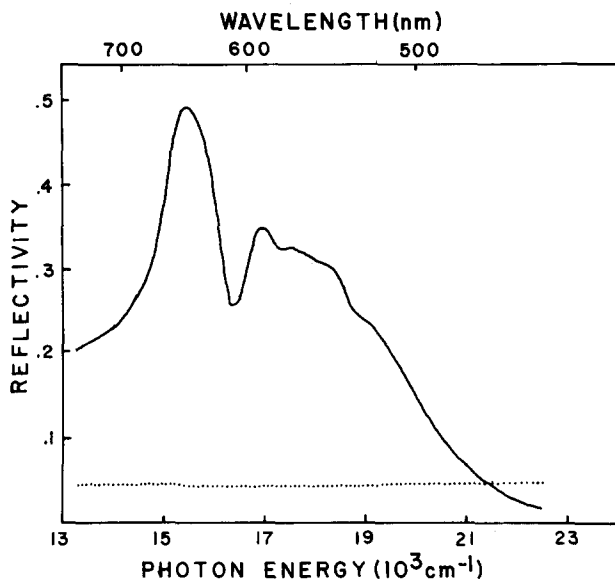


FIG. 2. Normal incidence reflection spectra for IPUDO at 25 °C with the incident light polarized along the principal directions in the crystal face.

II. EXPERIMENTAL

The reflection spectra were obtained with apparatus described previously.³ The crystals were mounted on a brass block which is placed in a closed cell covered with a 0.2 mm thick fused quartz window. The block is heated resistively and a copper-constantan thermocouple is placed next to the crystal for control and measurement of the temperature.

The monomer samples were prepared from a reaction of 5,7-dodecadiyn-1,12-diol with isopropylisocyanate using triethylamine and dibutyltin-di-(2-ethylhexanoate) as catalyst. Crystals (mp 138 °C) used for the investigation were grown from a solution in ethylacetate. The monomer crystals were irradiated with 50 Mrad of ⁶⁰Co gamma rays which gave crystals of better than 99% conversion to polymer. It should be noted that the ETCD and TCDU polydiacetylene crystals yield only about 80% polymer on gamma irradiation. Residual solvent or monomer were not detectable by mass spectrometry when the crystal was warmed to 180 °C and respective mass peaks monitored.

The crystals studied were shiny golden elongated parallelepipeds which, upon microscopic examination after being mechanically deformed, were observed to break into smaller fibers parallel to the length of the original crystal. Optical principal directions were found to lie parallel and perpendicular to the crystal long axis through the temperature range from 25 °C to 160 °C. Two separate crystals were studied. The data obtained for each were in agreement within the limits of error of the experiment.

III. RESULTS

The normal incidence specular reflection spectra for IPUDO at 25 °C are shown in Fig. 2 for both principal directions in the crystal face studied. From these spec-

tra, it is clear that the transition moment must be parallel to the chain axis of the polymer because there is no observed structure in the direction perpendicular to the fiber axis. Since an x-ray structure is not available, it can only be inferred by use of the morphological information given above that this moment lies in the polymer chain direction.

In Fig. 3, a selection of the normal incidence reflectivity spectra of IPUDO as a function of temperature is shown for one cycle of heating and cooling. As in the case of the thermochromic polydiacetylene, ETCD¹ [R is $-(CH_2)_4OCONHC_2H_5$] the reflectivity is observed to change from a congested band system exhibiting a golden reflection to a less congested band system with an associated green lustrous reflection. The peak frequencies at the temperature extrema are given in Table I, where the values for the thermochromic ETCD are also presented.

The spectra show that the two forms yield characteristic spectra peaked at frequencies associated with the two tautomers but that in the transition temperature region the summation of the high and low temperature bands causes apparent frequency shifts. It is clear that the spectral transition occurs over a rather narrow temperature range and, when the case of ETCD is taken into account, it appears that this behavior is likely to be typical of thermochromic polydiacetylenes.

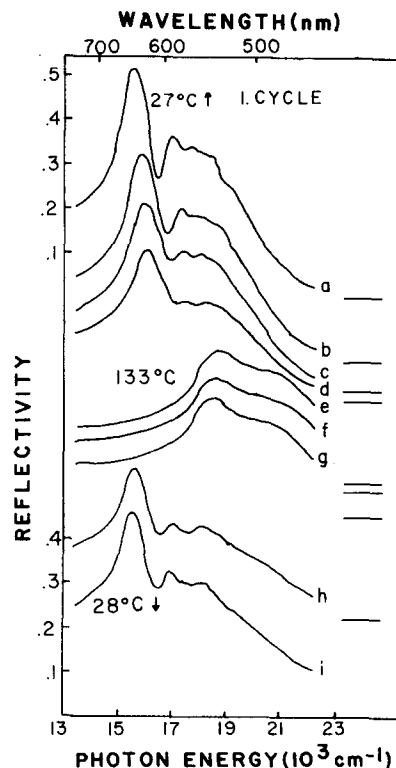


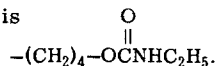
FIG. 3. Normal incidence reflection spectra of IPUDO as a function of temperature for the first cycle. The uppermost curve is obtained for the initially polymerized material. Left ordinates are for room temperature spectra. Origins for the higher temperature spectra are indicated by the horizontal lines on the right which are in the same sequence as the alphabetically indexed curves.

