effects of the changes in the polymerization conditions. The UV analyses were performed in CH_2Cl_2 at room temperature at 225 to 325 nm, using a Beekman DK-2A ratio recording spectrophotometer.

Acknowledgment. The financial support of this research project by the National Research Council of Denmark (Statens tekniskvidenskabelige Forskningsråd) is gratefully acknowledged. Many thanks are due to Professor Peter H. Plesch for the help with developing the experimental technique during a 2-week stay in 1976 at the University of Keele by one of us (S.H.). A gift of the triethyloxonium hexafluorophosphate by Dr. Patricia Dreyfuss, University of Akron, is appreciated, and finally many thanks are due to Mr. Hans Spanggaard of this Institute for interesting and helpful discussions and suggestions with regard to the performed work.

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Kinetics and Mechanism of the Bulk Thermal Polymerization of (3-Phenoxyphenyl)acetylene

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ABSTRACT: The kinetics of the high-temperature bulk polymerization of (3-phenoxyphenyl)acetylene were examined over the temperature range 400 to 600 K, using differential scanning calorimetry. Analyses of samples polymerized over a wide range of temperature, using gel permeation chromatography, revealed that the polymer molecular weight is invariant with temperature. The absence of an observable temperature correlation for polymer molecular weight is examined in terms of a biradical mechanism in which the kinetic and molecular chain lengths are controlled by a first-order termination step involving cyclization of the growing polymer chain. Based upon the observed data and semiempirical thermochemical arguments, it is concluded that the molecular weight of poly(3-phenoxyphenyl)acetylene is controlled predominantly by steric and thermochemical factors rather than by the reaction energetics.

The mechanisms for thermal polymerization of arylacetylenes are of interest from both theoretical and technological viewpoints. These compounds, in particular phenylacetylene and its simple derivatives, polymerize spontaneously in the range 400 to 600 K, and initiation may involve biradical formation.[1,2] Also, the molecular weight of the resultant polymer is rather insensitive to polymerization temperature.[3,4] The lack of an appreciable temperature dependence for molecular weight has been interpreted in the past as arising from degradative chain transfer[5,6] and more recently as being the result of a size-dependent first-order deactivation of the polymer chains.[4,7]

The 3-phenoxyphenyl substituent in the related monomer, (3-phenoxyphenyl)acetylene, occurs frequently in complex acetylene-terminated oligomers[8] that are used in the synthesis of highly temperature-resistant polymers. Since (3-phenoxyphenyl)acetylene possesses a substituent present in the oligomers as well as a reactivity comparable to phenylacetylene,[9] it represents a useful model compound to examine in order to gain insight into the mechanism of polymerization of the acetylene-terminated oligomers. In this paper, we wish to report the kinetics of the bulk polymerization of (3-phenoxyphenyl)acetylene and discuss the mechanistic implications.

Experimental Section

The monomer was obtained from Midwest Research Institute and was purified by vacuum distillation prior to use. Analysis by IR spectroscopy and gel permeation chromatography (GPC) indicated that the monomer purity exceeded 99%.

For kinetic runs, conversion data were determined from isothermal and dynamic differential scanning calorimetry (DSC) measurements, using a Perkin-Elmer DSC-II calibrated against lead and indium at heating rates of 80, 40, 20, 10, and 5 K/min.

In addition, isothermal conversion data were obtained from near-IR measurements by observing the disappearance of the acetylenic C–H stretching motion at 3250 cm^{-1}.

DSC Kinetics. Dynamic DSC. For dynamic DSC, the disappearance of monomer was calculated from

$$-\frac{1}{W_0}\left(\frac{dW}{dt}\right) = \frac{1}{Q}\left(\frac{dq}{dt}\right) = A \times 10^{-E/\Theta}F(W) \qquad \text{(i)}$$

where dq/dt is the differential power output in mcal/s, Q is the total heat of reaction in mcal, W_0 is the initial weight of the monomer, and W is the weight of residual monomer at time t. The parameters A and E are the usual Arrhenius parameters and $\Theta = 2.303\ RT$ kcal/mol.

The quantity $F(W)$[10] in eq i represents a concentration variable and was assumed to have the form,

$$F(W) = (W/W_0)^n = (q/Q)^n = (1-\alpha)^n \qquad \text{(ii)}$$

where n is the reaction order and α, the degree of conversion at time t, is $(1 - W/W_0)$. The apparent rate constant, k_{ap}, is $A \times 10^{-E/\Theta}$; thus, eq i and ii were combined to obtain

$$d\alpha/dt = k_{ap}(1-\alpha)^n \qquad \text{(iii)}$$

The molarity of the reacting sample was defined as

$$M = \frac{X_0(1-\alpha)}{V_0 + \Delta V} = \frac{M_0(1-\alpha)}{1 + \Delta V/V_0} \qquad \text{(iv)}$$

where X_0 and M_0 are the initial moles and molarity of the neat monomer, respectively, V_0 is the initial volume, and ΔV is the volume change of the reaction. Density measurements for the pure monomer and solutions of polymer in monomer corresponding to 10% conversion indicated that ΔV approached 14% for 100% conversion.

The enthalpy of polymerization, ΔH_p, in kcal/mol was derived from

$$\Delta H_p = \Delta H_s\left(\frac{A_m}{A_s}\right)\left(\frac{W_s}{W_m}\right) \qquad \text{(v)}$$

where ΔH_s is the heat of fusion of the standard, A_m and A_s are areas of the exotherms, and W_m and W_s are weights of monomer and standard.

