Energetics and Mechanism of the Solid-State Polymerization of Diacetylenes

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Abstract: A calorimetric study of the thermal polymerization of crystals of 2,4-hexadiyne-1,6-diol bis(*p*-toluenesulfonate) (PTS) is reported. Both programmed and isothermal differential scanning calorimetry techniques are employed to evaluate the heat of polymerization (ΔH_p = -36.5 kcal/mol) and the activation energy (E_a = 22.5 kcal/mol). In addition, the isothermal results, in conjunction with low conversion extraction measurements, yield a quantitative characterization of the autocatalytic effect in PTS: α_{max}/α_0 = 300 ± 50, where α_0 is the rate constant for polymerization in the low conversion limit and α_{max} is the maximum value observed in the autocatalytic region. This result is independent of temperature. The E_a and ΔH_p values are used in a discussion of the energetics and mechanism of the thermal polymerization of diacetylenes. The results suggest a biradical dimer as the chain initiation species.

I. Introduction

The solid-state polymerization of diacetylenes is a prime example of a lattice-controlled solid-state reaction. Current interest in the diacetylenes is due in large part to the work of Wegner,[1-3] who identified the polymerization process as a 1,4-addition reaction:

$$n RC\equiv C-C\equiv CR$$
$$\rightarrow \underset{B}{+RC=C=C=CR+_n} \leftrightarrow \underset{A}{+RC-C\equiv C-CR+_n} \quad (1)$$
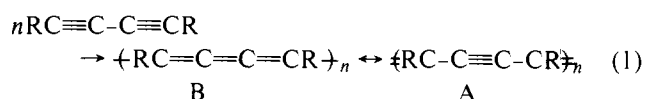
The polymer has a planar, fully conjugated backbone with an all-trans configuration.[4,5] X-ray structure determinations for five different polydiacetylenes (different R groups) are now available. Three have yielded the acetylene backbones (A) in a clear-cut manner.[4,6,7] Two have yielded structures best represented by the butatriene backbone (B).[5] Also, reversible phase transitions, B ↔ A, have been suggested based on spectroscopic considerations.[8,9]

The most thoroughly investigated diacetylene is PTS (R is $-CH_2SO_3C_6H_4CH_3$), both with regard to polymer properties[10,11] and polymerization kinetics.[3,12-16] PTS polymerizes quantitatively via thermal annealing[3,12] or high-energy irradiation.[15] The polymer crystal is nearly one-dimensional in its optical properties[10] and has the acetylene (A) bonding pattern.[6] The polymerization process in PTS is particularly interesting because of a dramatic "autocatalytic effect" observed in the polymer conversion vs. time curves obtained using monomer extraction techniques. At about 10% conversion to polymer, the polymerization rate increases dramatically (~100-fold) and the polymer conversion rapidly approaches 100%. This effect was first discovered by Wegner[3] and has since been investigated by a number of authors.[12-16] Even though the polymerization rate undergoes this dramatic increase at ~10% conversion, the activation energy for thermal polymerization (E_a = 22.5 kcal/mol) is apparently independent of conversion. This activation energy is primarily associated with the chain initiation event (rather than chain propagation), since activation energies for γ-ray and UV polymerization are quite small (~2 kcal/mol).[15]

In this paper, we present a detailed study of the polymerization kinetics of PTS using isothermal and programmed temperature differential scanning calorimetry (DSC). The use of these DSC techniques in the analysis of the kinetics of conventional polymerizations is now relatively commonplace.[17] To our knowledge, this work is first example of their *quantitative* application to a solid-state polymerization (or reaction). Barrall et al.[16] have used isothermal DSC to show that the PTS polymerization is exothermic, but did not present quantitative results and have presented only a rough analysis of the kinetics. In this paper, we determine the heat of polymerization, confirm previous activation energy measurements,[14,15] and provide a more quantitative characterization of the autocatalytic effect. In addition, we discuss the mechanism for thermal polymerization and show that a scheme based on a biradical dimer as the chain initiation species is consistent with the energetic parameters provided by our calorimetric experiments. A preliminary report of this work has appeared recently.[18]

II. Experimental Section

The procedure used in the preparation of PTS was essentially that of Wegner.[3] However, better results, in terms of product purity, have been obtained with some slight modifications of Wegner's procedure.[19] Conventional analysis techniques show little difference between PTS prepared by the modified procedure and PTS prepared by Wegner's procedure. However, the polymerization process is substantially affected, particularly in the autocatalytic region. This explains the discrepancies noted previously[14] in the t_{50} values (time to 50% polymer) of Preziosi,[19] who used Wegner's procedure, and Bloor et al.,[12] who also used Wegner's procedure but with extensive purification. Our results for t_{50} values are in good agreement with Bloor et al.[12] One problem with the extraction procedure noted previously[14] is the dissolution of some polymer. This effect, though small in any case, was not evident in the present work, since our extractant solutions were colorless. Our extraction procedure has been described elsewhere.[15]

