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An Examination of the Thermal Polymerization of a Crystalline Diacetylene Using Diffuse Reflectance Spectroscopy

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Abstract: Diffuse reflectance spectroscopy is used to investigate the thermal polymerization of 2,4-hexadiyne-1,6-diol bis(*p*-toluenesulfonate), PTS. Polymerization proceeds via a solid-state 1,4-addition to form a fully conjugated polymer chain. The polymerization rate is determined on a relative basis by monitoring the evolution of the optical band system which is characteristic of the PTS polymer. The temperature dependence of the polymerization rate, in the limit of low polymer conversion, is quite accurately described by an Arrhenius expression over the temperature range of the experiments reported here, 35–80 °C, which yields a 200-fold change in rate. The activation energy in this low conversion range is 21.9 ± 0.6 kcal/mol, which is about the same as that estimated at high conversions using polymer extraction techniques. At low conversions, the polymerization rate is constant at constant temperature. However, at higher conversions, an "autocatalytic" effect is observed as a tenfold increase in polymerization rate. This result is shown to require at least a tenfold increase in chain propagation length in the autocatalytic region.

Though diacetylenes have been known to polymerize for some time, the current interest in the polydiacetylenes stems largely from the recent work of Wegner, who identified the polymerization as a solid-state, 1,4-addition reaction.[1,2] In a number of instances this polymerization process has been shown to result in high perfection, large dimension polymer crystals.[3,4] The backbone is fully conjugated with two mesomeric representations, acetylene (=RC-C≡C-CR=) and butatriene (-RC=C=C=CR-), both of which have now been observed.[5-8] The polymer crystals are fully chain aligned and are effectively one dimensional in their optical properties.

The polymer of 2,4-hexadiyne-1,6-diol bis(*p*-toluenesulfonate), PTS (R is $-CH_2SO_3C_6H_4CH_3$), exists as the acetylenic structure[5] and is now described in a rather extensive literature concerned with optical properties,[9-13] photoconduction,[14-16] and the polymerization process.[2,4,17,18] The polymerization process is particularly interesting in PTS because of the "autocatalytic" effect first reported by Wegner[2] and since reexamined by Bloor et al.[17] In both cases, an extraction procedure was used in which the weight fraction of insoluble polymer was determined as a function of exposure time at a particular temperature (60, 70, and 80 °C in the experiments of Bloor et al.[17]). After ~10% conversion to polymer, conversion vs. time curves show a rapid—almost discontinuous—rise to nearly 100% conversion to polymer. From these data, one can estimate that the polymerization rate increases by a factor of 100 or more in this autocatalytic region,[2,17] i.e., $\gamma_{\max}/\gamma \gtrsim 100$ where γ is the polymerization rate in the low conversion limit. A reliable determination of $\gamma_{\max}/\gamma$ is quite important if a successful theoretical model for the autocatalytic effect is to be developed. The estimate from the extraction experiments cannot be considered very reliable because of a number of problems inherent in the extraction technique. First, the published data simply lack the accuracy that would be required for a reliable estimate. Also, a detailed study of the autocatalytic region is inhibited by the tedium of the extraction procedure. Finally, at low conversions where the crystals collapse on extraction, an unknown amount of polymer is lost by dissolving in the solvent (as we will discuss later) and by simply passing through the filter. At high conversions where the crystal integrity is maintained an unknown amount of monomer can be trapped in the lattice. (Intense grinding of the polymer with multiple extractions will eliminate this problem to some extent.)[17] Both of these problems would lead to overestimates of $\gamma_{\max}/\gamma$, even if the accuracy of the data were improved. In this paper, we examine the thermal polymerization of PTS using diffuse reflectance spectroscopy and establish at least a firm lower limit for $\gamma_{\max}/\gamma$. In addition, we accurately determine the activation energy for thermal polymerization of PTS and discuss the evolution of the spectra during polymerization.