In a typical dynamic DSC run, a sample of the freshly degassed monomer (2–4 mg) was transferred to a standard DSC pan and scanned under nitrogen at the appropriate heating rate. Data reduction and analysis were obtained with computer programs described previously.[11]

Isothermal DSC. For isothermal DSC runs, a sample of the monomer was rapidly heated (heat rate = 320 K/min) to the desired temperature, and the total output, dq/dt, was monitored continuously until apparent completion of the exotherm. At this time, the sample was rescanned to establish a base line, the rate given by the difference between the base line and total output. The partial heat of reaction at time t_i was determined by stepwise integration, using

$$q_i = (M_m/W_m)\sum (dq/dt)\Delta t \qquad \text{(vi)}$$

where M_m is the molecular weight of monomer, and Δt is the observation time. GPC analysis of these samples indicated the presence of residual monomer; therefore, conversions were calculated from eq vi by normalization with the total heat, Q, determined from the dynamic analysis.

IR Measurements. Additional isothermal experiments were conducted by monitoring the disappearance of the monomer by IR spectroscopy. In these runs, samples of the monomer were weighed into DSC pans, which in turn were placed in 10 × 0.25 in. polymerization tubes. The polymerization tubes were purged with nitrogen and placed in a silicone oil bath maintained at 500 ± 0.2 K. At periodic intervals, the tubes were removed from the oil bath, and the reaction was quenched by submersion of the tubes in liquid nitrogen. The contents of the DSC pans were dissolved in carbon tetrachloride, and the residual monomer was determined from IR at 3250 cm^{-1}.

Molecular Weights. Molecular weight data were obtained with a Waters Model 244 liquid chromatograph, using 10^4, 10^3, 2 (5×10^2), and 10^2 Å μ-Styragel columns. The GPC columns were standardized against low-molecular-weight polystyrene standards, as well as isolated fractions of poly(3-phenoxyphenyl)acetylene. All samples used for the GPC calibration were standardized against benzil with a Mechrolab vapor phase osmometer. Weight- and number-average molecular weights as functions of temperature and conversion were determined from the areas of the GPC curves.

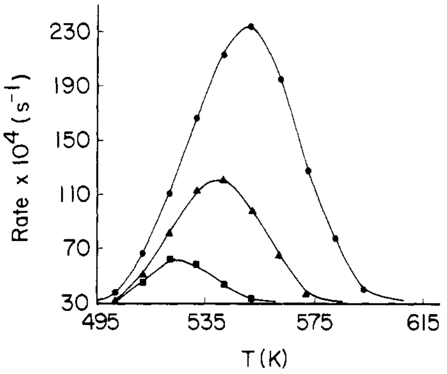


Figure 1. Reaction exotherms for thermal reaction of (3-phenoxyphenyl)acetylene. Heat rate (K/min): ●, 80; ▲, 40; ■, 20.

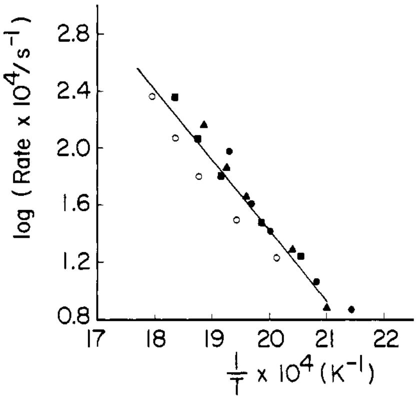


Figure 2. Composite Arrhenius plot for thermal reaction of (3-phenoxyphenyl)acetylene from 467 to 557 K. 100α: ●, 10; ▲, 20; ■, 40; ○, 60.

Results and Discussion

DSC Kinetics. Dynamic DSC. Figure 1 illustrates the reaction exotherms obtained for the dynamic DSC runs for three of the five heating rates. Representative rate data in the range 10 to 60% conversion and the total number of data points obtained from each exotherm are summarized in Table I. The temperature dependence of the rate data was evaluated by combining eq i and iii to obtain

$$\log\left(\frac{d\alpha}{dt}\right) = \frac{-E}{2.303R}\left(\frac{1}{T}\right) + \log A(1-\alpha)^n \qquad \text{(vii)}$$

At constant conversion, and assuming A and n constant, eq vii should yield a linear relation between log $(d\alpha/dt)$ and T^{-1}. Therefore, the apparent activation energy, E, may be obtained from the slope of eq vii at each level of conversion. An Arrhenius plot of eq vii for the data of Table I is shown in Figure 2. In Figure 2, the data obtained at each of the different conversion points fall essentially on lines of the same slope and indicate that E is independent of conversion. In order to evaluate A and n, eq i and iii were combined to derive

$$\log AF(W) = \log A(1-\alpha)^n = n \log (1-\alpha) + \log A \qquad \text{(viii)}$$

Values of $AF(W)$, calculated from the average activation energy and the rate data at each heating rate, were

Table I
Summary of Dynamic DSC Data for Thermal Polymerization of (3-Phenoxyphenyl)acetylene

heat rate, K/min	$\alpha \times 100$	T, K	$(d\alpha/dt) \times 10^3$, s^{-1}	total data pts
80	10	518	9.87	
	20	530	15.4	
	30	538	19.8	
	40	545	23.0	
	50	551	23.3	
	60	557	22.4	
				122
40	10	508	4.13	
	20	520	7.46	
	30	527	9.45	
	40	534	11.5	
	50	539	11.9	
	60	545	11.7	
				170
20	10	500	2.67	
	20	510	4.59	
	30	516	5.47	
	40	522	6.18	
	50	528	6.34	
	60	533	5.95	
				152
10	10	480	1.15	
	20	490	1.97	
	30	498	2.58	
	40	504	2.96	
	50	509	3.19	
	60	515	3.10	
				169
5	10	467	0.74	
	20	476	1.21	
	30	482	1.50	
	40	487	1.70	
	50	492	1.79	
	60	497	1.76	
				125