A Perkin-Elmer DSC-2 instrument with automated data processing was employed for all measurements of the thermal polymerization of PTS. All experiments were carried out in an argon atmosphere. Absolute calibrations were achieved using an indium standard under conditions which were identical with those of the various PTS experiments. The sample holder was a crimped aluminum pan. Sample weights were in the range of 8-13 mg. (We find that sample weights in excess of ~25 mg lead to distortions in the DSC curve shapes owing to the poor thermal conductivity of PTS). Absolute temperatures quoted herein for DSC experiments are accurate to ±0.5 K. Both isothermal and programmed temperature techniques were employed. In a typical isothermal experiment the instrument was set at the desired temperature, the sample was introduced, and the DSC signal was recorded as a function of time until polymerization was complete. The software for the DSC-2 was not set up for integration of isothermal DSC scans (to obtain the heat of polymerization, ΔH_p). Therefore, the traces were digitized and stored for further analysis on another calculator system (an HP9825 calculator on which all calculations described herein were performed). In the programmed temperature experiments, the sample was heated from 300 K at heating rates of 0.31-2.5 deg/min until polymerization was complete. In this case, ΔH_p was determined immediately by the DSC-2 calculator, which also automatically corrected for baseline drift. In these
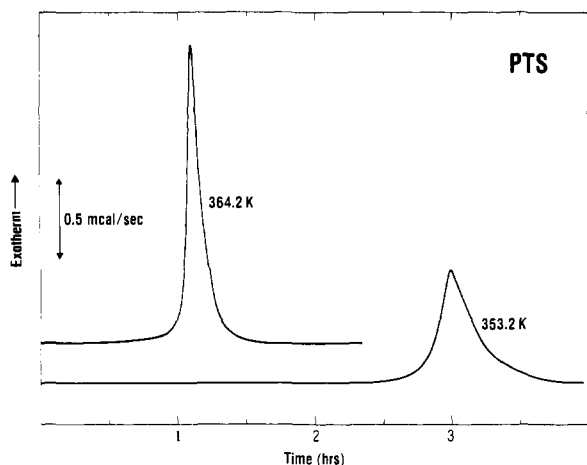
Figure 1. Typical isothermal DSC scans showing the exothermal polymerization of PTS. The sample weights are 10.54 and 10.99 mg for the 364.2 and 353.2 K curves, respectively. The curves are arbitrarily offset.
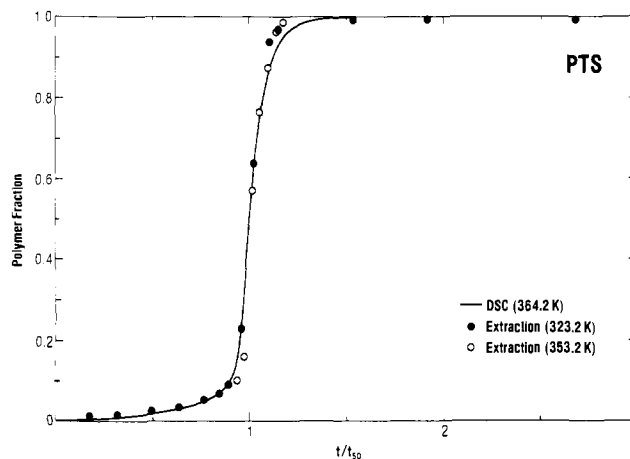

Figure 2. Polymer fraction vs. time obtained from the 364.2 K DSC curve by fitting $P(t) < 0.25$ portion of extraction results obtained at 323.2 K. The t_{50} normalization constant is the time required to reach 50% polymer: $t_{50} = 1.15$ h at 364.2 K, 62.6 h at 323.2 K (extraction), and 3.20 h at 353.2 K (extraction).

programmed experiments, the samples were preannealed (outside the instrument) for various times at 323.7 K (±0.1 K).

In a number of instances samples used in the isothermal and programmed experiments were rescanned to ensure that polymerization was complete. In the course of these experiments we have not seen any evidence for significant degradation of PTS polymer at the temperatures (<393 K) and for the time scales employed in these experiments.[20] We observe rapid degradation of PTS polymer with DSC at ~490 K, in agreement with Bloor et al.[12]