TABLE I. Thermochromic change for polydiacetylene crystals.

	IPUDO		
	ETCD ^{a,b}	(First cycle)	(Second cycle)
High temperature peak frequency of reflectivity	18 500	18 650	18 650
Low temperature peak frequency of reflectivity	15 750	15 400	15 550
Temperature of transition	115 ± 2 °C	116 ± 2 °C	95 ± 2 °C

^aReference 1.

^bR is



Upon cooling, the crystal reverts to a spectrum closely resembling that of the initial 25 °C spectrum. Hysteresis is evident and has been plotted in Fig. 4. The curve marked with numeral one refers to the first cycle of heating and cooling. This curve is obtained by plotting the reflectivity at the peak frequency of the low temperature form (15 400 cm⁻¹) as a function of the temperature of the crystal. The reflectivity does not return to the original low temperature reflectivity.

Because of this lack of agreement, the cycle was repeated. In this set, the reflectivities are lower than they were for the first cycle. However, the band shapes are still essentially those observed in the first cycle (see Fig. 3).

A striking change is observed in the second (labeled 2) hysteresis curve of Fig. 4 which was obtained during the second temperature cycle in the same fashion as the first hysteresis curve. The transition temperature now occurs 20 deg lower than that observed in the first cycle. Also, within the error of the experiment, the reflectivity for this cycle has returned to its initial value which was the reflectivity at the conclusion of the first cycle. The

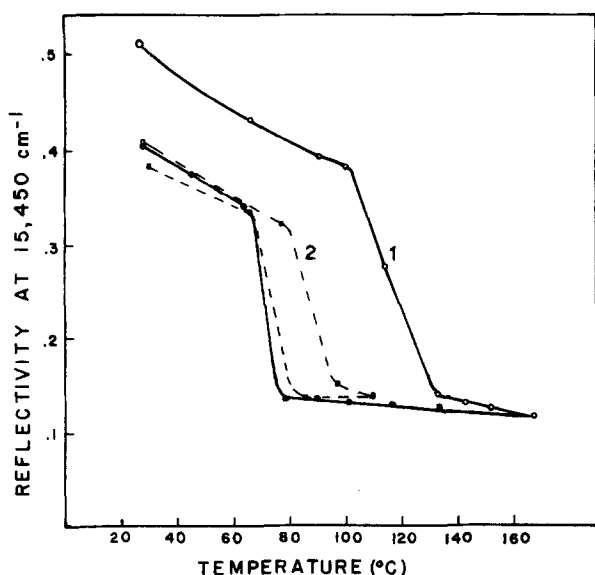


FIG. 4. Hysteresis loops for the reflectivity which is the peak at room temperature. The solid line represents the loop for the first cycle and the dashed is that for the second cycle. Cycles were taken in clockwise directions around the loops.

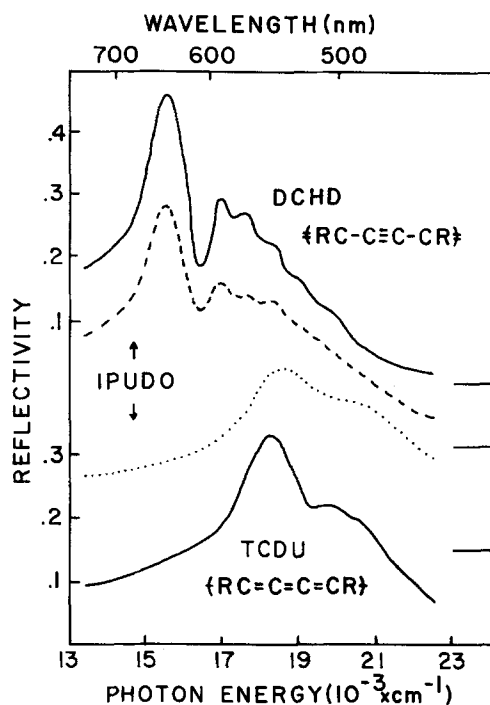


FIG. 5. Normal incidence reflection spectra for DCHD, TCDU, and IPUDO above and below the phase transitions. The dashed spectrum is for IPUDO above the transition whilst the dotted was that obtained below the transition. The observed backbone bonding sequences for the prototypes are represented. Origins are represented by horizontal lines to the right.

cooling section of the curve is, however, virtually identical to that of the first cycle. Thus, in both cases, the "cooling" transition temperature is 70 °C. In these experiments, the rate of heating was ~3 °C/min with the temperature held for ~20 min before the particular spectrum was obtained. The latter took ~30 min. For comparison, the reflection spectra for the high and low temperature forms of IPUDO are presented in Fig. 5 along with the reflection spectra for DCHD and for TCDU.