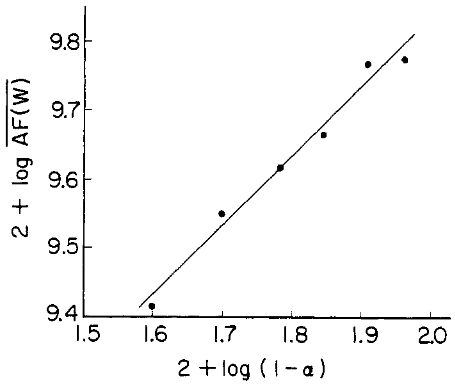


Figure 3. Dynamic DSC reaction order plot for thermal reaction of (3-phenoxyphenyl)acetylene from 467 to 557 K.

combined with the conversion data, and n and A were determined from the slope and intercept of eq viii. The order plot derived from eq viii is shown in Figure 3. Over the interval of 400 to 600 K from 20 to 60% conversion, the reaction was determined to be approximately first order ($n = 1.09$), and least-squares analysis of the rate data resulted in

$$\log (k_{\mathrm{ap}}/\mathrm{s}^{-1}) = (7.6 \pm 0.5) - (23.2 \pm 1)/\Theta \qquad \text{(ix)}$$

where $\Theta = 2.303RT$ kcal/mol. The error estimates correspond to one standard deviation.

The enthalpies of polymerization, ΔH_p, calculated for four of the five exotherms of the dynamic DSC data from eq v are summarized in Table II. The agreement between the values of ΔH_p obtained at each heating rate indicates that the reaction is independent of the heating rate.

Table II
Heat of Polymerization of (3-Phenoxyphenyl)acetylene

heat rate, K/min	$T_{\max}$,[a] K	$-\Delta H_p$, kcal/mol
80	552	35.4
40	542	36.7
20	532	37.0
10	514	36.6
		av 36.4 ± 1

[a] $T_{\max}$ is the temperature at the maximum of the exotherm.

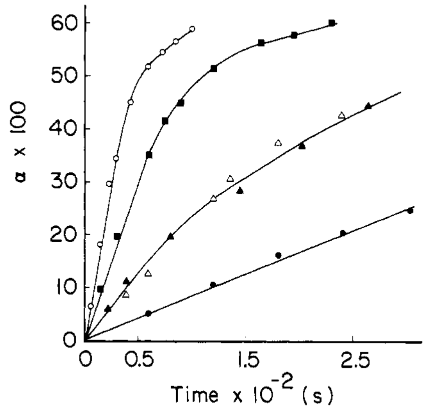


Figure 4. Isothermal conversion time curves for thermal reaction of (3-phenoxyphenyl)acetylene. DSC: ●, 480 K; ▲, 500 K; ■, 520 K; ○, 540 K. IR: △, 500 K.

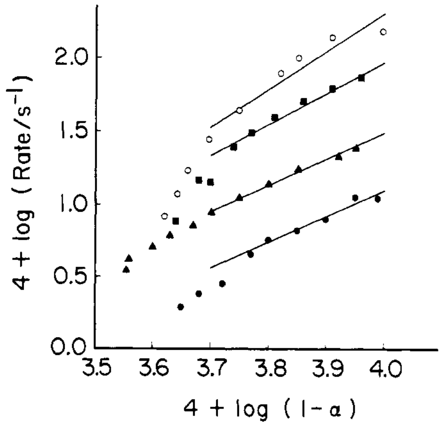


Figure 5. Isothermal reaction order plots for thermal reaction of (3-phenoxyphenyl)acetylene: (—) 0 to 50% conversion; ●, 480 K; ▲, 500 K; ■, 520 K; ○, 540 K.

Isothermal DSC. Conversion-vs.-time data obtained from the isothermal DSC measurements over the temperature range 480 to 540 K as well as that obtained at 500 K from IR measurements are plotted in Figure 4. The excellent agreement between these two techniques for the runs at 500 K confirms that the exothermicity of the reaction is associated with the loss of the acetylenic moiety. Reaction-order plots based upon the logarithmic form of eq iii for the isothermal data up to 70% reaction are shown in Figure 5, where the indicated slopes were chosen to reflect the best overall fit to the observed data. Over the first 50% of the reaction, least-squares analysis resulted in reaction orders of 2.5, 2.9, 2.9, and 2.3 at 480, 500, 520, and 540 K, respectively. The reason for the disparity between these observations and the apparent first-order monomer dependence obtained from the dynamic method is unknown, although it may be related to a difference in the activity of the monomer at higher conversion associated

Table III
Summary of Isothermal DSC Data for Thermal Polymerization of (3-Phenoxyphenyl)acetylene

T, K	W_0, mg	$(d\alpha/dt) \times 10^4$, s^{-1}	reaction order
540	2.2	133	2.5
520	2.1	64.3	2.9
500	3.7	27.0	2.9
480	3.6	8.33	2.3

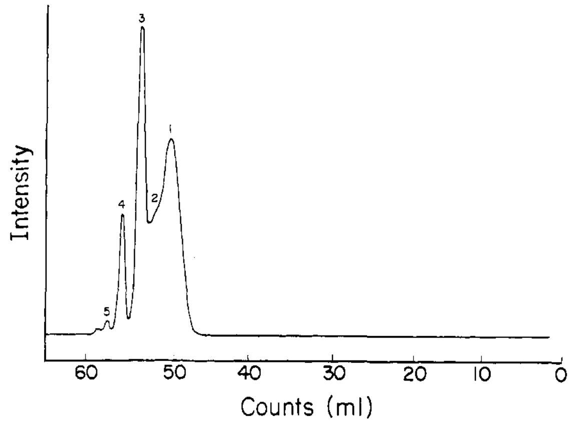


Figure 6. GPC trace for thermal reaction of (3-phenoxyphenyl)acetylene at 480 K: (1, 2) polymer; (3) oligomer; (4) dimer; (5) monomer.

with the dynamic experiments.