III. Results

A. Isothermal DSC. Typical isothermal DSC scans for PTS monomer are shown in Figure 1. The polymerization is exothermic with a long "induction period". The integral of these curves gives the heat of polymerization ΔH_p (see eq 1). However, care must be taken in choosing the baseline for integration, since it is well established, both by extraction[3,12,15] and spectroscopic measurements,[14] that PTS polymerizes at a slow, constant rate during this period. If the constant level in Figure 1 is used as the baseline, only a lower limit for ΔH_p can be obtained. Extrapolating back from the level region after the reaction is over is not accurate enough. Further analysis at this point requires that we make an assumption regarding the nature of the polymerization process, namely, that the product formed at all times along the conversion curve is the same energetically, i.e., that ΔH_p is independent of the polymer fraction $P(t)$. More specifically, we will assume that the heat evolved per polymerized monomer unit in the "induction" region is essentially the same as that in the high-conversion (autocatalytic) region. It is well established that the initial polymer chains formed in the monomer lattice are highly strained (elongated by ~5%) in the polymer chain direction.[12] In fact, it has been convincingly shown that it is the release of this strain that leads to the autocatalytic behavior.[21] Therefore, the above assumption cannot be rigorously true, because of these strain energy considerations. However, the strain energies involved are quite small (<2 kcal/mol)[21] compared to ΔH_p and this effect can be safely ignored. In fact, the validity of this assumption, within the uncertainty of our measurements, will be more apparent in the next section, when we compare the results of these isothermal experiments to those of the programmed temperature experiments, where there is no baseline ambiguity.

Therefore, assuming that ΔH_p is independent of $P(t)$, we obtain the polymerization rate [$\gamma \equiv dP(t)/dt$] from the height, h, in mcal/s at any point along the DSC curve as

$$\gamma = hM/w \, (-\Delta H_p) \tag{2}$$

where M is the molecular weight of PTS (418), w is the sample weight, and ΔH_p is given as

$$\Delta H_p = \frac{-M}{w} \int_0^\infty h \, dt \tag{3}$$

since the reaction is quantitative. The polymer fraction, $P(t)$, is given by

$$P(t) = \int_0^t \gamma \, dt = \int_0^t h \, dt \bigg/ \int_0^\infty h \, dt \tag{4}$$

Therefore, the unknown baseline can be obtained by fitting eq 4 to previous extraction measurements. We choose to vary the baseline level until the best fit is obtained over the range $P(t)$ = 0–0.25, where the extraction experiments are most reliable. The results of such a procedure are shown in Figure 2 for the 364.2 K curve of Figure 1. The fit is quite good except in the high conversion region where the extraction results are most suspect. Similar results for the 352.2 K curve of Figure 1 were given previously.[18] The final baseline adjustment was 0.004 mcal/s for the 353.2 K data[18] and 0.01 mcal/s for the 364.2 K data. We have used extraction measurements at 323.2 K for comparison, since these represent our most extensive measurements. (It has been shown previously[12,15] that conversion curves obtained by monomer extraction do not change substantially from 303.2 to 353.2 K.) The time scales are therefore adjusted by normalization to t_{50} values. The t_{50} value obtained for the 353.2 K DSC curve in Figure 1 is 3.02 h[18] compared to 3.2 and 3.3 h from the extraction measurements of Chance and Patel[15] and Bloor et al.,[12] respectively. This is quite reasonable agreement, since this 6–9% discrepancy between DSC and extraction translates to a temperature discrepancy of only about 0.8 K at 353.2 K (using an activation energy of 22.5 kcal/mol).[14,15]

The ΔH_p values derived from the DSC experiments of Figure 1 are given in Table I and are in good agreement within our crudely estimated uncertainties. This measurement of ΔH_p provides an important missing link in the analysis of the energetics of diacetylene polymerization. We will discuss the energetics in some detail in section IV.

Also shown in Table I are the time required to reach the exotherm peak, t_{max}, and the maximum polymerization rate, γ_{max}, for isothermal DSC experiments over the temperature range 343.2–364.2 K. The time t_{max} is slightly less than t_{50} and, in fact, would correspond to t_{42}, since our analysis of the 353.2 and 364.2 K data of Figure 1 yields $P_{max} = 0.42 \pm 0.01$, where P_{max} is the polymer fraction at the maximum polymerization
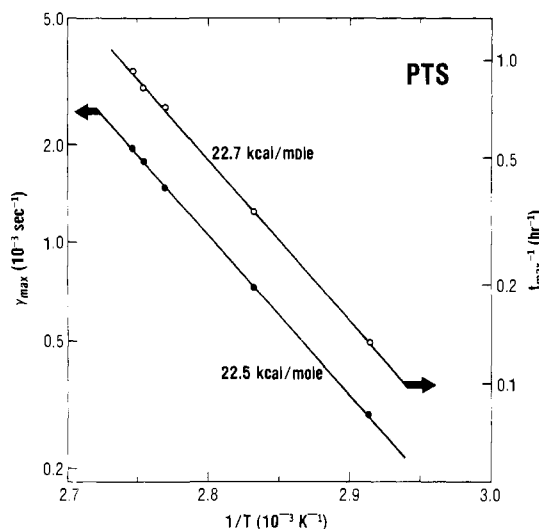
Figure 3. Arrenhius plots for the temperature dependence of γ_{max} (maximum polymerization rate) and t_{max} (time to the maximum rate) from Table I.

