Thermal Polymerization of Diphenyldiacetylene

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SUMMARY

Thermal polymerization of diphenyldiacetylene in the absence of a catalyst is a second-order reaction. The rate of polymerization is proportional to the square of monomer concentration, and the resultant molecular weight of the polymer is independent of the monomer concentration. The results suggest a mechanism in which bimolecular initiation and bimolecular termination steps are involved. The IR, NMR, UV, EPR, and mass spectral properties of the polymer are described.

The polymerization of acetylene compounds has received continuing interest. Polymerization through the addition of the triple bond should yield conjugated polyenes. The polymers do not, however, resemble other polyenes, such as the carotenoids, and the polymerization gives only low molecular weight materials. Various explanations for these anomalies have been offered,

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including the inactivation of the growing radical chain through delocalization of the conjugated polyene radical [1]. The thermal polymerization of acetylene is amply documented in the literature [2-4], and there have been two reports on the thermal polymerization of diphenyldiacetylene [5, 6]. Our interest in the thermal polymerization comes from the results of some theoretical calculations [7, 8], which reconfirm the interest in acetylene derived polymers and the possibility of devising a polymerization technique leading to a typically conjugated polymer. In this paper, we wish to report our observations on the polymerization kinetics of the thermal polymerization of diphenyldiacetylene and the properties of its polymer.

EXPERIMENTAL

Material

Diphenyldiacetylene was supplied by Farchan Research Laboratories. It was recrystallized from reagent grade methanol twice, mp 86-87.5° (uncorrected). Both IR and NMR spectra revealed no impurity.

Polymerization Procedure

To 1.4 g of diphenyldiacetylene in a 100-ml tube was added 1.5 ml of dry, redistilled benzene. The tube was connected to a vacuum manifold, flushed with prepurified nitrogen three times at -78°, degassed by three cycles of freezing-thawing, and evacuated at 10^{-2} mm Hg for 2 hr before being sealed in vacuo. The tube was submerged in a constant temperature oil bath, controlled to ±0.5° throughout the 120-140° range. At the end of the reaction the tube was cooled and broken under nitrogen atmosphere in a polyethylene glove box. All subsequent handlings were done under nitrogen atmosphere. The polymer was poured into 150 ml methanol, filtered, redissolved in benzene, and precipitated by dropwise addition of the benzene solution to excess methanol. The precipitate was dried in a vacuum oven at 50° for 16 hr. Per cent yield was determined gravimetrically. Molecular weights were determined either by a vapor pressure osmometer by Schwarzkopf Microanalytical Laboratory or cryoscopically in benzene in this laboratory.

RESULTS AND DISCUSSION

Polymerization Studies

Thermal Polymerization in Dimethylformamide. Data for experiments on the thermal polymerization of diphenyldiacetylene in N,N-dimethylformamide are given in Table 1. Below about $100°$ no thermal polymerization was observed. The number-average molecular weights of the polymers vary from 445 to 1286. The absence of nitrogen in the polymers was established by elemental analysis (Dumas) on the polymer. No carbonyl absorption around 1700 cm^{-1} in the IR was detected. It is, therefore, concluded that incorporation of nitrogen or carbonyl containing fragments from the solvent into the polymer by either initiation or transfer is not involved.

Table 1. Thermal Polymerization of Diphenyldiacetylene in N,N-Dimethylformamide

Monomer (mole/l)	Temperature (°C)	Reaction time (hr)	Polymer yield (%)	$\overline{M}_n$ (osm.)
9.85	80	94.5	0	—
9.85	100	8.5	0	—
9.85	107	123	0.92	1286
9.85	120	94.5	10.6	924
9.85	140	67.8	22.9	445
9.85	150	15.3	6.3	—

Thermal Polymerization in Benzene. Table 2 summarizes data for the thermal polymerization of diphenyldiacetylene in benzene. As shown in Fig. 1, polymerization is preceded by an induction period, the length of which depends on the polymerization temperature. The higher the temperature, the shorter the induction period as is characteristic of free radical polymerizations. Conversion increases with reaction time and temperature. The initial parts of the curves are linear, implying polymerization proceeds at a constant rate. The initial rate of thermal polymerization is taken as the initial slope of the curves. The initial slopes, calculated by least squares analyses of the data, are 0.416, 0.755, and 1.099 (%/hr) and the rates are