The application of diffuse reflectance spectroscopy is now commonplace,[19] particularly in inorganic chemistry where it can be used, for example, to eliminate effects of solvent on the coordination sphere of metal ions.[20] For organic materials, solvent effects are usually more subtle and applications of diffuse reflectance have generally been limited to the study of adsorbed species.[21,22] Kinetic studies in either area are quite rare.[23,24]

The theoretical basis for diffuse reflectance spectroscopy was established some time ago by Kubelka and Munk.[25] Though there are a number of more elaborate theoretical treatments of the problem,[26] the Kubelka-Munk (KM) theory remains a quite successful and widely used approach. According to KM theory, the ratio of the absorption coefficient (k) to the scattering coefficient (s) is given by

$$k/s = (1 - R)^2/2R \tag{1}$$

where R is the diffuse reflectance as measured against some nonabsorbing standard. This standard is often the dispersal medium for the absorbing material of interest. (In that case, eq 1 is sometimes rewritten to show explicitly the proportionality of k/s to the concentration of absorbing material.) Since s is independent of wavelength for moderately sized particles,[21,26] the absorption spectrum can be obtained from diffuse reflectance within an unknown scaling factor, s. The KM formulation has been shown in many instances to have quantitative applicability over a limited concentration range.[19,26,27] At high concentrations, specular reflection becomes important and this is the failure point for most theories, including KM theory. There are two ways of reducing this effect. First, one can dilute the sample in the nonabsorbing standard. A number of white materials have been used including filter paper,[28] which is used here. A second method is to use crossed polarizers for excitation and collection.[26,29] Ideally, the diffuse component is completely depolarized, while, for certain crystal orientations and collection angles, the specular component retains its polarization and is eliminated by the crossed polarizer. However, only if the collection sphere is limited to normal incidence (which is not the usual experimental arrangement) would the specular component be entirely eliminated by the crossed polarizers—and then only for isotropic crystals. The polydiacetylenes are highly anisotropic (essentially one dimensional) in their optical properties. Therefore, we will utilize here both methods for reducing specular reflection.

Our experimental arrangement and data collection procedures are described briefly in the Experimental Section. In the Results and Discussion, the results for the thermal polymerization of PTS are presented and discussed.

Experimental Section

Though commercial instruments are now available for measuring diffuse reflectance, we chose to set up the more flexible system described here. The excitation source was a 150-W xenon lamp with two ¼-m monochromators (Schoeffel 250D system) in tandem. The excitation bandwidth was 0.8 nm for all spectra reported here; this resolution is more than adequate to faithfully reveal all important features of the PTS spectrum above room temperature. (A subtle band splitting of ~200 cm^{-1} can be revealed at room temperature with high-resolution reflection spectra or using modulation techniques.[12]) The beam is linearly polarized with a Polaroid HNP'B polarizer and focused onto the sample—PTS crystals dispersed in filter paper (Whatman, 3M). The sample was sandwiched between a glass plate and a copper block. A dummy arrangement on the reverse side of the copper block had two 0.002 in. diameter copper-constantan thermocouples (front and back of dummy sample) connected to a Leeds and Northrup Electromax III temperature control system (±0.1 °C). The sample was located at one focal point of the elliptical collection mirror, which had a 5/16 in. diameter hole in the center for excitation. A photomultiplier tube (Bailey 4283B; S20 response) was located near the second focal point (~10 in. away). The angular collection range was 65° from normal in all directions, except for the small area blocked by the sample housing. A second polarizer was positioned between the sample and the PMT and, for all measurements reported here, was crossed with respect to the first polarizer. A beam splitter was located before the sample to provide a normalization signal from a second PMT. The signals from the two PMTs were amplified, ratioed, and plotted against wavelength. After normalizing to the results for the filter paper alone, the reflectance spectrum was obtained. The filter paper had a polarization ratio of essentially zero and an absolute reflectance of >93% throughout our spectral range, as determined using Eastman white reflectance standard no. 6091 ($BaSO_4$).

The PTS monomer was prepared by the method due to Wegner[2] and purified by several recrystallizations. A 0.07 g/mL solution of PTS in acetone was prepared, as well as 10:1 and 20:1 dilutions of this solution. We will refer to these solutions according to their relative concentrations, C_r = 1.0, 0.1, and 0.05. The filter paper with a thickness of 0.33 mm (further increase in this thickness did not increase the reflectance) was dipped in one of the solutions and the solvent was allowed to evaporate at 10 °C. The sample was then mounted in the sample holder (also at 10 °C to avoid any significant polymerization prior to measurement) and immediately inserted into the vacuum chamber. Spectral analysis reveals that the sample at this point contains less than 0.01% polymer. The sample contained ~1.5 mg of PTS (~0.1 g/cm^3) for C_r = 1.0 and proportionately less for the dilute samples. Though some experiments were conducted under high vacuum (<10^{-5} Torr), for all results reported, a modest vacuum of ~10^{-2} Torr was employed. The low thermal conductivity of the filter paper caused some problems and a number of sample holder designs were tried. In the final design, the two thermocouples on the dummy sample indicated a tolerable 3–4 °C temperature gradient through the sample at the highest temperature employed (80 °C). Since our thermocouple arrangement would tend to exaggerate the gradient, the actual gradient across the PTS sample was certainly less. The temperatures reported here represent the average of the readings from the front (glass/paper) and back (copper/paper) of the dummy sample.