Table I. Isothermal Polymerization of PTS

polymerization temp, K	t_{max}, h	γ_{max}, 10^{-3} s^{-1} [a]	$-\Delta H_p$, kcal/mol
343.2	7.48	0.292	>31.1[b]
353.2	2.95	0.717	36.5 ± 0.7[c]
361.2	1.42	1.478	>32.6[b]
363.2	1.23	1.778	>30.9[b]
364.2	1.08	1.956	36.7 ± 0.9[c]

[a] Determined as $h_m M / w(-\Delta H_p)$, where h_m is height of exotherm peak in mcal/s, M is the molecular weight of PTS (418), and w is the sample weight. [b] No corrections for polymerization during "induction period" so that only a lower limit estimate of $-\gamma H_p$ is possible. The integrals are obtained by weighing traces of the DSC curves. [c] Corrections made for polymerization during "induction period" by fitting polymer conversion curve obtained from extraction measurements. (See Figure 2 and ref 18). The error estimate is derived crudely from the goodness of these fits. Prior to this correction the lower limit estimates were 33.5 and 32.2 kcal/mol at 353.2 and 364.2 K, respectively.

rate. In determining γ_{max}, the baseline adjustments necessary to fit the conversion data are unimportant, since they are less than 1% of the peak. The direct accessibility of γ_{max} is a major point in favor of DSC over other techniques, such as the extraction and spectroscopic methods which are sensitive to the integral of the polymerization rate rather than the rate itself.

Arrhenius plots of the γ_{max} and t_{max} data are shown in Figure 3; they yield E_a = 22.5 ± 0.5 and 22.7 ± 0.6 kcal/mol, respectively. The γ_{max} data are, of course, quite sensitive to the autocatalytic behavior. On the other hand, the major contribution to t_{max} is the "induction period". The fact that the E_a values are the same and are in good agreement with previous results strongly supports the previous conclusion[14,15] that the detailed shape of the conversion vs. time curves is independent of temperature, i.e., that E_a is independent of conversion. The various activation energy results are summarized in Table II. (The programmed DSC results will be discussed in the next section.) If we merge all the Table II results, we can conclude that an Arrhenius expression with an activation energy of 22.5 kcal/mol yields an excellent description of the temperature dependence of the polymerization rate over the temperature range 291–364 K, i.e., with a factor of 2400 change in rate!

Table II. Summary of Activation Energy Determinations for the Thermal Polymerization of PTS

method	E_a, kcal/mol	measured quantity
extraction[a]	22.2 ± 0.4	time to 50% polymer (303–353 K)
extraction[a]	22.5 ± 0.8	time from 10–50% polymer (296–353 K)
extraction[b]	22.8 ± 1.0	polymerization rate at low conversions (<3% polymer; 303–353 K)
spectroscopy[c]	21.9 ± 0.6	time evolution of absorption coefficient at polymer absorption peak (308–353 K)
spectroscopy[d]	22.8 ± 0.6	time evolution of integrated absorption spectrum (291–353 K)
isothermal DSC[e]	22.7 ± 0.6	time to maximum polymerization rate (343–364 K)
isothermal DSC[e]	22.5 ± 0.5	maximum polymerization rate (343–364 K)
programmed DSC[f]	22.6 ± 0.4	temperature of maximum polymerization rate

[a] Reference 15; experimental data from ref 12 and 15. [b] Low conversions measurements from ref 12 and 15. [c] Reference 14. [d] Reference 15. [e] This work. See Figure 4. [f] This work. E_a value given above is the average of 32 determinations of E_a (95% confidence limits) by computer simulation of programmed DSC experiments.

An important characterization of the autocatalytic effect in PTS is the increase in polymerization rate in the autocatalytic region, i.e., γ_{max}/γ_0, where γ_0 is the polymerization rate at low conversions (during the induction period). Previous estimates are $\gamma_{max}/\gamma_0 \sim 100$ from extraction measurements and $\gamma_{max}/\gamma_0 > 10$ from spectroscopic measurements;[14] in both cases, it is the measurement of γ_{max} that presents the major problem. Just the opposite is true in the DSC experiments. To obtain γ_0 from our isothermal DSC scans, one must extrapolate back from the constant level after the polymerization is complete. Our sensitivity is such that this procedure cannot be carried out in a reliable manner. However, two experiments carried out at 353.2 K under optimal conditions for such a measurement yielded $\gamma_0 \sim 1.0 \times 10^{-5}$ s^{-1} and $\gamma_0 \sim 6 \times 10^{-6}$ s^{-1}, i.e., $\gamma_{max}/\gamma_0 \sim 100$. From the baseline adjustment (0.004 mcal/s) necessary to fit the extraction results for the 353.2 K data (Figure 1),[18] we have $\gamma_0 \sim 4.2 \times 10^{-6}$ and $\gamma_{max}/\gamma_0 \sim 170$. However, this latter result is obviously not independent of the extraction measurements.