Table 2. Rate Studies of Thermal Polymerization of
Diphenyldiacetylene in Benzene

Monomer (mole/l)	Temperature (°C)	Reaction time (hr)	Polymer yield (%)	$\overline{M}_n$ (osm.)
4.62	120	17.0	0.04	
		25.0	2.15	
		40.0	8.28	
		47.7	15.50	
		65.0	21.54	
		79.3	24.02	
		90.4	30.55	811
4.62	130	8.0	0.50	
		16.0	4.17	
		24.0	7.91	
		32.0	25.20	
		46.0	33.90	
		63.3	38.94	721
				913 (cryos.)
4.62	140	5.0	6.43	
		15.0	16.52	1410
		23.7	23.42	1240
		38.0	46.88	632
		46.5	48.84	1268
		89.2	60.74	1243
		117.0	60.64	

5.34, 9.69, and 14.10 $\times$ 10^{-4} mole/l-sec at 120, 130, and 140°C,
respectively.

The order of thermal polymerization at 140°C was determined by vary-
ing the monomer concentration at constant temperature according to the
equation

$$V = k(DPDA)^n$$

where V is the rate of polymerization, k the specific reaction rate constant,
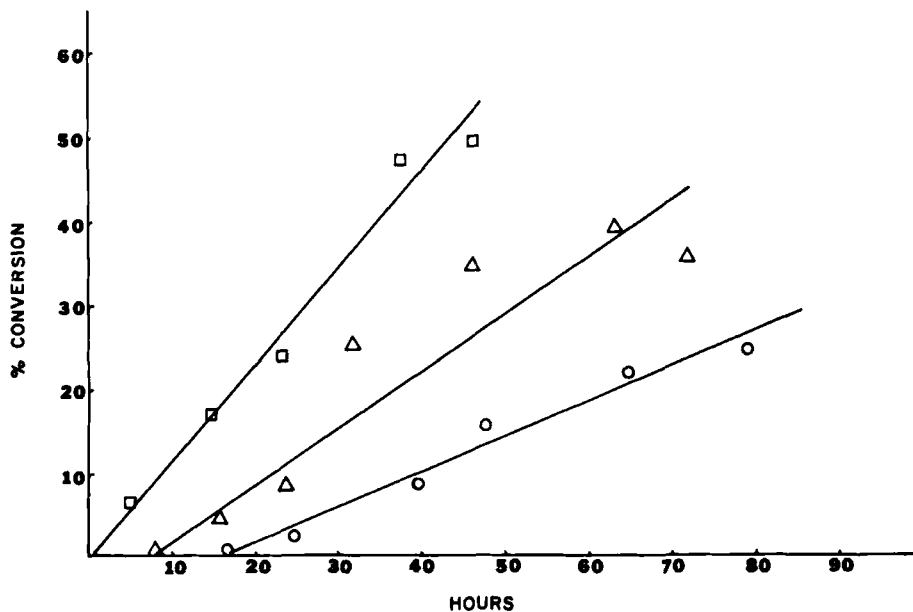and n the order of reaction. The dependence of rate on monomer

Fig. 1. Initial rate of thermal polymerization of diphenyldiacetylene. (○) 120°, (△) 130°, (□) 140°.

concentration is shown in Table 3. A plot of log rate of polymerization against log monomer concentration is given in Fig. 2. A straight line is obtained with a slope of 1.92, the order of the reaction, and an intercept

Table 3. Order of Reaction for the Thermal Polymerization of Diphenyldiacetylene at 140°C for 15 Hr