One set of samples for C_r = 1.0, 0.1, and 0.05 was examined by scanning electron microscopy for an estimate of the crystallite size. In each sample a range of crystallite sizes from ~0.1 μ to greater than 10 μ was observed. The concentrated sample was dominated by the large crystallites. The least concentrated sample was composed mainly of crystallites in the 0.1–1.0 μ range.

Results and Discussion

A test of KM theory (eq 1) is shown in Figure 1. The PTS sample (C_r = 1.0) was heated to 76 °C for 35 min and the spectrum recorded after returning to room temperature. According to the extraction results of Bloor et al.,[17] this treatment would give ~0.8% insoluble polymer. The agreement with the absorption spectrum for a single crystal with 0.1% insoluble polymer from Bloor and Preston[11] is remarkably good and, in fact, the curves are essentially superimposable. Therefore, the scattering coefficient, s, may be considered to be independent of λ, as has been shown to be the case in many systems where the crystallite dimensions are greater than the excitation wavelength.[21,26]

When the same sample is soaked in acetone the monomer is extracted and the lower curve in Figure 1 results. (Further treatment with hot acetone reduced this spectrum by less than 5%.) The spectral shift to shorter wavelengths and the spectral broadening are not unexpected. With the collapse of the crystals on extraction, the polymer chains would not be expected to retain their planar, fully conjugated conformation, so that an average conjugation length, which is shorter than the actual chain length, results.[30] Hence, the spectrum is broadened and blue shifted.[31] The large decrease in absorption is surprising since, by analogy to the polyenes,[32] we expect the absorption coefficient to be roughly proportional to conjugation length.[33] As a consequence, the integral under the absorption bands for the extracted and unextracted samples should be similar. However, it may be that a significant portion of the conjugation lengths are short enough so that they absorb below 400 nm, i.e., less than about five monomer units in length.[32] Spectral analysis of the extractant solution from this same sample (and also from experiments following the procedure in ref 2 and 17) definitely shows the presence of some polymer. This solution spectrum is quite similar to the extracted spectrum of Figure 1, except slightly more structured with broad

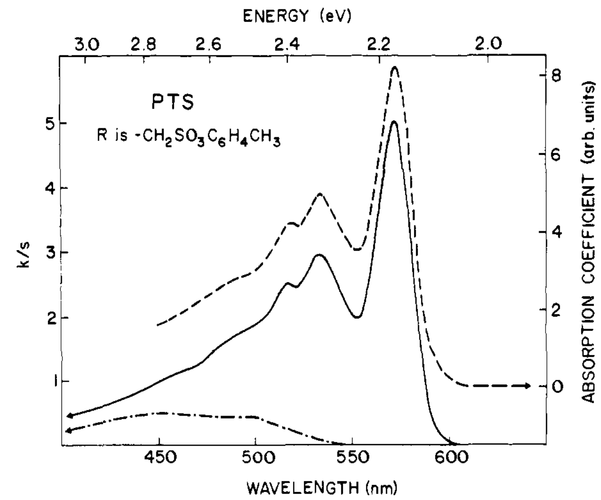

Figure 1. Absorption spectrum from diffuse reflectance (solid curve) (eq 1) for a PTS sample (C_r = 1.0) which was exposed to a temperature of 76 °C for ~35 min (~0.8% polymer).[17] The lower curve (- · · ·) results after extraction of the same sample with acetone. The upper curve (- - -) is from transmission measurements[11] on a single crystal containing ~0.1% polymer.

absorption peaks at ~500 and ~460 nm. A repeat of this experiment with ~½ the exposure time at 76 °C gave approximately a factor of 2 reduction in all three spectra. We have not measured quantitatively the polymer fraction which dissolves but, as stated earlier, we believe that it could be large enough to affect the results of Wegner[2] and Bloor et al.[17] There is no doubt, however, that an insoluble fraction does remain, which presumably contains the longer chains.

The evolution of the reflection spectra at 76 °C is shown in Figure 2 for C_r = 1.0. At low conversions the polymer concentration is expected to vary linearly with time as is the absorption coefficient, k. An analysis of the data shown in Figure 2 (including spectra taken at shorter time intervals but not shown in the figure) reveals that k/s from KM theory varies linearly with time until ~0.6 h at the peak absorption (572 nm) and for much longer times at shorter wavelengths. Thus, through this experiment and much more stringent tests of the time evolution of k/s monitored continuously at a single wavelength, the quantitative application of KM theory in the low conversion range is strongly justified.