To obtain a reliable estimate of γ_0 we have reexamined the low conversion (<3%) extraction measurements of Chance and Patel[15] and Bloor et al.[12] We obtain E_a = 22.8 ± 1.0 kcal/mol (see Table II) over the temperature range 303.2–353.2 K. (At 353.2 K, the extraction measurements yield γ_0 = 4.3 × 10^{-6} s^{-1}.) Fixing E_a at 22.5 kcal/mol, we may summarize the γ_0 and γ_{max} results as

$$\gamma_0 = (3.55 \pm 0.45) \times 10^8 \exp(-E_a/RT) \text{ s}^{-1} \qquad (5)$$

and

$$\gamma_{max} = (6.15 \pm 0.15) \times 10^{10} \exp(-E_a/RT) \text{ s}^{-1} \qquad (6)$$

Thus, we have γ_{max}/γ_0 = 175 ± 25—a result which is independent of temperature. The ratio of rate constants, α, has more physical significance. The first-order rate equation for γ is[15]

$$\gamma \equiv \frac{dP(t)}{dt} = \alpha[1 - P(t)]$$

$$= nq\xi \exp(-E_a/RT)[1 - P(t)] \qquad (7)$$

where n is the propagation length in monomer units, q is the probability that the thermally generated intermediate state
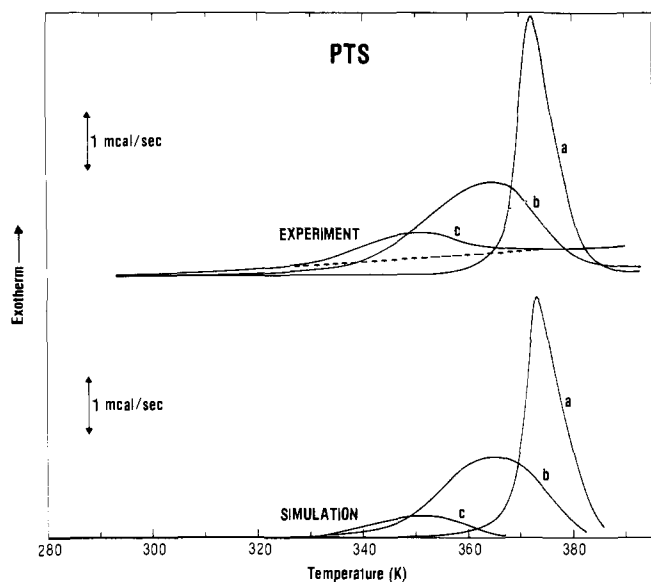
Figure 4. Programmed DSC results for PTS polymerization. The annealing times (at 323.2 K), heating rates, and sample weights are respectively (a) 52 h, 2.5 °C/min, and 11.41 mg; (b) 56.5 h, 2.5 °C/min, and 11.44 mg; (c) 56.5 h, 0.63 °C/min, and 11.76 mg. No baseline corrections have been made for the experimental curves (dashed line of curve c).

Figure 5. Residual heat of polymerization vs. annealing time at 323.7 K (t_{50} = 59.6 h) from Table III. The conversion, obtained by monomer extraction, vs. annealing time at 323.2 K is also shown (t_{50} = 62.6 h).

initiates a chain, and ξ is the frequency factor governing the population of the intermediate state. Since P_{max} = 0.42 ± 0.01, we have

$$\alpha_0 = (nq\xi)_0 = (3.55 \pm 0.45) \times 10^8 \exp(-E_a/RT) \text{ s}^{-1} \quad (8)$$

and

$$\alpha_{max} = (nq\xi)_{max} = (1.06 \pm 0.04)$$
$$\times 10^{11} \exp(-E_a/RT) \text{ s}^{-1} \quad (9)$$

The ratio of rate constants is α_{max}/α_0 = 300 ± 50. Though there is little doubt that an increase in chain length is a major contributor to α_{max}/α_0, the apportionment to the different factors (n, q, and ξ) has not been sorted out. It is interesting to consider the case where q and ξ are independent of conversion. From the previous lower limit estimate of the low conversion chain length (n > 24 units)[14], the lower limit for n in the autocatalytic region is 7200 units or a chain length of 3.5 μm! This chain would have a molecular weight of greater than 3×10^6. This situation seems unlikely; however, there is no additional experimental information to rule out this possibility.

Very recently McGhie et al.[22] have independently examined the thermal polymerization of PTS using isothermal DSC. Their results, E_a = 22 kcal/mol and ΔH_p > 32 kcal/mol, are in good agreement with the results presented herein, though there are some relatively minor differences in interpretation.