Monomer concentration (M)	Polymer yield (%)	Rate (mole/l-sec)	$\overline{M}_n$ (osm.)
2.27	7.76	3.26×10^{-5}	1740
4.62	16.54	14.15×10^{-5}	1410
5.90	16.60	18.14×10^{-5}	1450
9.67	29.35	52.48×10^{-5}	1303

of 5.96×10^{-6}, the reaction rate constant. The uncatalyzed thermal polymerization of diphenyldiacetylene is, thus, second order. This is in accord with the observation that the uncatalyzed thermal polymerization of styrene is second or third order [9].
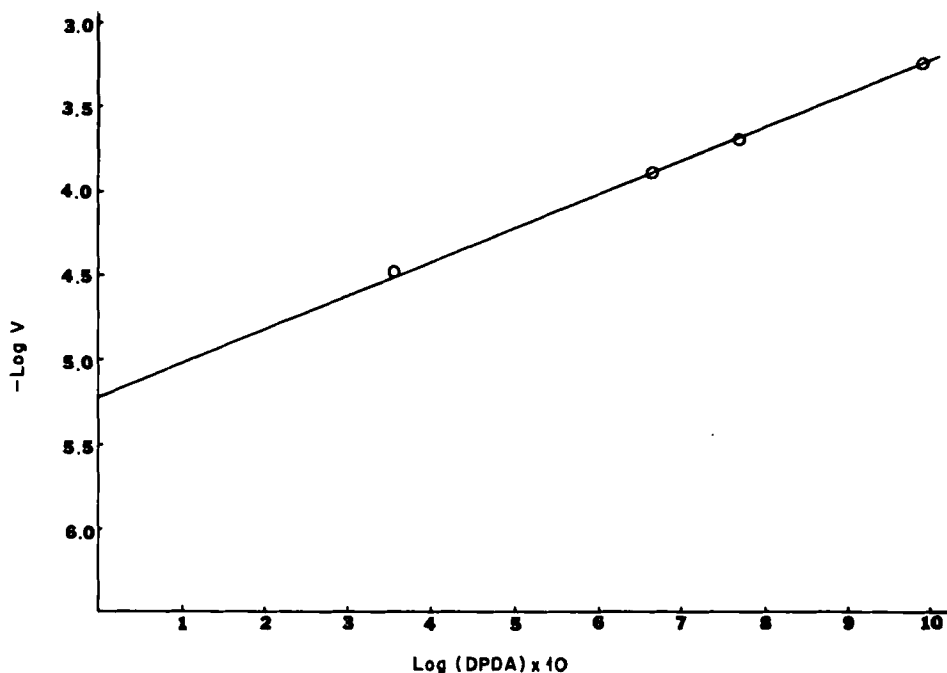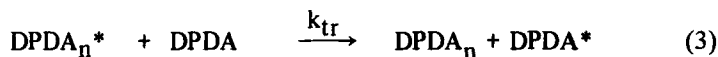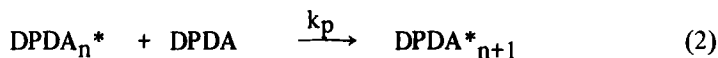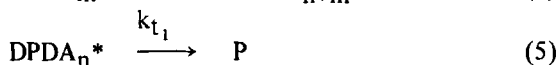

Fig. 2. Dependence of rate of polymerization on monomer concentration.

Kinetic analysis of the reaction mechanism of the above thermal polymerization data shows that the second power dependence of rate on monomer is consistent with a mechanism of bimolecular initiation and bimolecular termination. It further requires that the molecular weight of the polymer be independent of the monomer concentration.

$$2DPDA \xrightarrow{k_i} 2DPDA^* \qquad (1)$$

$$DPDA_n^* + DPDA \xrightarrow{k_p} DPDA^*_{n+1} \qquad (2)$$

$$DPDA_n^* + DPDA \xrightarrow{k_{tr}} DPDA_n + DPDA^* \qquad (3)$$

$$\text{DPDA}_n^* \; + \; \text{DPDA}_m^* \; \xrightarrow{\; k_{t_2} \;} \; \text{DPDA}_{n+m} \qquad (4)$$