Rate data determined from the initial slopes of the conversion plots in Figure 5 are summarized in Table III. These data were subjected to least-squares analysis to obtain

$$\log (k_{ap}/\mathrm{s}^{-1}) = (7.9 \pm 0.6) - (24.0 \pm 1.3)/\Theta \quad \text{(x)}$$

which is in good agreement with the preferred result, eq ix, obtained from the dynamic measurements.

The observed activation energies, $E = 23.2 \pm 1$ and 24.0 ± 1.3 kcal/mol from the dynamic and isothermal DSC analyses, respectively, are in good agreement with those expected from data previously reported for similar monomers,[2] namely, phenylacetylene ($E = 26.2 \pm 1$ kcal/mol) and 2-methyl-5-ethynylpyridine ($E = 20.4 \pm 1$ kcal/mol).

Polymer Characterization. A representative cumulative differential molecular weight distribution obtained from GPC analysis at 243 nm for monomer polymerized at 480 K is shown in Figure 6. The total reaction products were dissolved in chloroform, and the major components consisting of fractions 1 and 2 were isolated by precipitation with methanol. The IR and ^{1}H NMR spectra of these fractions were similar to those previously reported for the trans-cisoidal isomer of poly(phenylacetylene).[12-14] Low-pressure reduction of fraction 1 with a Pd/charcoal catalyst resulted in the uptake of 4.6 mol of H_2/mol of polymer based upon a VPO molecular weight of 2300. For a polyene structure of the same molecular weight, one would expect an absorption of $\simeq$11 mol of hydrogen for a quantitative reduction. For comparison, a sample of poly(phenylacetylene) ($M_n \simeq 2000$) prepared under identical conditions absorbed 4.3 mol of H_2/mol of polymer. Based on these data, it is concluded that the polymer is a polyene with a trans-cisoidal conformation.

Fractions 3–5 were all soluble in methanol, and resolution was achieved from repetitive collections of the GPC fractions. The ^{1}H NMR spectrum relative to Me_4Si of the major methanol-soluble component, fraction 3, exhibited a complex multiplet centered at 7.2 ppm and a singlet at 7.9 ppm with intensity ratios consistent with that expected for the trimer, 1,3,5-tris(3-phenoxyphenyl)benzene.

Table IV
Influence of Temperature and Conversion on the Molecular Weight of Poly(3-phenoxyphenyl)acetylene

T, K	M_0,[a] M	$(1 + \Delta V/V_0)$	$\alpha \times 100$[b]	M_n	M_w
540	2.65	0.921	51	1113	1301
520	2.76	0.960	26	1008	1099
500	2.80	0.980	13	973	1043
		0.970	19	947	1107
		0.956	28	971	1155
		0.941	38	912	1064
		0.934	43	1120	1374
		0.923	45	1091	1246
480	3.00	0.956	26	973	1131
460	3.14	0.970	19	1034	1201
450	3.31	0.967	21	985	1097
		0.969	20	960	1095
			av	1007 ± 68	1159 ± 101

[a] Bulk molarity of the monomer. [b] Determined from disappearance of the acetylenic moiety at 3250 cm^{-1}.

Mass-spectral analysis revealed that fraction 4 was a dimer. The GPC retention volume of fraction 5 was identical with that of the monomer.

Molecular weights of the polymer distribution consisting of fractions 1–4 at several conversions and temperatures determined from the GPC analyses are summarized in Table IV. For second-order termination, M_w/M_n should vary from 1.5 to 2.0, depending upon the amount of polymer formed by disproportionation. All of the data in Table IV exhibit $M_w/M_n \simeq 1.2$ and are similar to those observed for poly(phenylacetylene).[7] In view of the uncertainty associated with the GPC analysis of the ratio, M_w/M_n, it seems inappropriate to draw conclusions related to the termination mechanism from these measurements. On the other hand, the number-average molecular weights exhibit, at best, only a marginal temperature dependence. This observation strongly implies that the kinetic and molecular chain lengths are governed by a first-order termination step, as opposed to a second-order mechanism which would be reflected by a sizable temperature dependence for molecular weight.

In addition to the data given in Table IV, two samples of monomer diluted with o-xylene ($M \simeq 1.8$) were polymerized at 400 K. The average molecular weights of these samples were not significantly different from those obtained in bulk; thus, chain transfer can be excluded as a significant factor in controlling molecular weight.

Proposed Reaction Mechanism. Based upon the sum of our experimental data and the combined observations of Erhlich et al.[7] for the azobis(isobutyronitrile)-initiated reaction of phenylacetylene and those of Berlin and coworkers[2] for the corresponding thermal reaction, we propose the simple biradical mechanism shown below for (3-phenoxyphenyl)acetylene:

initiation

$$2\mathrm{M} \rightarrow \cdot\mathrm{M}_2\cdot \quad (1)$$

propagation

$$\mathrm{X}_i + \mathrm{M} \rightarrow \mathrm{X}_j \quad (2)$$

termination

$$\mathrm{X}_j \rightarrow \mathrm{X}_k \quad (3)$$

elimination

$$\mathrm{X}_k \rightarrow \mathrm{X}_l + \Phi \quad (4)$$

termination

$$2\mathrm{X}_l \rightarrow (1 + \beta)\mathrm{P} \quad (5)$$

In the proposed mechanism, $\cdot M_2\cdot$ is a biradical, X_i and X_j are growing polymeric radicals, X_k is a cyclic radical formed by intramolecular cyclization of radical X_j, X_l is an open-chain radical formed by unimolecular elimination of a cyclic trimer, Φ, from species X_k, P is polymer, and β is an unknown factor that may vary from zero to unity which represents the fraction of polymer formed by disproportionation.

