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POLYMERIZATION OF ARYLACETYLENIC COMPOUNDS

by

Joseph Y. C. Lee

A dissertation submitted to the Graduate Faculty in Chemistry in partial fulfilment of the requirements for the degree of Doctor of Philosophy, The City University of New York.

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I wish to express my sincere gratitude to Professor Richard H. Wiley for his guidance, advice and encouragement, and to the members of my Supervisory Committee for their help.

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1. INTRODUCTION

The polymerization of acetylenic compounds has received continuing interest. In principle, the polymerization of acetylenic monomers through addition of the triple bond will give polymers with conjugated double bonds, known as polyenes. The polyenes are an interesting class of material. A characteristic feature of the polyenes is the great degree of delocalization of the π-electrons possible in the macromolecule. The delocalization gives rise to a decrease of the internal energy of the system and a decrease of the energy of electronic excitation resulting from the decrease in the energy difference between the highest filled electronic level and the lowest unfilled level.[1] The decrease in internal energy results in a molecular structure of greater thermodynamic stability. The decrease in the energy of excitation is reflected in semiconducting, magnetic,and color properties. In fact, many polyenes are semiconductors.[2] Nevertheless, Dewar has pointed out that the single and the double bonds in polyenes can be treated as localized to explain the collective properties of the polyenes as a linear function of the bond properties.[3] In this sense, the bonds in the polyenes are "localized" even if there are significant interactions between the single and the double bonds, so long as the interactions between two adjacent bonds are the same in different polyenes.

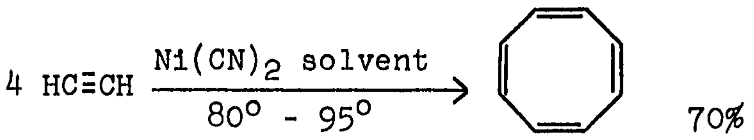
It is well known that polyenes are very sensitive to air, oxygen, light, and heat.[4] Divinylacetylene is notoriously difficult to handle. Some naturally occurring acetylenes decompose violently on melting. A search in the open literature reveals that the polymerization of acetylenic compounds is rather ill-defined. It almost always involves a solvent-soluble and a solvent-insoluble fraction,[5] and the conditions of the polymer isolation and recovery have seldom been specified in terms of the elements to which the polyenes are sensitive.

It is the objective of this work to prepare polymers of acetylenic compounds under very carefully controlled conditions by various techniques and to see if the chemical and physical properties of the products formed are distinct from those prepared by other means. The specific monomers are phenylacetylene, diphenylacetylene, diphenyldiacetylene, and 2-ethynylnaphthalene.

2. HISTORY

The polymerization of acetylene has been studied much less than ethylene. There has been a tremendous amount of literature concerning the polymerization of ethylene, the high pressure process which employed oxygen or peroxide to give low density polyethylene and the low pressure process which employed transition metals or organometallics to give high density polyethylene.[6] The reason is perhaps one of economics since at present the price of ethylene is 5 to 8 cents per pound while for acetylene, it is 20 to 25 cents per pound.[7] On the other hand, the polymerization of acetylene yields a range of products; benzene, cyclooctatetraene, polyacetylene, and an intractable cuprene. Cuprene is a dark brown powder that shows practically no crystallinity, and is believed to be formed by the action of oxygen on polyacetylene into a three-dimensional structure.[8] The process of polymerizing a triple bond may be more complicated than that for a double bond. A more complex array of products would be expected from phenylacetylene than styrene.

The earliest reported polymerization of acetylene dates back to 1866 when Berthelot trimerized acetylene to benzene thermally.[9] Subsequently, Reppe and his co-workers[10] made the startling discovery that acetylene may be polymerized in the presence of nickel salts to a mixture of cyclopolyalkenes, the major portion of which is cyclooctatetraene-1,3,5,7.