$$\text{DPDA}_n^* \; \xrightarrow{\; k_{t_1} \;} \; \text{P} \qquad (5)$$
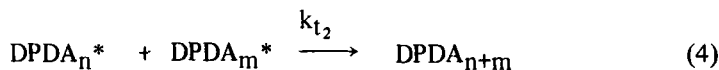
Reaction (1) is chain initiation and cannot be first order in the absence of catalyst. Flory [10] has shown that in such a case the energy requirement is too great. It can be second or third order. Reactions (2) and (3) are the chain propagation and transfer steps, and are second-order processes. Reactions (4) and (5) are chain termination steps, and can be bimolecular or unimolecular. It can be shown that at steady-state conditions, the rate of polymerization, V, and the kinetic chain length, ν for a bimolecular initiation and termination mechanism are:

$$V = k_p \left[\frac{k_i}{k_{t_2}} \right]^{0.5} \left[\text{DPDA} \right]^2$$

$$\nu = k_p \left[\frac{k_{t_2}}{k_i} \right]^{0.5}$$

A termolecular initiation or a unimolecular termination is not consistent with our data.

The apparent energy of activation is calculated from the slope of Fig. 3, and is found to be 6.4 kcal/mole. This value is comparatively low compared to the value 10.3 kcal/mole of methyl methacrylate and other thermal polymerizations in the literature.

Properties of Polymers

Polydiphenyldiacetylenes obtained by thermal polymerization are dark brown in color, and have a number-average molecular weight in the 632-1740 range. They are all soluble in aromatic solvents so that a three-dimensional cross-linked structure can be excluded. The melting point in a capillary seems to be 270-300°. There is no sharp endotherm observed in differential thermal analysis.

The conjugated double bond system in the thermal polymer was confirmed by the color test with antimony trichloride in chloroform [11]. This color test has been extensively used for testing of vitamin A and β-carotenoids which are known to contain a conjugated double bond system [12]. The monomer diphenyldiacetylene does not give coloration

with the reagent. IR absorption also supports the presence of such a system. There is an increase in intensity of the 1600 cm^{-1} absorption. The 1600 cm^{-1} absorption has been assigned to indicate fully conjugated double bonds while the 1665 cm^{-1} absorption is assigned to isolated double bonds [13, 14].
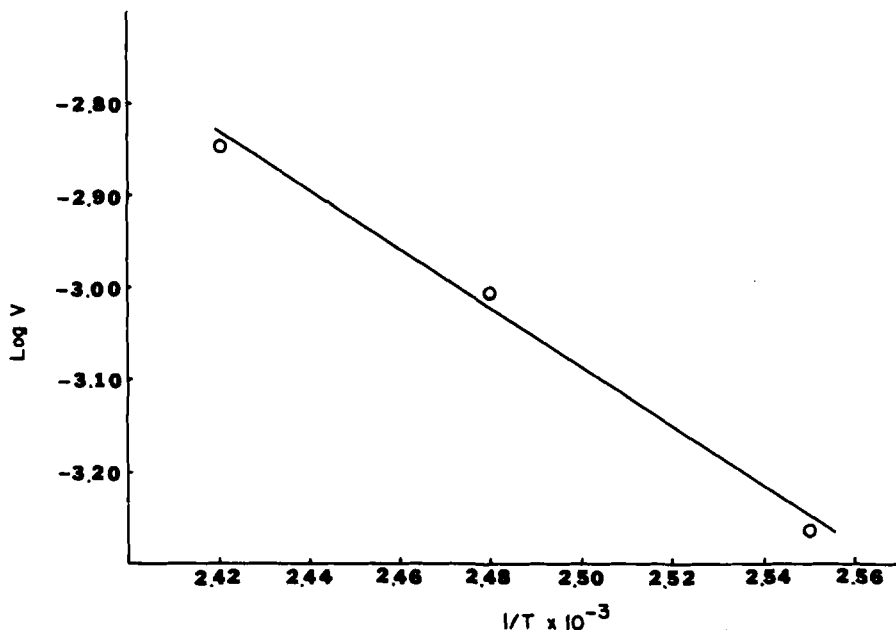

Fig. 3. Arrhenius plot for thermal polymerization of diphenyldiacetylene.