B. Programmed Temperature DSC. Programmed temperature DSC is a particularly useful technique for evaluating heats of polymerization.[17] The advantage over isothermal techniques is that there are well-defined points on the programmed DSC curve where the polymerization rate can be taken as zero, i.e., there is no ambiguity in the location of the baseline. In the PTS case, the polymerization rate is completely negligible at 300 K, the starting point for our programmed temperature experiments. This locates the starting point for integration to obtain ΔH_p; the end point is determined as some point well beyond the exotherm peak. The integration with baseline corrections is performed automatically with our calculator system.

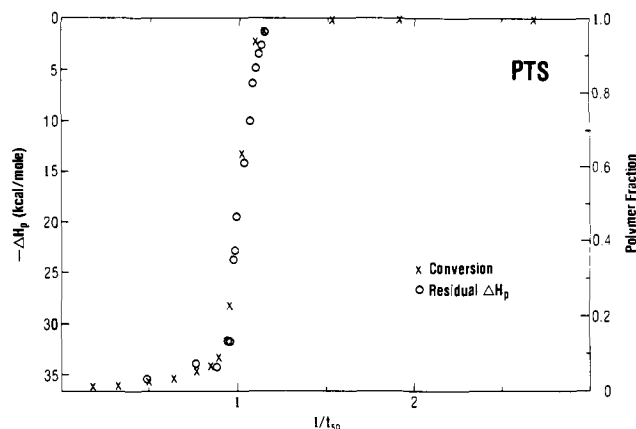A complication arises in the application of programmed

DSC techniques to PTS polymerization which is not usually a problem with conventional polymerizations. If we heat PTS monomer at 10 °C/min, a melting endotherm is observed at 366 K (ΔH_{fusion} = 11.3 kcal/mol). At this high heating rate no significant polymerization occurs prior to melting. Obviously, this melting must be avoided in the study of the polymerization. Melting is still a problem with a heating rate of 0.63 °C/min but is apparently avoided if we further decrease the heating rate to 0.31 °C/min; however, we cannot state this with certainty, since 0.31 is our lowest available rate. These low heating rates are undesirable, in any case, since our sensitivity decreases in proportion to the heating rate.

We avoid the melting problem in the programmed DSC experiments by using samples which have been preannealed outside the instrument. This allows the completion of polymerization with reasonable heating rates prior to reaching the melting point. We are aided by the observation[23] that the "apparent" melting point, T_m (determined with a 10 °C/min heating rate) increases monotonically with polymer conversion $P(t)$.[24] Programmed DSC scans for suitably preannealed PTS show no evidence of melting.

Typical programmed DSC scans are shown in Figure 4. These curves show the sensitivity to the sample pretreatment conditions and to the heating rate. The integral of the DSC scans yields the residual heat of polymerization, ΔH_p^R, which should equal $\Delta H_p(1 - P_a)$ where P_a is the polymer fraction appropriate for the annealing conditions of the experiment. This again requires the assumption, stated earlier in the discussion of the isothermal results, that ΔH_p is independent of $P(t)$. Averaging the results for the seven samples for which P_a was measured by extraction, we find ΔH_p = 36.4 ± 1.3 kcal/ mol (95% confidence limit) in good agreement with the isothermal results. (Restricting our considerations to only the low conversion samples in this group, $P(t) \leq 0.134$, we find ΔH_p = 36.4 ± 0.5 kcal/mol). The ΔH_p^R values are plotted in Figure 5 vs. annealing time and are compared with extraction measurements. The good agreement illustrated in Figure 5 and the good agreement between ΔH_p determined by programmed and isothermal DSC support our assumption that ΔH_p is independent of conversion. However, our experiments cannot completely rule out a significant difference between ΔH_p in the induction region and ΔH_p in the high conversion region, though certainly none is indicated.

The programmed DSC experiments also yield a measure of the activation energy for polymerization. We do this by performing a computer simulation of the DSC experiment. The necessary input is the heating rate, the annealing time and temperature, and the conversion curve previously determined at 323.2 K.[15] The only assumption necessary is that the shape
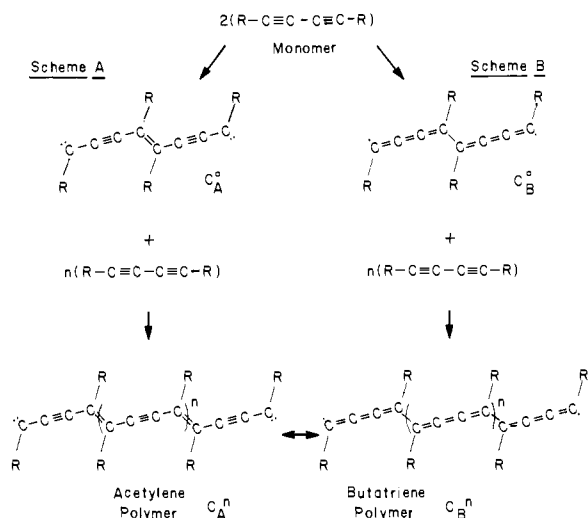
Figure 6. Carbene and radical schemes for the thermal polymerization of diacetylenes.