The first observation of a linear polymerization of acetylene was made by Nieuwland.[11] He found that when acetylene is passed into a saturated solution of sodium or ammonium chloride and cuprous chloride, vinylacetylene, and divinylacetylene are obtained.

$$\mathrm{CH{\equiv}CH} \xrightarrow[\mathrm{NH_4Cl}]{\mathrm{CuCl_2}} \mathrm{CH{\equiv}CH^*}$$

$$\mathrm{CH{\equiv}CH^*} + \mathrm{CH{\equiv}CH} \longrightarrow \mathrm{HC{\equiv}C\text{-}CH{=}CH_2}$$

$$\mathrm{CH{\equiv}CH^*} + \mathrm{HC{\equiv}C\text{-}CH{=}CH_2} \longrightarrow \mathrm{CH_2{=}CH\text{-}C{\equiv}C\text{-}CH{=}CH_2}$$

The manufacture of vinylacetylene is an industrially important process that led to the first commercially successful synthetic rubber, neoprene, poly(2-chloro-1,3-butadiene), by hydrohalogenation of vinylacetylene to chloroprene, 2-chloro-1,3-butadiene. Divinylacetylene is used for preparation of drying oils of unusual properties, and is an important raw material. It is very unstable and decomposes with violence.

2.1 Thermal Polymerization of Acetylenes

The most characteristic product of the thermal polymerization of acetylene is benzene which forms a major part of the liquid product from 20-90 percent. Between 400-600°, Pease[12] found that the reaction is second order. Schlapfer and Brunner independently arrived at the same conclusion.[13] Two bimolecular reactions accompanied by ring closure constitute a more probable mechanism for benzene formation especially in the vapor state than the simultaneous union of three acetylene molecules. In addition to benzene, other aromatic products have been detected including styrene, naphthalene, anthracene;[14] toluene, diphenyl, fluorene, pyrene, chrysene;[15] acenaphthene, phenanthrene;[16] m- and p-xylene, 1,4-dimethylnaphthalene, tetrahydronaphthalene;[17] o-xylene, pseudocumene, mesitylene, hydrindene, fluoranthene,[18] and higher hydrocarbons of undetermined structures. In brief, it may be stated that the thermal polymerization of acetylene leads primarily to aromatic products, principally benzene. The formation of higher aromatic hydrocarbons may be accounted for by assuming either substitution in the resulting benzene ring or cyclization of aliphatic chains containing more than six carbon atoms.

Experimental data on the thermal polymerization of acetylene showed that the composition of the end products varies widely with changes in conditions of reaction. For example, the course and extent of polymerization depend on the temperature, the pressure, the time of heating, the dilution of acetylene, the catalytic effect of deposited carbon due to decomposition, or added metals.

Early workers have stressed the importance of the reaction temperature. Berthelot first observed that a complex mixture of aromatic hydrocarbons was formed on heating acetylene for half-hour at the softening point of glass, but as the temperature of the glass became bright red, hydrogen and decomposed carbon predominated.[9] Walker reported slow condensation of acetylene to a liquid hydrocarbon mixture at 400-450°, but more rapid at 550°.[19] Bone and Coward found that polymerization reached a maximum at 600-700°, and above 800°, decomposition and methane formation became the principal reaction.[20] In contradiction, Kovache found that the optimum temperature for acetylene polymerization was 950°.[21] It appears that no reliable conclusion can be drawn concerning the effect of temperature on acetylene polymerization unless the length of the heating period, the purity and the pressure are also specified.

Results of diluting the acetylene with other gases depend on the nature of the diluent. Inert diluents would be expected to retard the bimolecular reactions of polymerization. Pease has reported a decrease in the rate of polymerization of acetylene diluted by nitrogen in the temperature range 400-650°.[12] Fischer, Bangert and Pichler noted that a higher temperature was necessary to obtain the same liquid hydrocarbons from acetylene diluted with nine times its volume of methane or hydrogen.[22] Hydrogen, which has been most frequently used as a diluent, undoubtedly reacts with acetylene and its polymer as well as producing the effects ascribed to added inert gases. Berl and Hoffman obtained the highest recorded yield, 98.8% of liquid products by passing acetylene mixed with 15% of steam at 740° through a glass tube packed with porcelain beads.[23] Fischer and his co-workers found that the dilution of acetylene with carbon dioxide before heating resulted in raising the proportions of "light oils" in the product.[22] It should be remembered that traces of water and also hydrogen from decomposition reactions are probably present in nearly all the experiments on thermal polymerization of acetylene.

Changes in the course of acetylene polymerization induced by variation in the pressure of the gas have been little studied, but theoretically increased pressures would be expected to promote the process. Fischer and his group found no observable effect by reducing the pressure from 750 to 200 mm. Hg. Dangerous explosions result on increasing the pressure of acetylene much above one atmosphere at the same temperature.[22] A patent, however, claims that acetylene may be polymerized to give a very high yield of liquid hydrocarbons while dissolved in an inert oil under a pressure of 10-200 atmospheres in the presence of finely divided iron or magnesium bromide as a catalyst.[24] The effect is not very clear since a metal catalyst was used.