The electronic spectrum of the thermal polymer showed no discrete absorption maxima but a broad absorption around 255-290 mμ. There is continuous absorption from UV into the visible region in the form of a gradual slope. The intensity is stronger at short wavelength. Such behavior can be attributed to polymers in which a number of chromophores exist, each having different absorption maxima according to the length of the conjugated system. No discrete maxima would be expected unless one particular chromophore dominated the structure of the polymer. We may take the broad absorption peak at 255-290 mμ as due to the benzene chromophore, and the continuous absorption from UV to visible as due to the conjugated system.

The NMR spectra of the thermal polymers are quite diffuse and feature-less except for the broad peak of the phenyl protons absorbing around

2.9 τ but in a broad band. This is to be expected since the polymer contains only phenyl protons and consists of many species of different conformations and molecular weight.

Polydiphenyldiacetylene is paramagnetic. The monomer, however, does not show an EPR signal so that the radical nature of the polymerization is further substantiated. The number of paramagnetic particles per gram of polymer is one order of magnitude larger than β-carotene, a control which is known to have eleven conjugated double bonds. Results of the EPR measurement on the polymer and the polymer-complexes are given in Table 4.

The EPR curve of the thermal polymer showed no resolved hyperfine structure but a singlet with a g value of 2.033, very close to that of a free electron. Upon formation of charge-transfer complexes, the line width decreases while the spin concentration increases. The Lorentzian line shape of the EPR curve permits the calculation of T_2, the spin-spin relaxation time, in the polymer by the equation

$$T_2 = 1/(1.52 \times 10^7)\Delta H$$

Since the range of ΔH for polydiphenyldiacetylene is from 4.8 to 13.6, the range of spin-spin relaxation time is from 1.4 to 0.5×10^{-8} sec.

The mass spectrum for monomer diphenyldiacetylene (DPDA) which has not previously been reported, and polydiphenyldiacetylene are given in Figs. 4, 5, and 6. As with diphenylacetylene (DPA) [15], diphenyldiacetylene shows: 1) a strong molecular ion peak, at 202 amu with ^{13}C peaks of appropriate intensity at 203 (16.9%) and 204 (1.3%) amu, 2) a set of peaks at 150-1-2 (6, 2, and 1%) amu, and 3) a peak at 126 (2.5%) amu. The intensity of the low mass peaks for DPDA is considerably less relative to the molecular ion than it is for the DPA peaks. There is also a relatively intense peak at 101 m/e (5%) which may be either the doubly charged molecular ion or a C_8H_5 fragment or both. The 150 amu peak results from a characteristic benzenoid loss of two C_2H_2 fragments from the molecular ion. There is a peak of lesser intensity at 176 m/e corresponding to the loss of one C_2H_2 fragment. The 122-126 m/e peaks correspond to the loss of a third C_2 fragment.

The mass spectrum for polydiphenyldiacetylene (PDPDA), given in Fig. 5, was obtained using techniques developed with other polymers [16-18]. Initially, at sample temperatures of about 200°, the 202 m/e (monomer) peak is most intense. At the end of the heating cycle, with the sample temperature at 380°, the most intense peak is the tropylium peak at 91 m/e. It is

Table 4. EPR Measurements on Thermal Polydiphenyldiacetylene and Related Compounds