Two possible structures for the biradical consist of the *trans*-1,4-bis(3-phenoxyphenyl)-1,3-butadiene-1,4-diyl and the *cis*-1,3-bis(3-phenoxyphenyl)-1,3-butadiene-1,4-diyl species,

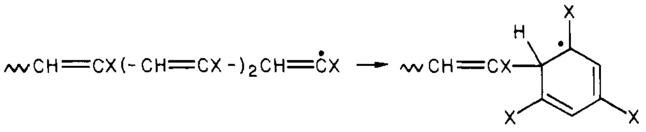
$$X\dot{C}{=}CHCH{=}\dot{C}X \text{ and } X\dot{C}{=}CHC({=}\dot{C}H)X$$

where X is identified with the 3-phenoxyphenyl substituent. While thermodynamic and structural considerations favor the trans species formed by tail-to-tail addition of monomer as the preferred structure, the cis-1,3 biradical obtained from head-to-tail addition should not be totally excluded.

Propagation is assumed to occur from a monoradical or pseudomonoradical source. The initiating species could result from either subsequent reactions which produce simple monoradicals or from steric and/or conformational effects associated with one of the radical sites in $\cdot M_2\cdot$. However, in either case, one would still expect the rate-determining step of the reaction to be dominated by formation of the biradical, $\cdot M_2\cdot$.

Reactions 2, 3, and 4 are assumed to exert major control over the kinetic and molecular chain lengths, while reaction 5 does not. Reaction 3, first proposed for polymerization of phenylacetylene,[7] represents first-order termination of the growing polymer chain. This is consistent with the polymer characterization data and the fact that the polymer molecular weight is rather insensitive to the polymerization temperature.

If propagation is exclusively head-to-tail, then reactions 3 and 4 may be represented as



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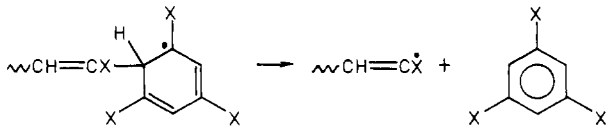
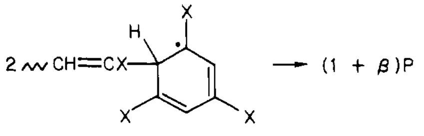


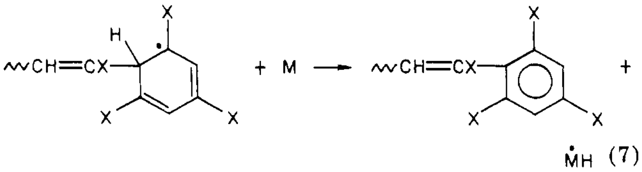
respectively. The conjugated radical, X_l, formed by reaction 4 could then re-initiate the kinetic chain or disappear through reaction 5 by radical recombination and disproportionation.

The significance of competing termination steps involving the proposed cyclohexadienyl radicals, for example, by either the second-order reaction,



(6)

or the monomer-transfer reaction,



(7)

may be assessed from consideration of appropriate relative rates. With respect to reaction 4, the relative rates of reactions 6 and 7 are $R_4/R_6 = k_4/(2k_6[X_k])$ and $R_4/R_7 = k_4/(k_7[M])$. From related thermochemistry,[15] it is likely that $k_4 \geq k_6 \simeq k_7$; therefore, the relative rates simplify to $R_4/R_6 \geq (2[X_k])^{-1}$ and $R_4/R_7 \geq [M]^{-1}$. Reaction 6 may be excluded from further consideration since this would require an unusually large molar concentration for X_k; i.e., $[X_k]$ would vary from 0.05 to 0.5, in order for the relative rate to be in the reasonable range of $0.1 \leq R_6/R_4 \leq 1$. Competition between reactions 4 and 7 is more feasible since $R_7 = R_4$ when $[M] = 1$; however, reaction 7 can still be excluded from the mechanism since appreciable chain transfer with *o*-xylene was not observed. Thus, the sequence of reactions 3-5 in the proposed mechanism would account for the observed product distribution, which consists primarily of linear polymer and cyclic trimer, as well as the marginal temperature dependence observed for the polymer molecular weight.

Evaluation of the Ratio k_p/k_t. Application of the usual steady-state hypothesis to the proposed mechanism assuming short kinetic chains leads to

$$-\frac{dM}{dt} = R_i\left\{1 + \frac{k_p}{k_t}M\right\} \tag{xi}$$

where R_i is the rate of initiation and k_p and k_t are specific rate constants for propagation and termination. Equation xi represents the net disappearance of monomer but simplifies to the more common long-chain approximation, i.e., $-dM/dt \simeq (k_p/k_t)R_iM$, when $(k_p/k_t)M > 1$.

Since the kinetic chain length, λ, is $(-dM/dt)/R_i$, eq xi may be rearranged to obtain

$$\lambda = 1 + \frac{k_p}{k_t}M \tag{xii}$$

From eq xii, one would expect a small temperature dependence for the kinetic chain length since k_p and k_t could have similar activation energies. The kinetic chain length is related to the number-average degree of polymerization, DP_n, by

$$DP_n = \frac{2}{(1+\beta)}\left\{1 + \frac{k_p}{k_t}M\right\} \tag{xiii}$$

Replacing M in eq xiii by eq iv yields

$$DP_n = \frac{2}{(1+\beta)}\left\{1 + \frac{k_p}{k_t}\left[\frac{M_0(1-\alpha)}{1 + \Delta V/V_0}\right]\right\} \tag{xiv}$$

which relates the number-average degree of polymerization at steady-state conditions to the extent of the reaction and the volume contraction.