Acetylene is known to polymerize with free radicals generated by peroxides. Landers polymerized acetylene with methyl radicals generated by di-t-butyl peroxide.[25] The rate of polymerization was proportional to the first power of acetylene and to the square root of the peroxide concentration. This is exactly required by the conventional free radical polymerization mechanism, and he suggested unimolecular decomposition of peroxide into free radicals, propagation by radical addition to the triple bond, and termination by radical combination.

Substituted acetylenes also thermally polymerize with more or less ease, depending on the structure of the monomer. Besides polymers, some of the products are substituted benzenes and as in the acetylene case, 4 and 8 member cyclic rings can also form. Coming back to the specific monomers here studied, the literature on the thermal polymerization of phenylacetylene was very much less than that of acetylene. Korshak reported polymerization of phenylacetylene in low yield (3-60%) in presence of peroxides under 1-6000 atmospheres pressure from 70-200°.[26] The structure was unknown but the polymer was a brittle orange solid which became a yellow powder on precipitation from benzene. Berlin has reported polymerizing phenylacetylene thermally to a yellow solid with high thermal stability.[27] The assumed structure was that of a conjugated polyvinylene. Shantarovich,[28] found that thermal polymerization of phenylacetylene was a second order reaction like that reported for acetylene by Pease. He obtained a polymer containing 6-17 monomeric units, and some 1,3,5-triphenylbenzene. Okamoto studied the solvent effect of thermal polymerization of phenylacetylene in 1961.[29] A remarkable feature was that no cyclization occurred when polymerization was conducted in solvents and only 1% of 1,3,5-triphenylbenzene was obtained when polymerization was done in bulk (no solvent). His results are reproduced in Table 1.

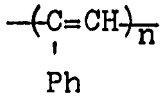
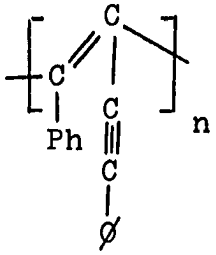
He assigned a conjugated structure of  $-\!\!\left(\underset{\underset{\mathrm{Ph}}{|}}{\mathrm{C}}=\mathrm{CH}\right)_{n}$ in mostly trans configuration. Barkalov studied the rate of polymerization of phenylacetylene in the presence of benzoyl peroxide at 60-80°C., and found that the rate increased linearly with the concentrations of peroxide and phenylacetylene.[30] He obtained an apparent activation energy of 21 Kcal/mol. Higashiura,[31] reported that the initial rate of thermal polymerization of phenylacetylene in benzene between 130-170° increased with 2.32 power of phenylacetylene concentration, having an apparent activation energy of 23.9 Kcal/mol. Finally, the structures of thermally polymerized phenylacetylene have been studied by Berlin,[32] who found by infrared, X-ray measurements to be a linear molecular with trans configuration in agreement with Okamoto, by Ehrlich,[33] who by X-ray diffraction pattern and electron spin resonance signal found it to be an amorphous polymer, with termination by chain transfer to the monomer, and by Kern,[34] who by infrared spectroscopy studied the isomerization of polyphenylacetylene and found the polymer

Table 1 Polymerization Conditions and Physical Properties of Phenylacetylene[29]

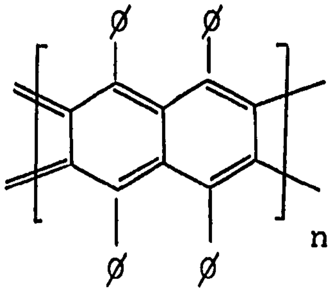
Solvent	Reflux Temp. (°C.)	Reaction Time (hrs.)	m.p. of Crude Polymers (°C.)	Average M.W.	Found	
					% C	% H
Decalin	175-195	22	188-195	550	93.32	6.29
Xylene	140-160	65	100-135	485	93.82	6.35
Diglyme	165-180	65	100-115	482	90.78	6.48
Chlorobenzene	130-145	48	145-150	1020	93.95	6.04
None	145-160	18	195-205	973	93.58	5.90

consisting of cis and trans units with respect to the chain backbone, and not mainly trans as others reported.