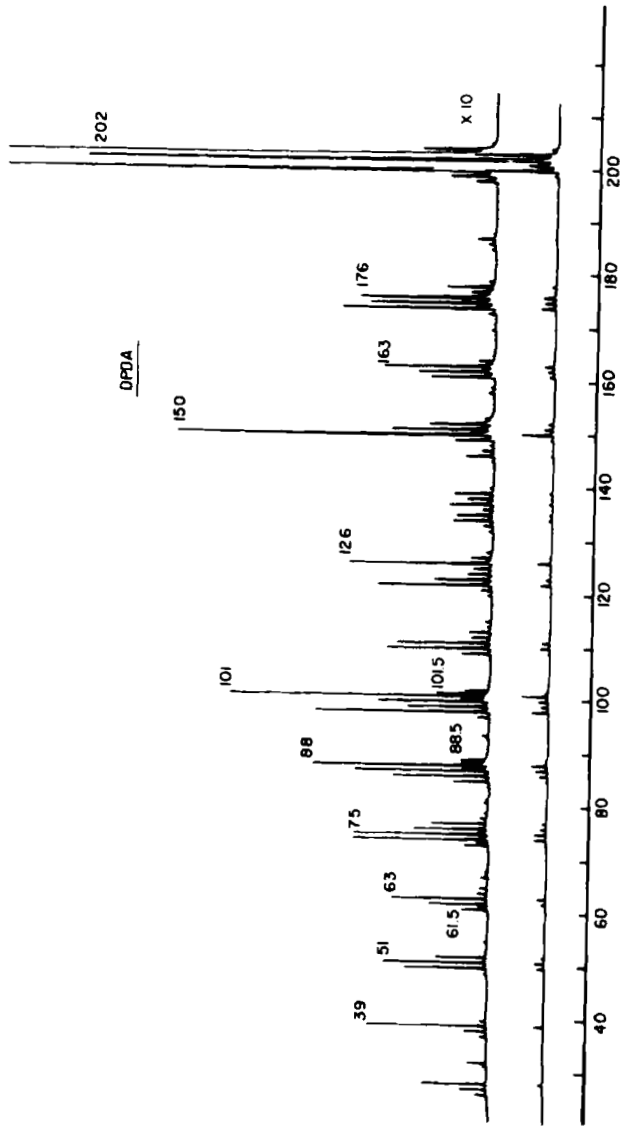| Polymer	Complex	Line width ΔH (Gauss)	Line shape	Spin concn (spins/g)
Polydiphenyldiacetylene	–	13.6	Lorentzian	3.10×10^{17}
	+ NbCl$_5$	4.8	″	8.41×10^{17}
	+ SbCl$_3$	5.6	″	10.8×10^{17}
	+ I$_2$	6.0	″	79.8×10^{17}
β-Carotene	–	22.0	Gaussian	6.80×10^{16}
	+ NbCl$_5$	13.0	″	7.60×10^{16}
	+ SbCl$_3$	12.7	″	9.90×10^{16}
	+ I$_2$	11.7	″	31.0×10^{16}