At higher conversions, KM theory breaks down for this concentrated sample owing to specular reflection (among other things, perhaps).[26] This effect causes an artificial sublinear variation of k/s at 572 nm with time and eventually a decrease with time (t > 4.2 h). The unstructured spectrum at t = 4.2 h in Figure 2 is symptomatic of that often observed when there is a significant contribution from both diffuse and specular reflection. Since the two components are complementary (diffuse, minimum at absorption peak; specular, maximum at absorption peak) a relatively unstructured spectrum results. The absorption spectrum obtained by Bloor et al.[17] from diffuse reflectance measurements on high conversion (~12%), extracted PTS (undiluted) shows a similar loss of structure. Their spectrum also shows an increase in absorption in the blue region as would be obtained, for example, from the inappropriate application of KM theory to our final $t \geq 6.2$ h curve. (A much larger increase would be obtained from the analogous curve for unpolarized light.)

All of the features in the final reflectance curve for complete polymerization can be attributed to specular reflectance. The correlation to the normal incidence reflectivity from Eckhardt et al.[12] is even more obvious if the two polarizers in our experiment are arranged parallel, in which case R increases by about a factor of 5. This dominance of the specular component is unusual in the diffuse reflectance literature, particularly in a crossed polarizer configuration. However, it is not surprising for the polydiacetylenes, since they are highly anisotropic and show metallic-like reflection with light polarized parallel to the chain direction. Therefore, even for normal incidence, the reflected light will in general be elliptically polarized. A simple calculation which illustrates this point is described in Appendix I.

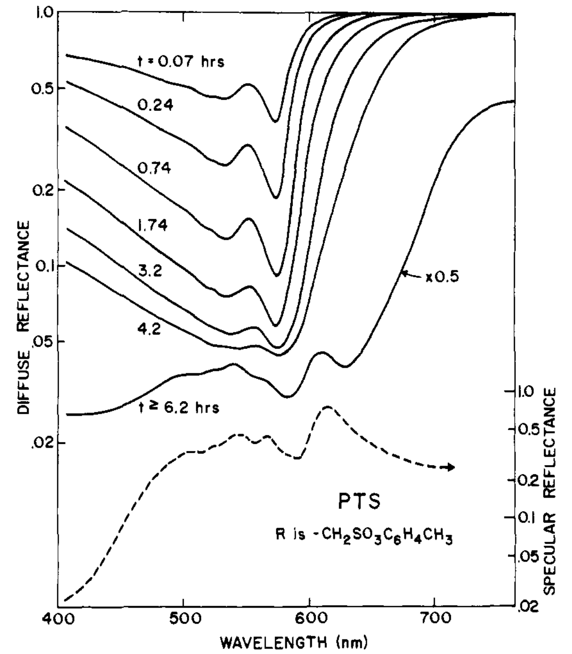

Figure 2. Evolution of diffuse reflectance spectra of PTS for various times at ~ 76 °C. All data were taken on the same sample (C_r = 1.0) and in a crossed polarizer configuration. The dashed curve is the normal incidence reflectance spectrum of fully polymerized PTS from Eckhardt et al.[12] for incident light polarized parallel to the chain direction.

The spectral evolution for PTS shows the growth of a band system (peaked at 572 nm) with no observable shift in frequency over the conversion range which this peak can be unambiguously determined in the diffuse reflectance spectrum. As is evident from the final curve in Figure 2, the absorption peak at complete conversion is located at ~615 nm, i.e., the maximum in the specular reflection region. These results are in general agreement with the transmission data of Bloor et al.[17] However, we see no evidence for a continuous shift of the 572-nm transition to 615 nm, as Bloor et al.[17] have inferred from their transmission data. In fact, our results cannot rule out the possibility that the 572-nm band system becomes buried under the 615-nm system, the latter making its appearance in the autocatalytic region.

With the quantitative applicability of KM theory established for our problem at low polymer conversions, we can now move on to the important problem of determining the activation energy (E_a) for thermal polymerization. We can write the following relation for the polymerization rate at low conversion:

$$\gamma \equiv \frac{d[P]}{dt} = n\alpha = n\alpha_0 \exp(-E_a/RT)$$

$$= \frac{A(n,\lambda)}{C_r} \frac{d(k/s)}{dt} \tag{2}$$

where [P] is the normalized polymer concentration, α is the polymer initiation rate constant, n is the average chain length (in monomer units), C_r is relative concentration, as before, and k/s is from eq 1 at some wavelength, λ. Note that we have ignored the factor (1 − [P]) that would multiply $n\alpha$ assuming first-order kinetics, since it is negligible at low conversions.