There has been no English literature recorded to date on the thermal polymerizations of diphenylacetylene and diphenyldiacetylene. Only two references appeared in Russian so far. In 1967, Berlin and his school reported a thermal polymerization of diphenylacetylene in bulk at 300-400° for 3-10 hours.[35] They dissolved the polymer in benzene and precipitated in methanol. The molecular weights were 940-1200. The heat stability was greater than the corresponding polyphenylacetylene, with a softening temperature of 160-215°.

The earliest reported thermal polymerization of diphenyldiacetylene was in 1965 by Davydov.[36] He found the thermal polymer was very stable to heat, not decomposing even at 500°. Irrespective of the time and temperature of polymerization, the molecular weight is always 1100. In 1967, Berlin,[37] reported the thermal polymerization of diphenyldiacetylene without solvent under argon at 80-400°. At 400°, diphenyldiacetylene exploded. So he employed a two-stage process by first heating the system at 195° and then heating it to 400°. He proposes a structure of 

at low temperature of polymerization which cyclized to a ladder-like structure on heating to a higher temperature.



No literature concerning the thermal polymerization of naphthylacetylene can be found to date.

2.2 Polymerization of Metal Catalysts

Much more information on the catalytic polymerization of acetylene is available than on the thermal polymerization. Most of the catalysts are transition metal compounds which could complex with the acetylene molecule. These metal-acetylene complexes are involved in the catalytic addition of the acetylene in cyclization, oligomerization and polymerizing reactions. Much interest has been generated in the chemistry of these complexes, both in their molecular geometry and in the products they help to catalyze. Consequently, transition metal complexes involving acetylene can be classified according to Rutledge as:[38]

1. Nast products in which the metal-acetylene bonds are normal σ bonds[39] as in $K_6\left[Ni(C{\equiv}C\text{-}\phi)_8\right]$.

2. Complexes in which the triple bond is unchanged as in $(PtCl_2 \cdot t\text{-}BuC{\equiv}Ct\text{-}Bu)_2$.[40]

3. Complexes in which acetylene is a chelating ligand as in platinum complexes in which one acetylenic compound can replace another ligand in a solution at room temperature.[41]

   $$Pt(P\phi_3)_2ac + ac' \rightleftharpoons Pt(P\phi_3)_2ac' + ac$$

   where ac and ac' are different acetylenes.

4. Complexes in which acetylene forms cyclic structures as in benzene,[42] cyclobutadiene,[43] cyclooctatetraene.[10]

5. Complexes in which acetylene forms linear structures with conjugated double bonds which lead to linear oligomers[44] and high polymers.[45]

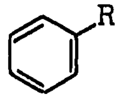
It is the complexes under the last heading that are of interest here, although the same complex can catalyze either linear polymerization or cyclization depending on conditions, or both reactions occurring simultaneously. Donda and Moretti have compared the activity of Ziegler catalyst and Luttinger catalyst under the same conditions and the two catalysts can cyclotrimerize acetylenes as well as polymerizing them.[46]

The polymerization of acetylene to a high molecular weight linear polyene of predominantly trans structure was first described by Natta.[47] In heptane at -30 to +80°, Et_3Al-$Ti(OPr)_4$ gave 90-95% of dark crystalline polymer, completely insoluble. At Al:Ti ratio of 2.5, 98.5% of the acetylene is polymerized. Similarly, Ziegler catalysts polymerize other acetylenic hydrocarbons.[48] The first systematic study of Ziegler catalysts for the polymerization of acetylene and 1-alkynes was made by Watson.[49] He determined the optimum ratio of organometallic to transition metal halide, $Al(i\text{-}Bu)_3:TiCl_4 = 2.0\text{-}2.5$; $BuLi:TiCl_4 = 4.0$; $ZnEt_2:TiCl_4 = 2.5\text{-}3.0$. As the reaction temperature increases, more acetylene polymerizes and the percentage of soluble polymer increases. The ratio of soluble to insoluble polymer is a linear function of the catalyst concentration, and increases with increasing catalyst. At about the same time, Lutz found that reaction of acetylene with Ziegler catalysts also gave benzene besides linear polyacetylene.[50] He concluded that both the high polymerization and the cyclotrimerization of acetylene took place without the breaking of the metal-carbon bonds of the catalyst. Ikeda made the important discovery that one end group of the polyacetylene molecules comes from the groups belonging to the organometallic catalyst; the alkyl group of the product alkylbenzenes comes from the groups also belonging to the organometallic catalyst; and using ^{14}C organometallic catalyst, the product benzene also contains radioactive ^{14}C.[51,52] He suggested a mechanism for acetylene cyclization, oligomerization and polymerization as follows.