At ordinary temperatures, formation of polymer in reaction 5 would be expected to occur predominantly by radical combination. On the other hand, considering the rather high temperatures used to induce polymerization,[16] one would infer similar size distributions for the intermediates and the resultant polymer. Thus, the unknown fraction, β, was equated to the average value of 0.5, and the molecular weight and conversion data in Table IV were combined in eq xiv to obtain the data for k_p/k_t summarized in Table V.

Examination of the block of data in Table V obtained at 500 K reveals a small correlation for k_p/k_t and the extent of reaction as expected from consideration of eq xiv. Comparison of the average of the data at 500 K to the other entries over the entire temperature range indicates

Table V
Influence of Temperature and Conversion on the Ratio k_p/k_t

T, K	$\alpha \times 100$	k_p/k_t, M^{-1}
540	51	2.4
520	26	1.4
500	13	1.1
	19	1.2
	28	1.3
	38	1.4
	43	2.1
	45	2.1
480	20	1.1
460	19	1.2
450	21	1.1
	20	1.0
		av 1.5 ± 0.5

a negligible correlation with temperature.

The lack of an observable temperature correlation for k_p/k_t is not inconsistent with the suggestion based upon eq xii that the kinetic and molecular chain lengths might exhibit a small temperature coefficient arising from similar activation energies for propagation and termination. For the related monomer, phenylacetylene, Erhlich and coworkers[4,7] have suggested that the temperature independence of the polymer molecular weight is due to a size-dependent electronic rearrangement rather than an exponential temperature dependence of rate constants. While this suggestion would apply equally to (3-phenoxyphenyl)acetylene, we believe that the temperature independence of the molecular weight for both polymers may also be rationalized from kinetic and thermochemical arguments outlined below.

Entropy changes for both propagation and termination vary as $\overline{\Delta C^\circ_p} \ln (T/298)$, where $\overline{\Delta C^\circ_p}$ is the average heat capacity change of the reaction, and T is the absolute temperature. Changes in $\overline{\Delta C^\circ_p}$ are usually small; for example, thermochemical considerations[17] suggest that $\overline{\Delta C^\circ_p}$ for propagation is close to zero. In contrast, however, for termination (see Appendix) an additional increment arises from the loss of hindered internal rotation about carbon–carbon σ bonds of the polyene chain in formation of the cyclohexadienyl species in reaction 4 which results in $\overline{\Delta C^\circ_p} = -3.5$ cal/K mol. Therefore, the temperature dependence of the entropy change for termination should exceed that for propagation as determined by $\overline{\Delta C^\circ_p} \ln (T/298)$.

Since the magnitude of A_p/A_t is governed by the difference in entropy changes of propagation and termination, i.e., $\Delta S^\circ_p - \Delta S^\circ_t$, the latter considerations suggest that A_p/A_t should increase at higher temperature.[18] From the thermodynamic data of Table VI and the thermochemical considerations outlined in the Appendix, and assuming tight or product-like transition states[19] for propagation and termination, one can estimate that $\log (A_p/A_t/\mathrm{M}^{-1}) = (-1.8 \pm 0.5) + 0.8 \ln (T/298)$ over the range 298 to 800 K.

Combining the estimate of $\log (A_p/A_t)$ with the average value, $k_p/k_t = 1.5$ M^{-1}, from Table V at 500 K leads to

$$\log \left(\frac{k_p}{k_t} \Big/ \mathrm{M}^{-1} \right) = (-1.8 + 0.8 \ln (T/298) \pm 0.5) + (3.6 \pm 1)/\Theta \quad \text{(xv)}$$

for the predicted explicit temperature dependence of k_p/k_t.

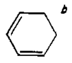
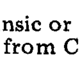
The suggested temperature dependence of A_p/A_t would be negligible at ordinary temperatures for a polymerization consisting of long chains; however, it would be quite significant at high temperature when $\lambda \leq 10$. In fact, from the simple model given in the Appendix used to derive eq xv, one expects A_p/A_t to increase by a factor of 1.4 over the range 450 to 540 K. In order for k_p/k_t to remain constant, a change in $E_p - E_t$ on the order of 0.2 kcal/mol would be required, which is well within the experimental uncertainty of the data of Table V. The predicted increase in A_p/A_t would effectively cancel the decrease associated with $(E_p - E_t)/\Theta$ at higher temperature so that k_p/k_t remains essentially unchanged over the entire temperature range. Thus, it follows that $\mathrm{DP}_n = 6 \pm 2$ estimated from eq xiv by using k_p/k_t evaluated from eq xv over the range 450 to 540 K compares favorably with $\mathrm{DP}_n = 5 \pm 0.5$ determined by the molecular weight data given in Table IV. Similar arguments might also account for the temperature independence of the molecular weight of poly(phenylacetylene).