Because it has been proposed that the thermochromic change is due to a change of electronic structure from the acetylenic (I) tautomer to the butatriene type (II) tautomer, it is of interest to compare the absorption line shapes as well as the absorption cross sections for the two. The frequency dependence of the real and imaginary parts of the dielectric constant obtained by Kramers-Kronig transform of the reflection data are presented in Fig. 6 for the low temperature form of the IPUDO crystal. Because of the difference in reflectivity from the initial low temperature form, the reflectivity data are taken from the curve obtained at 25 °C at the end of the second cycle.

The imaginary dielectric constant band shape bears strong resemblance to that obtained for the prototype acetylenic (I) polydiacetylene DCHD.⁶ The intense low energy peak occurs at 15 500 cm⁻¹ with a prominent secondary peak at 16 900 cm⁻¹. Prominent shoulders are observed at 17 500 and 18 050 cm⁻¹. The progressions are also reminiscent of DCHD with an approximate 600 cm⁻¹ progression in the secondary band system which is

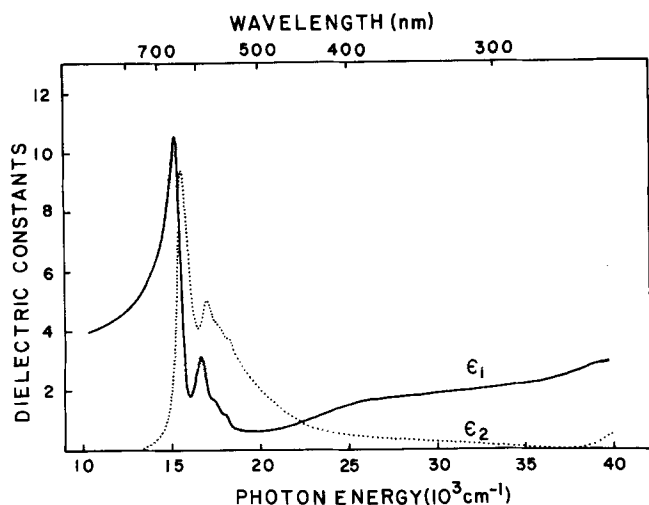


FIG. 6. Real (ϵ_1) and imaginary (ϵ_2) parts of the dielectric constant for IPUDO at 25°C. ϵ_1 (solid line) and ϵ_2 (dotted line).

characteristic of the acetylenic polymer electronic spectra. Examination of the real dielectric constant shows that its value remains everywhere positive. In the other acetylenic systems, the real part of the dielectric constant ϵ_1 does go negative over a narrow region. However, it is clear that in this case it comes close to doing so and that with slightly higher values of the reflectivity, perhaps closer to the higher values obtained at the beginning of the first cycle, a negative region of ϵ_1 probably would develop. This is of interest since this would indicate a region of quasimetallic reflectivity⁸ and the possibility of surface polaritons.⁹ Thus, both of these properties have the potential of being thermally controlled in these systems.

In Fig. 7, the real and imaginary parts of the dielectric constant are presented for the high temperature phase. Here the spectra are in strong agreement with those obtained for the prototype "butatriene" (II) polydiacetylene TCDU.¹⁰ Here the peak occurs at 18 800 cm^{-1} with a shoulder at 20 000 cm^{-1} . The curve for ϵ_1 fails to go negative in this case also.

Calculation of the absorption cross sections for the two forms affords some additional insight into how closely the states involved in the thermochromic transition resemble those of the prototype systems. Since the transition moment is sensitive to the nature of the electronic states of the two types, strong deviations in cross sections would weaken the identity of the states in the thermochromic material with those of the prototype systems. Since the observed energies of the high and low temperature transitions are consistent with those of the prototypes, close agreement of their intensities to those of the prototypes would strengthen the case for I \rightarrow II transformations. Since reflectivities are not reliable indicators of intensity, it is necessary to obtain this information from the Kramers-Kronig transforms of the reflection spectra.