For cyclization to benzene and alkyl benzene:

$$[\text{Cat}]\text{-R} + \text{CH}\equiv\text{CH} \longrightarrow [\text{Cat}]\text{-CH=CH-R}$$

$$[\text{Cat}]\text{-CH=CH-R} + \text{CH}\equiv\text{CH} \longrightarrow [\text{Cat}]\text{-CH=CH-CH=CH-R}$$

$[\text{Cat}]\text{-CH=CH-CH=CH-R} + \text{CH}\equiv\text{CH} \rightarrow [\text{Cat}]\text{-H} +$ 

$$[\text{Cat}]\text{-H} + \text{CH}\equiv\text{CH} \longrightarrow [\text{Cat}]\text{-CH=CH}_2$$

$$[\text{Cat}]\text{-CH=CH}_2 + \text{CH}\equiv\text{CH} \longrightarrow [\text{Cat}]\text{-CH=CH-CH=CH}_2$$

$[\text{Cat}]\text{-CH=CH-CH=CH}_2 + \text{CH}\equiv\text{CH} \rightarrow [\text{Cat}]\text{-H} +$ 

For oligomerization and high polymerization:

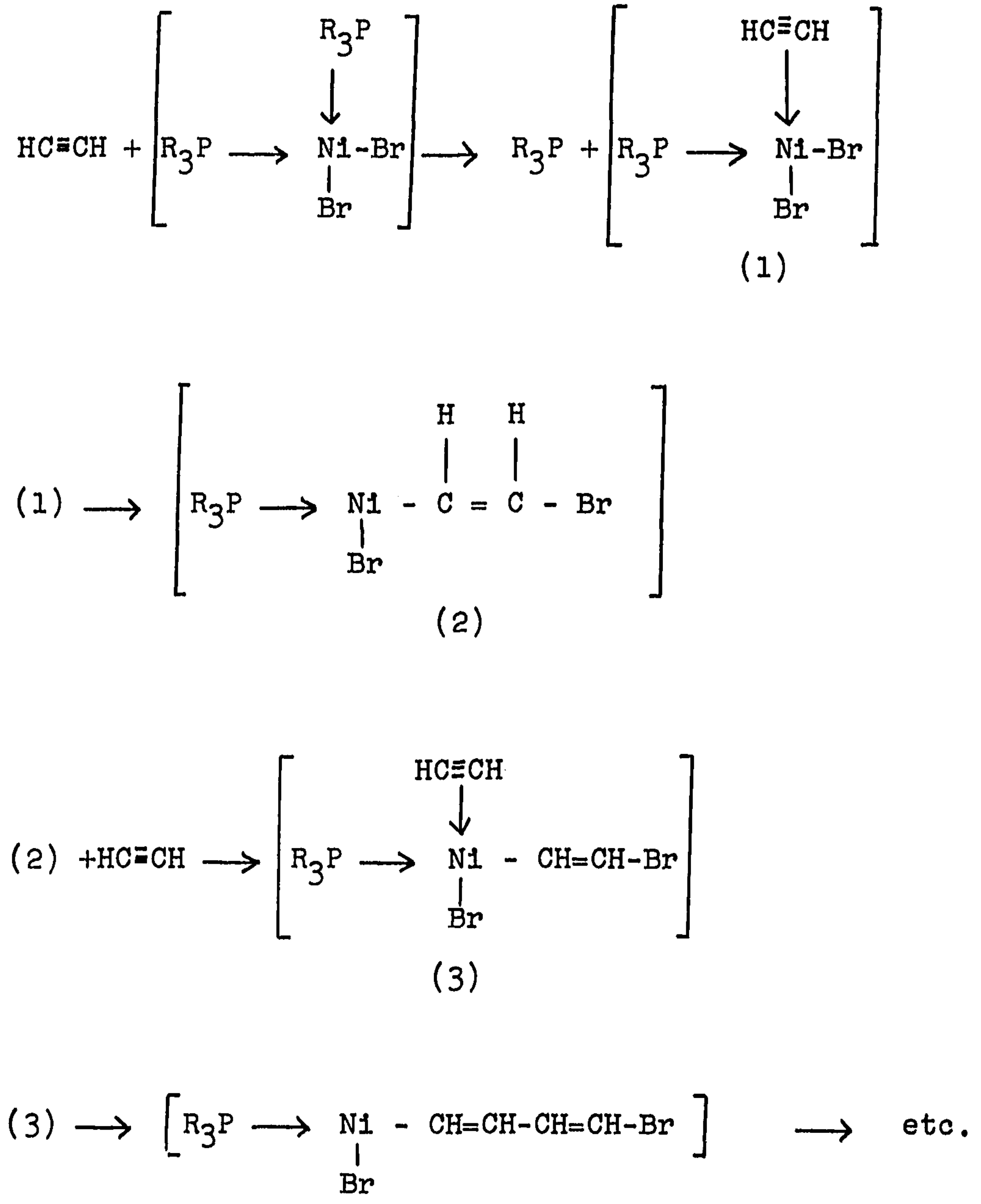
$$[\text{Cat}]\text{-R+CH}\equiv\text{CH} \longrightarrow [\text{Cat}]\text{-CH=CH-R}$$