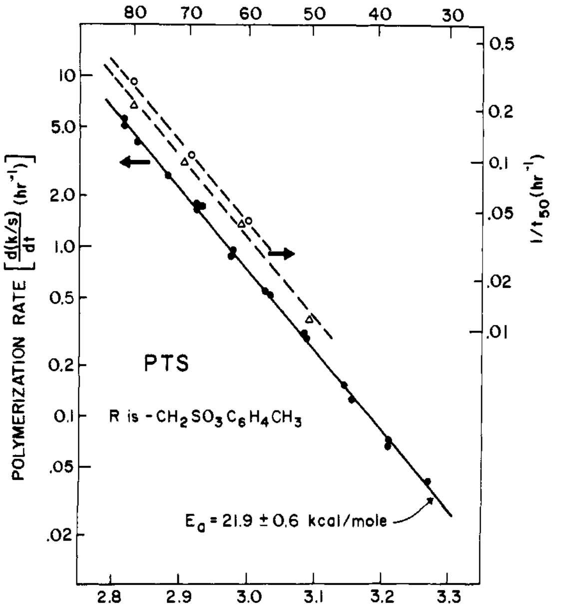

Figure 3. Polymerization rate vs. $1/T$. The solid line represents the best fit to an Arrhenius expression with $E_a = 21.9 \pm 0.6$ kcal/mol. The open circles and triangles are measurements of the time required to reach 50% polymer from Bloor et al.[17] and Preziosi.[34]

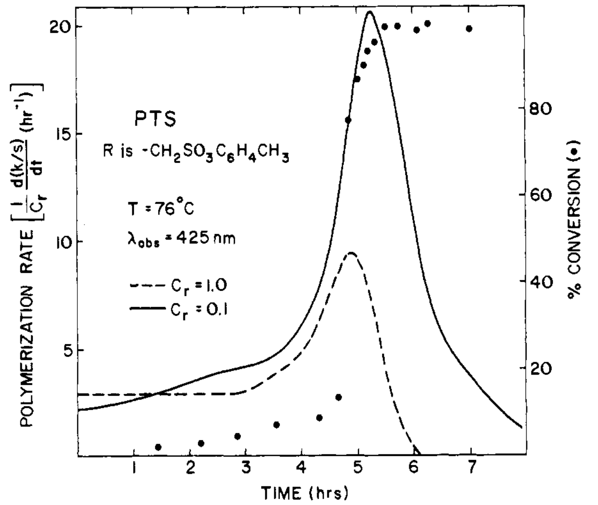

Figure 4. Polymerization rate vs. time at 76 °C. Note that the results are normalized by the relative PTS concentration, C_r. The autocatalytic effect is seen as the large increase in rate at $t \sim 4$ h. The solid points are taken from Bloor et al.[17] and have been corrected to our time scale, i.e., from 80 to 76 °C, assuming an activation energy of 21.9 kcal/mol. The small increase in polymerization rate at $t \sim 1$-2 h for $C_r = 0.1$ sample is thought to be an artifact due to the effect of small crystallite sizes on the polymerization kinetics.

$A(n,\lambda)$ is a constant for a particular n and λ and would be inversely proportional to the absorption spectrum of a chain of length n. Substantial changes in n would be expected to be accompanied by measurable frequency shifts in the absorption spectrum (red shift with increasing n). Since there are no spectral shifts in the low conversion range, we assume that n and $A(n,\lambda)$ for a particular λ are constants in this range. The same argument also allows us to ignore any further growth of "living" chain ends, at least in this low conversion range. The proportionality of $d(k/s)/dt$ to C_r in eq 2 was tested for $C_r = 1.0$, 0.1, and 0.05 in numerous instances in the course of these experiments. Deviations as large as a factor of 2 were occasionally observed; this was probably due to variations in sample preparation, since there seemed to be no systematic deviation from a simple linear proportionality.

We have assumed in writing eq 2 that the measured E_a is associated entirely with the initiation step, i.e., that chain propagation and termination do not make major contributions to the measured E_a. This assumption seems quite reasonable, since the activation energy for UV polymerization of PTS has been estimated to be quite small.[2] (Our preliminary result for PTS is 3.0 ± 0.5 kcal/mol.)