Fig. 4. Mass spectrum of diphenyldiacetylene. Sample (inlet) temperature 75°C. Mass range 20-220 amu, pressure 4.6 × 10⁻⁷ Torr, electron energy 70 eV, ion energy 68 eV, upper trace at ×10.
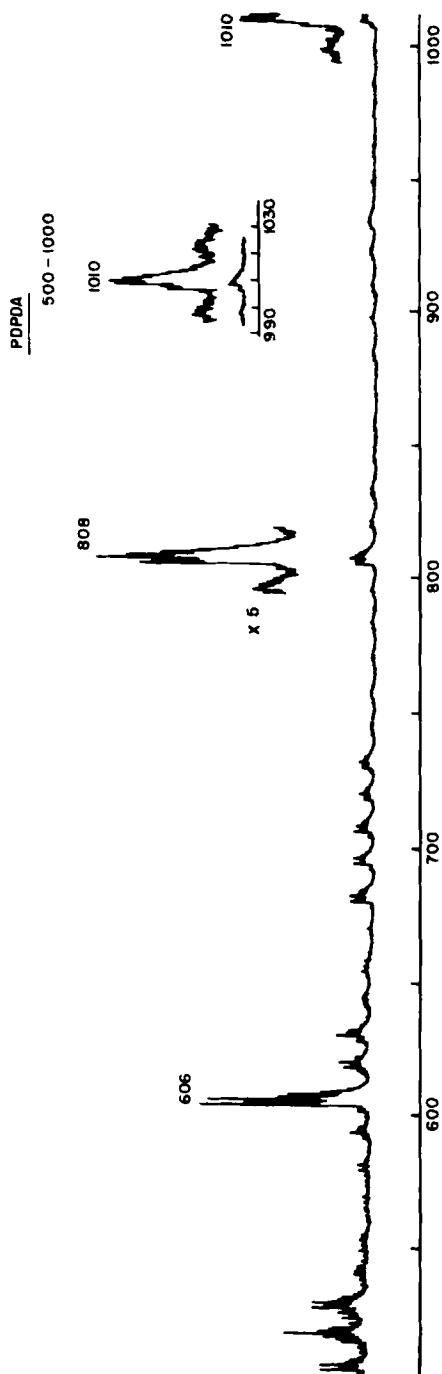
Fig. 5. Mass spectrum of polydiphenyldiacetylene. Sample temperature 380°C. Mass range 500-1000 amu (inset 990-1030 amu), pressure 4×10^{-7} Torr, electron energy 70 eV, ion energy 72 eV.
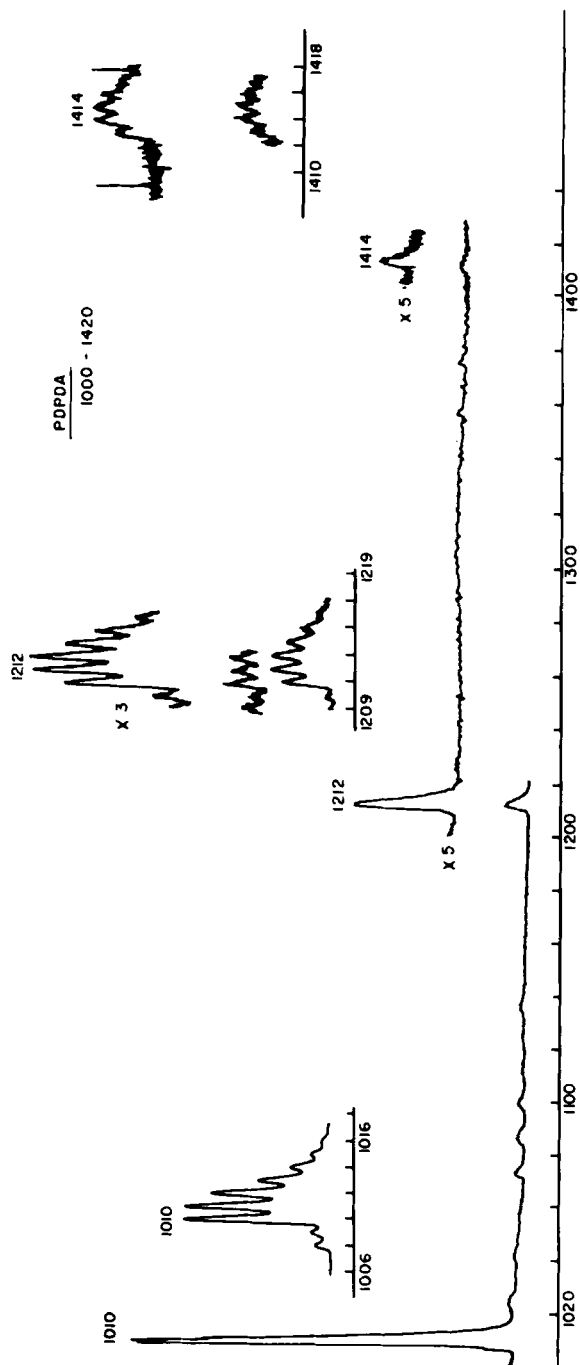
Fig. 6. Mass spectrum of polydiphenyldiacetylene. Sample temperature 250-300°C. Mass range 1000-1420 amu, pressure 3 × 10⁻⁷, electron energy 70 eV, ion energy 72 eV. Inset traces at high resolution and wide sweep width to show grouping of pentamer, hexamer, and heptamer peaks.

not known whether the monomer peak at 202 amu results from volatilized, unreacted monomer or from monomer formed in depolymerization. The high sample temperature spectra also show peaks at multiples of 202 up to 1212 m/e.

Three structures have been proposed previously [5, 6, 19] for polydiphenyldiacetylene. These involve 1,4- and 1,2-addition and ladder structures. There is no positive identification possible for any of these that is firmly established in our data for the thermal polymer.

ACKNOWLEDGMENTS

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