The proposed first-order termination step, reaction 4, is analogous to intramolecular propagation; therefore, the predicted temperature dependence for k_p/k_t given by eq xv should be comparable to cyclization ratios for monomers that cyclopolymerize by competing inter- and intramolecular propagation. This is supported experimentally by

$$\log \left(\frac{k_p}{k_c} \Big/ \mathrm{M}^{-1} \right) = (-3.5 \pm 0.8) + (2.3 \pm 1.2)/\Theta \quad \text{(xvi)}$$

for methacrylic anhydride,[20] where k_c is the specific rate constant for intramolecular propagation. The similarities of the ratios of the preexponential factors as well as the observed activation energy differences in eq xv and xvi provide additional support that termination involves intramolecular cyclization. Furthermore, this comparison is in accord with the expectation that A_t is greater than A_p, which suggests that the steric requirements for continued propagation exceed those for termination even though the activation energy for termination may be greater than that expected for propagation. This leads us to conclude that the kinetic and molecular chain lengths

Table VI
Summary of Ideal Gas Thermodynamic Properties

species	symmetry no. (σ)	S°_{int},[a] cal/K mol 298 K	C°_p, cal/K mol 298 K	800 K
$CH_2{=}CHCH{=}CHCH{=}CH_2$	2	80.74	28.04	53.54
	2	67.40	23.08	51.42
$CH_2{=}CHCH{=}CHCH{=}\dot{C}H$	1	79.02	26.90	50.09
	1	66.38	21.94	47.97

[a] The intrinsic or symmetry-corrected entropy, S°_{int}, is related to absolute entropy by $S^\circ_{\mathrm{int}} = S^\circ_{\mathrm{abs}} + R \ln \sigma$.
[b] Estimated from $CH_3(CH_2)_4CH_3$ by using ref 21, p 68.

of poly(3-phenoxyphenyl)acetylene are influenced more by steric and thermochemical effects than by those associated with reaction energetics.

Summary

The kinetics of the high-temperature bulk polymerization of (3-phenoxyphenyl)acetylene were studied with isothermal and dynamic differential scanning calorimetry, gel-permeation chromatography, and infrared spectroscopy. The apparent heat of polymerization at a mean temperature of 535 K was determined to be $\Delta H_p = -36.4 \pm 1$ kcal/mol. Least-squares analysis of the rate data was used to obtain the activation energy, $E = 23.2 \pm 1$ kcal/mol, and the preexponential factor, $A = 10^{7.6\pm0.5}$ s^{-1}.

GPC analyses of samples polymerized over a wide range of temperature indicated that the polymer molecular weight ($M_n = 1007 \pm 68$) is insensitive to the polymerization temperature. This was discussed in terms of a simple biradical mechanism in which molecular weight is controlled by a first-order termination step involving cyclization of the growing polymer chains.

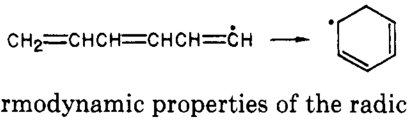
Analysis of the molecular weight data, based upon the proposed mechanism, resulted in $k_p/k_t = 1.5 \pm 0.5$ M^{-1}. The lack of an observable temperature correlation for k_p/k_t is consistent with a small but nonetheless significant temperature dependence for A_p/A_t estimated from semiempirical thermochemical considerations. It was suggested that the temperature dependence of A_p/A_t would cancel the decrease at higher temperature associated with $(E_p - E_t)/\Theta$ so that k_p/k_t remains essentially unchanged over the entire temperature range.

Based upon the internal consistency obtained by combining k_p/k_t with the semiempirical estimate of A_p/A_t and the favorable comparison to kinetic data for a similar monomer, it was concluded that the kinetic and molecular chain lengths of poly(3-phenoxyphenyl)acetylene are controlled primarily by steric and thermochemical factors.

Acknowledgment. Two of us, J. M. Pickard and E. G. Jones, gratefully acknowledge support of this work by the Air Force Systems Command, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio 45433, under Contract No. F33615-77-C-5175.

Appendix

The entropy change for termination was estimated for a model reaction of a polyene chain from group additivity[21] with the assumption that the entropy change is independent of the kinetic chain length and the nature of the pendant groups attached to the polymer backbone. Since the entropy change for termination depends largely upon the loss of hindered internal rotation about carbon–carbon σ bonds, termination may be approximated as



The thermodynamic properties of the radicals, for example, entropy, were obtained by the difference method,[22] using

$$S°(\dot{R}) = S°(RH) + \Delta S°_{vib} + \Delta S°_{\sigma} + \Delta S°_{e} + \Delta S°_{conj} \qquad (A1)$$

where $S°(\dot{R})$ is the entropy of the radical and $\Delta S°_{vib}$, $\Delta S°_{\sigma}$, $\Delta S°_{e}$, and $\Delta S°_{conj}$ are corrections to the hydrocarbon entropy, $S°(RH)$, for changes associated with vibrational degrees of freedom, symmetry, electronic state, and resonance, respectively, arising from the loss of a hydrogen atom in the parent hydrocarbon. The additional corrections associated with mass, barrier heights, and overall rotation were neglected. The model compounds consisted of 1,3-cyclohexadiene and 1,3,5-hexatriene.

Corrections for symmetry were taken as $R \ln \sigma$, where σ is the product of the total independent symmetry axes within the molecule. Electronic states were assumed to be doubly degenerate, and $\Delta S°_e$ was approximated as $R \ln (2S + 1)$ where S is the net electron spin. For both radicals, $\Delta S°_{vib}$ was associated with the loss of three vibrational degrees of freedom at 3000, 1150, and 700 cm^{-1}, while delocalization of the odd electron in the 1,3-cyclohexadienyl radical was equated to a three-electron torsion at 500 cm^{-1}. Appropriate corrections for $\Delta S°_{vib}$ and $\Delta S°_{conj}$ were obtained from tables tabulated by Benson and O'Neal.[22]