$$[\text{Cat}]\text{-CH=CH-R+nCH}\equiv\text{CH} \longrightarrow [\text{Cat}]\text{-}(\text{CH=CH})_{n+1}\text{R}$$

$$[\text{Cat}]\text{-}(\text{CH=CH})_{n+1}\text{R+CH}\equiv\text{CH} \rightarrow [\text{Cat}]\text{-H+C}_6\text{H}_5\text{-}(\text{CH=CH})_{n-1}\text{R}$$

If n is low, it is an oligomer, if n is large, it is a high polymer and if n is 1, we have alkylbenzene. When R is a hydrogen, it is benzene. The mechanism is the same as those advanced for the polymerization of 1-olefins with insertion of monomers into a coordinated complex with one important difference, that is, the aromatization of one end group in the polyacetylene chain. Another important feature is that aromatization, oligomerization and polymerization have the same mechanism, same initiation, propagation and termination through transfer with the monomer, (not recombination or disproportionation).

In addition to the well-known Ziegler catalyst, there are other catalysts which polymerize acetylene as well, especially the transition metal complexes of Group VIII elements. In 1960 Luttinger reported a new system for the high polymerization of acetylenes.[53] The system consists of an hydridic reducing agent like sodium borohydride plus a salt of a Group VIII metal like nickel chloride. The polymer obtained is like the one Natta obtained with Ziegler catalyst. When a Group VIII complex like bis(tri-n-butylphosphine) nickel dichloride, $(n\text{-}Bu_3P)_2Ni(Cl)_2$ was used, one mole of catalyst can polymerize several thousand moles of 1-alkynes in a few minutes. We should, however, recall that Reppe also used nickel carbonyltrialkylphosphine complexes $(R_3P)_2Ni(CO)_2$ to prepare a number of aromatic products from acetylene and monosubstituted acetylenes.[42] What Luttinger did was to add a co-catalyst, the hydridic reducing agent, to the same complex, and he obtained both cyclization and polymerization. Green independently reported a similar system. The phosphine complexes of nickel or cobalt salt, $(R_3P)_2MX_2$ reduced with $NaBH_4$ in tetrahydrofuran.[4] The catalyst $(Pr_3P)_2NiCl_2$ shows well-defined proton resonance absorption characteristic of hydrogen bound directly to transition metals, indicating that the active catalyst is a species with metal-hydrogen bonds, in support of Ikeda's mechanism. Daniels found that nickel halide-tertiary phosphine complexes alone are catalysts for acetylene polymerization with iodide better than bromide better than chloride. Yet, cobalt, and palladium complexes, also of Group VIII metal, are completely inactive as a polymerization catalyst.[54] The reason is not clear. The resultant polyacetylene always contains nickel and halogen. While nickel can be removed by washing with HCl, the halogen is not removable, indicating that nickel and halogen are present as end groups of the chain, the former as labile organometallic and the latter as alkyl halide. The initial step in the polymerization is a displacement of one or more phosphine ligands by acetylene, to form a transient π-complexed acetylene intermediate which leads to polymer by a cycle of ligand insertion and monomer complexation.