Figure 7. Reaction diagram for the thermal polymerization of diacetylenes. The photopolymerization process is also indicated.[15]

of the conversion curve is independent of temperature.[15] The activation energy is then varied until the simulation correctly reproduces the observed temperature of the exotherm peak. The average, as shown in Table II, is $E_a = 22.6 \pm 0.4$ kcal/mol (95% confidence limits) in excellent agreement with the various E_a determinations in Table II. We have also performed similar computer simulations using the 353.2 K isothermal DSC curve of Figure 1 instead of the conversion curve so than an absolute scale in mcal/s is obtained. (The additional input of sample weights is also necessary, of course.) Three such simulations with $E_a = 22.5$ kcal/mol are shown in Figure 4 along with the corresponding experimental curves. The agreement with experiment is quite satisfactory.

In summary, the DSC experiments have shown that E_a is, to a high degree of accuracy, independent of polymer conversion. In addition they have provided an important quantitative characterization of the autocatalytic effect, namely, $\alpha_{max}/\alpha_0 = 300 \pm 50$. Most important, however, is the determination of ΔH_p (-36.5 kcal/mol) and the confirmation of previous E_a measurements (22.5 kcal/mol). These energetic parameters will be used in the next section to discuss the mechanism of diacetylene polymerization.

IV. Discussion

Before discussing the energetics of diacetylene polymerization, we must first consider whether the energetic parameters (E_a and ΔH_p) derived for PTS can be taken as being representative of all thermally reactive diacetylenes. Certainly the E_a value for PTS can be considered typical, since E_a estimates for ten different diacetylenes from Wegner and co-workers[25] and published[26] and unpublished work from our laboratory can be summarized as $E_a = 19$–25 kcal/mol.[27] In most of these compounds, the deviation from the E_a value for PTS has no statistical significance. Similar arguments for ΔH_p are not possible, since the PTS value represents the first such measurement for a polydiacetylene. We will attempt to make our point with a simple thermochemical calculation. For this purpose we choose to use Dewar's tabulation of carbon–carbon bond energies for different hybridizations.[28] We must consider a total of five bonds for the monomer and six bonds for the polymer; see Figure 6. (The C–C single bonds to the substituent group must be included, since their hybridization changes from sp-sp³ in the monomer to sp²-sp³ in the polymer.) The calculations yield $\Delta H_p = -29.4$ kcal/mol for the acetylene bonding sequence (scheme A of Figure 6) and -35.1 kcal/mol for the butatriene sequence (scheme B). We may take the
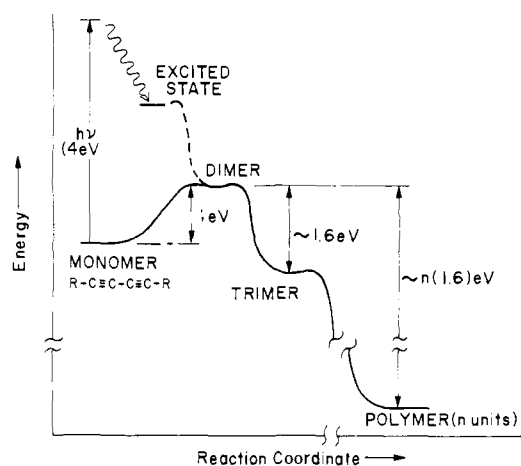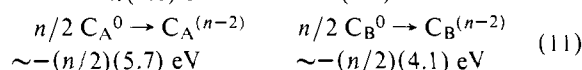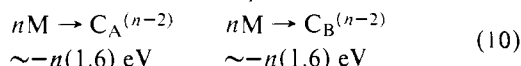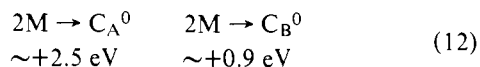
calculation one step further by constructing a bond length/bond energy relationship from Dewar's tabulation and considering the polymer bond lengths observed in X-ray structure determinations.[29] We obtain -30.6 kcal/mol based on average bond lengths for the three structure determinations which yielded acetylene bonding patterns,[4,6,7] -31.5 kcal/mol from the PTS structure (acetylene bonding),[6] and -31.0 kcal/mol for the two structure determinations[5] which yielded butatriene bonding sequences. A number of other methods for estimating ΔH_p are known,[30] but yield very similar results.[31] Thus the experimental ΔH_p value for PTS is in reasonable agreement with the result expected from thermochemical considerations and we doubt that future work on other diacetylenes will yield significantly different ΔH_p values. Thus, it seems safe to assume that the PTS results are typical for thermally polymerizable diacetylenes. For the remainder of this paper we find it convenient to change our energy units to eV: $E_a = 1.0$ eV and $\Delta H_p = -1.6$ eV.