For an E_a determination, R is monitored continuously at 572 nm while the temperature is changed stepwise from ~35 °C to ~80 °C. R is then converted to k/s and $d(k/s)/dt$ is determined at each temperature. At the end of the experiment extensive measurements at the highest temperature are conducted to ensure that all measurements have been made in the range where k/s is rigorously linear with time. Results are shown in Figure 3 for two complete temperature cycles. There was no systematic variation between the two temperature cycles. An Arrhenius expression accurately describes the data over a temperature range in which the polymerization rate changes by more than 2 orders of magnitude. In this low conversion limit, we find $E_a = 21.9 \pm 0.6$ kcal/mol. The error estimate includes (crudely) the temperature uncertainty mentioned in the Experimental Section. Results are also shown for the reciprocal time to 50% polymer ($1/t_{50}$) from the extraction experiments of Bloor et al.[17] and Preziosi.[34] The problems we mentioned earlier for the extraction procedure should not affect the temperature dependence of t_{50}. The high conversion, extraction results for E_a are seen to be in excellent agreement with our E_a determination at low conversions. Furthermore, Patel[35] has recently examined the autocatalytic region in more detail using extraction techniques. He determined the time required to go from 10 to 50% polymer over the temperature range 40-80 °C and found an activation energy of 22.5 ± 0.8 kcal/mol. We conclude, as Bloor et al.[17] have suggested, that there is little, if any, change in E_a in the autocatalytic region. Therefore, making the reasonable assumption that the preexponential factor α_0 in eq 2 remains unchanged in the autocatalytic region, we conclude that the chain initiation rate constant is unchanged throughout the polymerization. The large increase in polymerization rate must be attributed to an increase in chain length, i.e., to the factor n in eq 2. We will now determine a lower limit value for the increase in n.

In order to follow the polymerization rate as a function of time beyond the low conversion limit, we must reduce the contribution from specular reflection. We do this by sample dilution and by changing the observation wavelength to 425 nm, where specular reflection is much less. The results are shown in Figure 4. For the concentrated sample we obtain $\gamma_{max}/\gamma = 3.2$. However, specular reflection is still a problem, since $d(k/s)/dt$ becomes negative beyond 6.1 h. Dilution to $C_r = 0.1$ yields $\gamma_{max}/\gamma = 10$, as did two separate experiments (not shown) for $C_r = 0.05$. This further dilution also results in no further shift of γ_{max} to longer times. We, therefore, take $\gamma_{max}/\gamma = 10$ to be the limiting value as $C_r \rightarrow 0$. This value is a lower limit, however, because $A(n,\lambda)$ has changed with the increase of n and we neglected the unknown term $(1 - [P])$ in eq 2. Since we are monitoring $d(k/s)/dt$ in the blue region of the spectrum it is quite likely that $A(n,\lambda)$, which is inversely proportional to the absorption spectrum, will increase with an increase in n (red shift in absorption spectrum). The correction for $A(n,\lambda)$ could be expected to cause less than a factor of 2 increase[11] in γ_{max}/γ. The term $(1 - [P])$ cannot be taken from extraction data of Bloor et al.[17] shown in Figure 4 because of at least a 10% uncertainty in the time scales. However, if γ_{max} occurs at $P \leq 0.5$, which seems reasonable, a further increase of less than a factor of 2 is necessary in our γ_{max}/γ estimate.

Therefore, the length of the chains formed in the autocatalytic region is at least 10 times (and probably no more than 50 times) greater than those formed at low conversions. This increase in chain length is consistent with the ESR measurements of Stevens and Bloor[18] and with Wegner's viscosity measurements.[2]