$$HC\equiv CH + \left[R_3P \longrightarrow \underset{\substack{|\\ Br}}{\overset{\substack{R_3P\\ \downarrow}}{Ni}}\text{-}Br\right] \longrightarrow R_3P + \left[R_3P \longrightarrow \underset{\substack{|\\ Br}}{\overset{\substack{HC\equiv CH\\ \downarrow}}{Ni}}\text{-}Br\right]$$

(1)

$$(1) \longrightarrow \left[R_3P \longrightarrow \underset{\substack{|\\ Br}}{Ni} - \overset{\substack{H\\ |}}{C} = \overset{\substack{H\\ |}}{C} - Br\right]$$

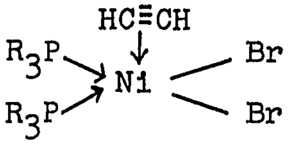
(2)

$$(2) + HC\equiv CH \longrightarrow \left[R_3P \longrightarrow \underset{\substack{|\\ Br}}{\overset{\substack{HC\equiv CH\\ \downarrow}}{Ni}} - CH{=}CH\text{-}Br\right]$$

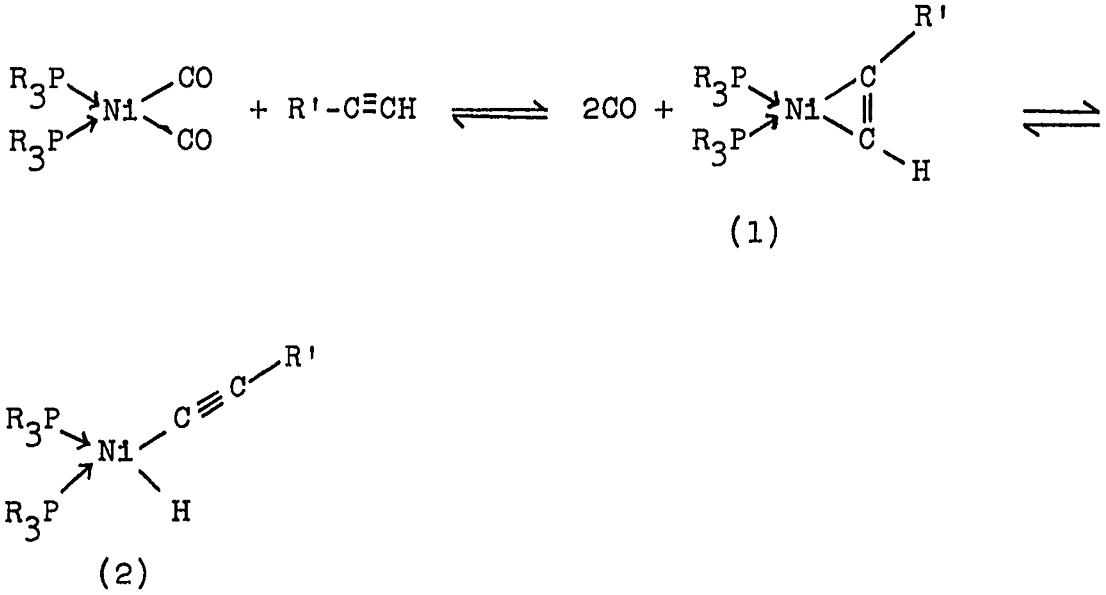
(3)

$$(3) \longrightarrow \left[R_3P \longrightarrow \underset{\substack{|\\ Br}}{Ni} - CH{=}CH\text{-}CH{=}CH\text{-}Br\right] \longrightarrow \text{etc.}$$

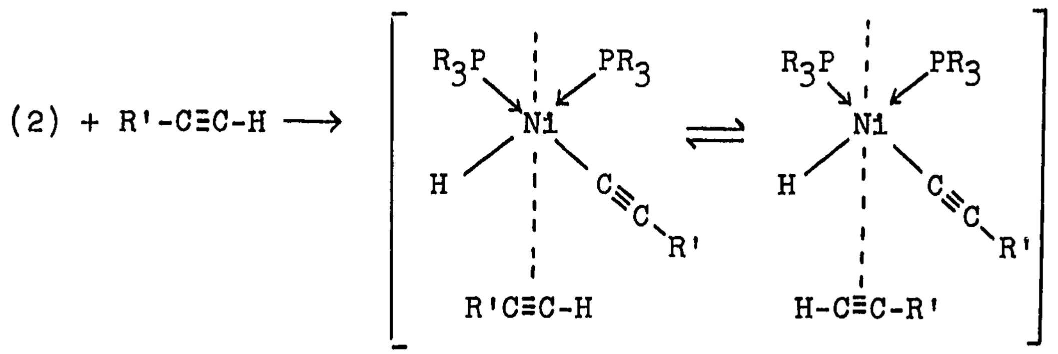
An alternative reaction path lies in direct acetylene complexation to form a pentacoordinate π-complex in which nickel has attained the Kr configuration, which can lead to polymer in the same way as (1).