An important first step in the discussion of the mechanism of diacetylene polymerization is to consider whether or not the initiation event (i.e., the dimerization in Figure 6) is a "thermally allowed" process based on molecular orbital considerations.[32] This is most easily accomplished within the radical scheme in Figure 6, since in that case changes in bonding are restricted to the plane of the backbone so that we may work in C_2 symmetry. Further simplification is possible if we consider the formation of the $(R)C\equiv C-\dot{C}=C(R)-(R)C\equiv\dot{C}-C\equiv C(R)$ resonance form of C_B^0 in Figure 6. With these simplifications our problem is completely analogous to the dimerization of ethylene to form a biradical, which is a thermally allowed process.[33] It seems reasonable to assume, therefore, that there is no orbital symmetry imposed barrier to the dimerization of two diacetylene monomer units. As a consequence, our E_a value should be a rough measurement of the difference in energy between two diacetylene monomers and the biradical (or bicarbene) dimer. The resulting reaction diagram for diacetylene polymerization is illustrated in Figure 7.

Assuming that the reaction of two C_A^0 units in Figure 6 will be exothermic by approximately a sp²-sp² double bond energy (5.7 eV) and that the reaction of two C_B^0 units will be exothermic by approximately a sp²-sp² single bond energy (4.1 eV),[28] we may estimate the energetic requirements of the dimerization event based on our ΔH_p measurement:

$$nM \rightarrow C_A^{(n-2)} \qquad nM \rightarrow C_B^{(n-2)}$$
$$\sim -n(1.6)\text{ eV} \qquad \sim -n(1.6)\text{ eV} \qquad (10)$$
$$n/2\,C_A^0 \rightarrow C_A^{(n-2)} \qquad n/2\,C_B^0 \rightarrow C_B^{(n-2)}$$
$$\sim -(n/2)(5.7)\text{ eV} \qquad \sim -(n/2)(4.1)\text{ eV} \qquad (11)$$

$$2M \rightarrow C_A{}^0 \qquad 2M \rightarrow C_B{}^0$$
$$\sim +2.5 \text{ eV} \qquad \sim +0.9 \text{ eV} \qquad\qquad (12)$$

where eq 12 is obtained with the appropriate manipulation of eq 10 and 11. The carbene scheme yields an unacceptably high E_a estimate of 2.5 eV. This can be expected qualitatively, since the formation of $C_A{}^0$ requires the disruption of two carbon-carbon π bonds.[15] The radical scheme gives a quite reasonable E_a estimate and from these simple energetic considerations would seem to be the most reasonable conceptualization of the polymerization mechanism.[34] Though these arguments obviously oversimplify the problem, we believe that the direction for future theoretical calculations of the energetics and pathway for diacetylene polymerization is clearly indicated.

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Electronic Excitation Energy Partitioning in Dissymmetric Dioxetane Thermolyses. The Absolute Chemiluminescence Yields and Triplet to Singlet Excited State Ratios for 3-Acetyl-4,4-dimethyl-1,2-dioxetane

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Abstract: 3-Acetyl-4,4-dimethyl-1,2-dioxetane (3) was prepared by the base-catalyzed rearrangement of 4-bromo-3-hydroxy-3,5,5-trimethyl-1,2-dioxolane (2). Thermal decomposition of dioxetane 3 to acetone and methylglyoxal proceeds with an activation energy of 26.0 ± 1.0 kcal/mol and a log A of 14.2. The enthalpy of activation and entropy of activation were determined to be 25.5 ± 1.0 kcal/mol and 4.0 ± 2.0 eu, respectively. The total yield of excited states produced in the thermal decomposition was determined to be $17 \pm 3\%$. Both excited-state acetone and excited-state methylglyoxal were detected. The excited-state multiplicities and yields follow: acetone triplet, $0.45 \pm 0.20\%$; methylglyoxal singlet, $1.6 \pm 0.5\%$; and methylglyoxal triplet, $15 \pm 3\%$. No singlet excited state acetone was detected. We suggest that the observed excited-state yields and the low triplet to singlet excited-state methylglyoxal ratio can best be rationalized in terms of the energetics of a stepwise biradical decomposition of the dioxetane 3.

Prerequisite to the logical design of efficient chemiluminescent systems is the detailed knowledge of the fundamental excitation steps in known chemiluminescent processes. The study of the unimolecular thermal decomposition of 1,2-dioxetanes,[2] subsequent to the isolation and characterization of the first dioxetane in 1969,[3] has provided considerable in-