Bloor et al.[17] conclude that the polymer chains are "effectively infinite" in length even at low conversions. This conclusion is based primarily on the insolubility of the polymer and the high viscosities obtained by Wegner.[2] The large frequency shifts observed in the optical spectra (572-615 nm) and the small frequency shift observed in the Raman spectra (+75 cm^{-1} for $\nu_{C\equiv C}$) are attributed to the release of a large degree of strain on the low conversion, polymer chain. This strain is due to the 5% elongation necessary for an isolated, infinite polymer chain to be commensurate with the monomer lattice. Mitra et al.[36] have studied the stress dependence of the Raman vibrational frequencies in monocrystalline fibers of the polydiacetylene, HDU (R is $-CH_2OCONC_6H_5$). This polymer has the acetylene structure[6] with bond lengths which are nearly equal to those in PTS.[5,6] The vibration frequencies in the double and triple bond regions vary linearly with elongation of the HDU fiber due to effects of bond anharmonicity. The largest measured shift was +32 cm^{-1} for $\nu_{C\equiv C}$ at 1.6% elongation. (At higher elongations the fibers broke.) This translates to 100 cm^{-1} for the 5% elongation of the low conversion PTS chains, in good agreement with the results of Bloor et al.[17] The Raman intensity in HDU was essentially independent of elongation. If the shift in the absorption maximum in HDU (not measured directly) were anywhere near the shift observed for PTS, large changes in Raman intensity would be expected owing to resonance enhancement effects. Also, as stated earlier in reference to Figure 2, we do not see the continuous shifts in absorption frequency as a function of conversion that would be required for a highly strained PTS chain. For these reasons, we do not believe that the blue-shifted absorption spectrum in low conversion PTS crystals can be entirely explained with strain arguments. Instead we suggest that either the initial chains are relatively short or the bonding sequence is different from the acetylene structure observed[5] for the fully polymerized crystals.

The simplest explanation of the low conversion absorption spectrum is that after initiation the chains will propagate only a relatively short distance because of the large (5%) mismatch between monomer and polymer repeat distances in the chain direction (*b* crystallographic direction).[17] As the concentration of these chains grows, the *b* axis repeat decreases owing to solid solution formation. (It is this effect which would be expected to cause continuous frequency shifts for a highly strained PTS chain in the monomer lattice.) Eventually the lattice mismatch is decreased to the point where the chains can propagate for much longer distances, i.e., at least 10 times further according to our results. This is essentially the model considered by Bloor et al.[17] However, the hypothesis that the initial chains are quite short was rejected previously, mainly because of solubility considerations and the high reduced viscosities measured by Wegner.[2] Based on a lowest energy optical transition of 572 nm, a chain length of roughly 24 monomer units can be estimated. It seems likely to us that a polydiacetylene chain of this length would be insoluble in common organic solvents. However, it is not clear that Wegner's viscosity measurements[2] can be rationalized with these relatively low molecular weight (~10 000) chains.

A final possibility is that the low conversion chain represents an intermediate state[1,2] with a different bonding sequence—butatriene, for example. Since a butatriene structure has now been observed,[7,8] this possibility deserves further consideration. In this regard it is interesting to point out that high pressure (~5 kbar) induces an butatriene to acetylene transformation in the polydiacetylene, TCDU [R is $-(CH_2)_4OCONHC_6H_5$][8] and that a 0.1% elongation at the thermochromic phase transition in ETCD [R is $-(CH_2)_4OCONHC_2H_5$] is observed directly in a thermal mechanical analysis.[37] As in TCDU, this phase transition in ETCD is believed to have associated with it a change in electronic structure which corresponds to an acetylene to butatriene transformation in backbone structure.[37] Therefore, it does not seem unreasonable that the elongation of the polymer chain in PTS at low conversions could result in the favoring of a butatriene bonding sequence. Though it may be fortuitous, the optical properties (both Raman and absorption) of TCDU in the butatriene form are quite similar to those of low conversion PTS.

In summary, we have demonstrated a new technique for analyzing the polymerization of diacetylenes. The method does not require large single crystals and avoids the tedium and inaccuracy associated with extraction techniques. The application to PTS has produced a more quantitative description of the experimental parameters associated with thermal polymerization in this material. A study of UV and γ-ray polymerization of PTS using diffuse reflectance spectroscopy is in progress.

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Appendix I

We will discuss briefly here the specular contribution to our reflection spectra. The reflection coefficients for one-dimensional materials at arbitrary angles of incidence have recently been worked out.[38] The formulas are quite complicated and their application to the problem here would offer no qualitative insight without elaborate computer calculations. Therefore, we will make the simplifying assumption that only normal incidence reflection is collected. In that case, the reflection coefficients reduce to the well-known Fresnel coefficients[39] and the calculation of $\mathcal{R}^+$ (crossed) and $\mathcal{R}^\parallel$ (parallel) is quite simple. We will further assume that all crystals are oriented with a face (containing the polymer chain) parallel to the *xy* plane. This assumption affects only the absolute magnitude of $\mathcal{R}^+$ and $\mathcal{R}^\parallel$ and not their ratio.