Detailed crystallographic data on IPUDO is not available but the unit cell parameters are known at 25°C. X-ray diffraction analysis shows that the polymer crys-

tals are orthorhombic. The space group is either $Pca2_1$ with cell parameters $a=10.87$, $b=4.89$, and $c=39.19$ Å or $Pbcm$ with cell parameters $a=4.89$, $b=10.87$, and $c=39.19$ Å. Four monomer units per unit cell agree with the calculated density of 1.164 g/cm^3 , which is in good agreement with the measured bulk density (1.166 g/cm^3). These data permit the calculation of a dipole strength of 1.76 Å² for the low temperature (I) form and 1.50 Å² for the high temperature (II) form. Since the high temperature lattice constants are not known, the latter value has been calculated using the 25°C values.

The intensities obtained by Kramers-Kronig transform of reflection spectra for the DCHD and TCDU prototypes give dipole strengths of 1.70 Å² and 1.69 Å² respectively.^{6,9} The agreement is quite good especially when the effects shown in the hysteresis experiments are recognized to influence the reflectivity of the high temperature form. The supporting quantitative evidence of both intensities and frequencies of the electronic transitions support the I \rightarrow II transition.

IV. CONCLUSIONS

The spectra for IPUDO support the earlier hypothesis of changes between tautomeric forms I and II for polydiacetylenes. In spite of the varied nature of the R groups in these studies, the band shapes and frequencies of the two forms are remarkably constant. Thus, it is reasonable to attribute the electronic spectra to transitions of the backbone π electrons of the polymer. This agreement is enhanced by the constancy of the absorption cross section.

In an earlier paper,¹ the influence of interchain interactions was suggested as the cause of the thermochromic change. Specifically, interchain interactions were discussed because the thermochromic ETCD has interchain distances which are significantly shorter than for other polydiacetylenes. Because such an interaction might be expected to also strongly influence the intensities of the transitions under consideration, other interactions which

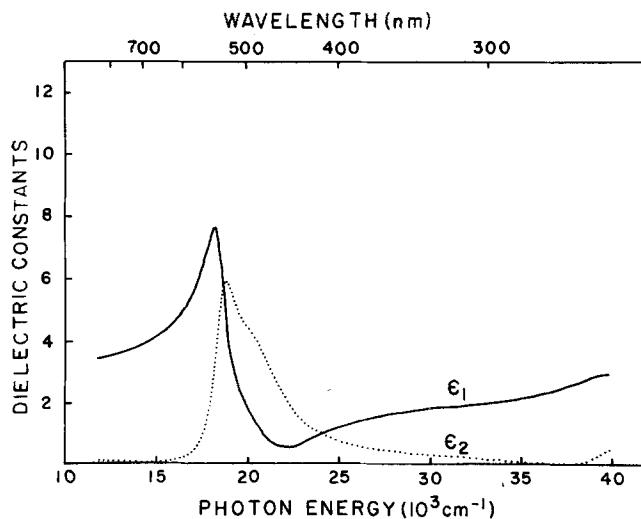


FIG. 7. Real (ϵ_1) and imaginary (ϵ_2) parts of the dielectric constant for IPUDO at 125°C. ϵ_1 (solid line) and ϵ_2 (dotted line).

do not involve the *direct* interaction of the chromophores (backbones) on different chains must be sought.

The change of the hysteresis upon cycling suggests that an annealing effect is operant. Since the butatriene configuration is that which simple molecular orbital considerations indicate would be most destabilized by nonplanarity, it is this structural property which is most likely to be affected by the annealing. The lack of change of the hysteresis on cycling in ETCD suggests that the nature of the pendant R groups may account for the hysteresis variability in IPUDO. Indeed, the two terminal methyl groups in the IPUDO may be expected to render packing of the chains more difficult because of the various orientations which they may assume upon reaction of the monomers. Thus, annealing the crystal may be expected to thermally activate the librations of these R groups sufficiently that the pendant groups might orient themselves in such a conformation which would allow maximal efficiency of packing and hydrogen bonding with the pendant groups above and below thereby inducing planarity.

Such an effect in a polar mixed solvent for the BCMU oligomer which spontaneously assumes a different configuration upon titration with a hydrophobic solvent has been demonstrated.¹¹ Since the BCMU also has a urethane group, it is reasonable to assume a similarity in behavior with the IPUDO. Additional evidence for this mechanism is given by the low temperature strain induced transition³ of the II type TCDU to an I type which gives the prototype spectrum. In this case, the strain is expected to force the pendent side groups into disarray, thereby favoring the I type backbone configuration.

The lowering of the transition temperature to the II form upon warming for IPUDO is consistent with this mechanism. The constancy of the low temperature transition may be attributed to the presence of strains at the

lower temperature which are sufficient to distort the polymer from the desired planarity.

When considered with the other data on the polydiacetylenes, the evidence for the thermally induced transitions between the I and II forms is strong. However, determination by x-ray crystallography remains the crucial experiment for confirmation of the model.

ACKNOWLEDGMENTS

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