Gas-phase thermodynamic properties of the parent model compounds and the radicals are summarized in Table VI. The absolute entropy change at 298 K, $\Delta S°_{298}$, for the ideal gas state at 1 atm is related to that at higher temperature by

$$\Delta S°_T = \Delta S°_{298} + \overline{\Delta C°_p} \ln (T/298) \qquad (A2)$$

where $\Delta S°_T$ is the entropy change at temperature T and $\overline{\Delta C°_p}$ is the average reaction heat capacity change over the observed temperature range. From the data given in Table VI, eq A2 yields

$$\Delta S°_T = (-12.6 \pm 0.5) - (3.5) \ln (T/298) \text{ cal/K mol} \qquad (A3)$$

for termination over the range 298 to 800 K. One should note that the mole change for termination is zero; therefore, the entropy change is independent of the standard state and should be unchanged in a condensed phase.[23]

The result for log (A_p/A_t) was evaluated from the assumption of tight transition states, i.e., assuming $\Delta S^{\ddagger} = \Delta S°$,[19] from

$$\log \left(\frac{A_p}{A_t}\right) = \frac{\Delta S°_p - \Delta S°_t - R \ln \Delta V}{2.303R} \qquad (A4)$$

where ΔV ($\simeq$0.14) is the volume change of polymerization. The entropy for propagation is not known precisely; however, it should be similar to that for related vinyl monomers, $\Delta S°_p \simeq -25 \pm 2$ cal/K mol.[19] With the latter assumptions, eq A3 and A4 lead to

$$\log \left(\frac{A_p}{A_t} \Big/ \text{M}^{-1}\right) = (-1.8 \pm 0.5) + 0.8 \ln (T/298) \qquad (A5)$$

over the range 298 to 800 K.

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(17) If variations in chain length are neglected, then $\overline{\Delta C^\circ_p}$ for propagation is given by the difference in heat capacity of the monomer and the repeat unit of the polyene chain. For polymerization of acetylene, group additivity considerations similar to those outlined in the Appendix yield $\overline{\Delta C^\circ_p} = +0.08$ cal/K mol over the range 298 to 800 K.
(18) This is analogous to use of the modified Arrhenius equation, $k = A'T^n e^{-E/RT}$. The variables A' and E' are related to the usual Arrhenius parameters A and E by $A = A'(eT)^n$ and $E = E' + nRT$, where n is a small positive or negative integer.
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Photoreaction of Benzophenone with the *n*-Alkanes: A Model for Bimolecular Reactions of Polymers

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ABSTRACT: The photochemical reaction between benzophenone and the *n*-alkanes has been examined. Rate constants have been obtained as a function of temperature for hexane through hexatriacontane. These show parallel Arrhenius plots with $E_a = 3.9 \pm 0.2$ kcal/mol for all chain lengths. At room temperature, the second-order rate constants increase linearly with chain length with a slope of 0.94×10^4 M^{-1} s^{-1} per CH_2 group. A model is proposed to account for this behavior.

Outside of enzyme kinetics, there have not been many kinetic studies of the reaction of small molecules with dilute solutions of polymers. Such studies are important in that they examine the consequence of the non-uniform distribution of reactants in solution. For example, imagine a polymer chain containing noninteracting catalytic groups along its backbone. A solution containing small amounts of this polymer would have regions of relatively high concentration of catalytic groups surrounded by regions containing no such groups. It is important to understand the way in which small molecules would react with such a polymer, if only to be able to use such knowledge to infer cooperative catalysis when appropriate deviations from this behavior were found.

There should be two limiting cases in such reactions. In the diffusion-limited case studied by Schnabel and his co-workers,[1,2] the rate of the reaction is limited by the diffusion of the reactive species into the region of space containing the polymer. Here it is effectively swallowed up by chemical reaction. An example is the reaction of ·OH generated by pulse radiolysis with poly(ethylene oxide) where $\sim\!\!\sim OCH_2\dot{C}HO\sim\!\!\sim$ refers to the site of the

$$\mathrm{HO\cdot + HO(CH_2CH_2O)_xH \xrightarrow[H_2O]{} H_2O + {\sim\!\!\sim}OCH_2\dot{C}HO{\sim\!\!\sim}} \tag{1}$$

polymer from which a hydrogen atom was abstracted by ·OH. The molar second-order rate constant for this reaction increased as (mol wt)$^{0.6}$, consistent with a simple diffusion model in which the rate increased in proportion to the radius of polymer presented to the approaching ·OH reactant.

In the other limit, the polymer and reactant encounter each other many times before reacting. Since the rate of the reaction is not limited by the rate of diffusion of the reactants together, the measured rate will be sensitive to other aspects of their interaction. These may include not only the details of bond breaking and bond making in the transition state of the reaction but perhaps other features as well, such as polymer chain length and conformation.

To examine these features, one should choose a reaction for kinetic studies that satisfies a number of important criteria: (i) The reaction should be much slower than diffusion controlled (i.e., the second-order rate constant should be less than 10^7–10^8 M^{-1} s^{-1}); (ii) the polymer should be capable of reacting at many sites along its backbone; but (iii) under the conditions of the kinetic study, no polymer should react more than once. In addition, the studies should be carried out at dilutions sufficient that no polymer–polymer interpenetration occurs. Among the examples of such reactions are those of polyethylene or poly(ethylene oxide) with hydrogen abstracting species much less reactive than ·OH, e.g., *tert*-butoxy radical or excited states of aromatic ketones.

Several years ago we reported preliminary results on the kinetics of reaction of photoexcited benzophenone with dilute solutions of the *n*-alkanes.[3] A peculiar saturation effect was observed such that for long chain alkanes, the second-order rate constant appeared to level off as the chain got longer. After many unsuccessful attempts to develop models that would explain this behavior, we began to question our original data. We have repeated our original measurements, extended our study to longer chain lengths, and examined the temperature dependence of the reaction between the *n*-alkanes and photoexcited benzophenone. Some of our original data were in error.[3] The saturation effect does not exist. The bimolecular rate constant for this reaction increases linearly with chain

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