The incident light propagates in the *z* direction and is linearly polarized along the *y* direction. If the chain makes an angle θ with respect to $\hat{y}$, then the reflected electric field is

$$\boldsymbol{E}^r = (r_\parallel - r_\perp)\sin\theta\cos\theta\,\hat{x} + (r_\parallel\cos^2\theta + r_\perp\sin^2\theta)\hat{y} \tag{A.1}$$

The terms $r_\parallel$ and $r_\perp$ are the Fresnel coefficients[39]

$$r_\parallel = (1 - n_\parallel - i\kappa_\parallel)/(1 + n_\parallel + i\kappa_\parallel) \tag{A.2}$$

and

$$r_\perp = (1 - n_\perp)/(1 + n_\perp) \tag{A.3}$$

where $n_\parallel$ and $n_\perp$ are the real parts of the refractive indices parallel and perpendicular to the chains, respectively; $\kappa_\parallel$ is the imaginary part of the refractive index and is related to the absorption coefficient (parallel to chain) as $\kappa_\parallel = k\lambda/4\pi$. In eq A.3 we have taken $\kappa_\perp = 0$, a good approximation for the polydiacetylenes in the visible region of the spectrum. This assumption does not affect the equations to follow.

With the second polarizer in the *x* direction (crossed) we will observe only the *x* component of $\boldsymbol{E}^r$ and may calculate $\mathcal{R}^+$ by integrating $|E_x{}^r|^2$ over θ. The properly normalized result is

$$\mathcal{R}^{+} = \tfrac{1}{8}(R_{\parallel} + R_{\perp}) - \tfrac{1}{4}Re(r_{\parallel}r_{\perp}) \qquad \text{(A.4)}$$

where $R_{\parallel}$ and $R_{\perp}$ equal $|r_{\parallel}|^2$ and $|r_{\perp}|^2$ and are the usual expressions for normal incidence reflectivity.[39] Similarly, with the second polarizer in the y direction (parallel), we find

$$\mathcal{R}^{\parallel} = \tfrac{3}{8}(R_{\parallel} + R_{\perp}) + \tfrac{1}{4}Re\,(r_{\parallel}r_{\perp}) \qquad \text{(A.5)}$$

Note that $\mathcal{R}^{+} + \mathcal{R}^{\parallel}$ gives $(R_{\parallel} + R_{\perp})/2$ as expected. Also, as expected, $\mathcal{R}^{+} + \mathcal{R}^{\parallel}$ gives 1 and ½ for the two limiting cases of perfect reflection in all directions ($r_{\parallel} = r_{\perp} = -1$) and perfect reflection in one dimension ($r_{\parallel} = -1$; $r_{\perp} = 0$). For the limiting case of an isotropic absorber with reflectivity R_{iso}, we find $\mathcal{R}^{+} = 0$ and $\mathcal{R}^{\parallel} = R_{\text{iso}}$, as required for the case of normal incidence collection.

Since $R_{\perp}$ is unstructured in the visible, $\mathcal{R}^{+}$ will more or less follow $R_{\parallel}$ as we observe in Figure 2. Also, since $r_{\perp}$ is real, $Re(r_{\parallel}r_{\perp})$ is always positive and the ratio $\mathcal{R}^{\parallel}/\mathcal{R}^{+}$ is always greater than 3. As stated earlier, we observe $\mathcal{R}^{\parallel}/\mathcal{R}^{+} \approx 5$. However, it is difficult to argue even qualitatively the effect on this ratio when all angles of incidence are included.

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Structure of Imerubrine, a Novel Condensed Tropolone–Isoquinoline Alkaloid

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Abstract: Imerubrine, $C_{20}H_{17}NO_5$, is an orange-red base obtained from *Abuta imene* and *Abuta refescens*. It crystallizes in space group $P\bar{1}$; cell dimensions $a = 11.368$ (1) A°, $b = 11.871$ (1) A°, $c = 13.058$ (1) A°, $\alpha = 94.23$ (1) °, $\beta = 100.87$ (1) °, $\gamma = 75.18$ (1) °. There are four molecules in the unit cell. The structure, solved by a novel direct methods approach, proves to be a new tropolone ether for which the general term "tropoloisoquinoline" is proposed. The possible biosynthesis is discussed.

Imerubrine, $C_{20}H_{17}NO_5$, is an orange-red base which has been isolated from the tropical American vines *Abuta imene* and *Abuta refescens*. On the basis of its spectroscopic properties, the tentative structures **1** or **2** were suggested for imerubrine.[2] We now report the results of a complete x-ray crystallographic analysis which shows that imerubrine has neither of these structures, but has instead the remarkable tropolone ether structure **3**. Imerubrine is thus the first example of a new isoquinoline alkaloid type, for which the general term "tropoloisoquinoline" is proposed.[3]