Using Reppe's catalyst, Meriwether and his coworkers,[55] have worked out a detailed scheme for the linear polymerization and aromatic cyclization of acetylene by nickel dicarbonyl-diphosphine complexes, $Ni(CO)_2(PR_3)_2$, the activity varying with the substituent R in a general way, $C_2H_4CN > C_6H_5 > H > OC_2H_5 > \text{n-alkyl} \gg OC_6H_5 \approx Cl$. The reaction mechanism is given as follows:

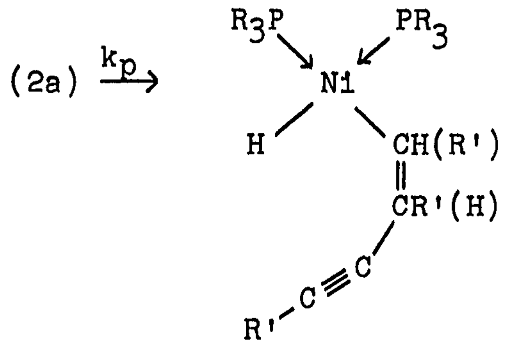


The acetylene (R'=H) replaces all the CO ligands. Complex (1) is initially formed, but converted to (2) readily which is the active catalyst for both polymerization and cyclization. In analogy to the Ziegler catalyst, a metal-hydrogen bond is present. (1) And (2) are planar complexes of nickel (II) that has a vacant P_z orbital, available to π-bonding with a second acetylene molecule.



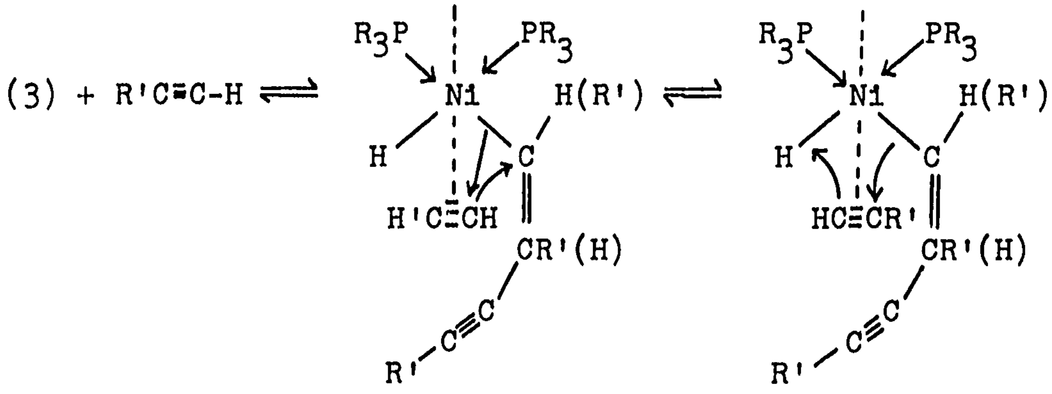
(2a)

(2) Reacts with acetylene monomer to (2a) involving π-complex formation between the triple bond and the nickel P_z orbital such that the z axis goes through the center of $C\equiv C$ bond with the acetylene molecule lying roughly parallel to the plane of the complex. The symmetry of the P_z orbital gives rise to stereospecific orientations of the linear acetylene relative to P_x and P_y axis, or relative to the $-PR_3$ and $-C\equiv C-R'$ groups. If $R' \neq H$, four reactions are possible, namely, cis insertion of the monomer between the nickel and acetylide carbon atoms such that (a) R' group is adjacent to the $C\equiv C$ bond, (b) to the nickel atom, (c) hydrogen exchange between the π complexed acetylene and the acetylide, and (d) dissociation of the π-complex. All four reactions can proceed from different conformations of the π-complex.



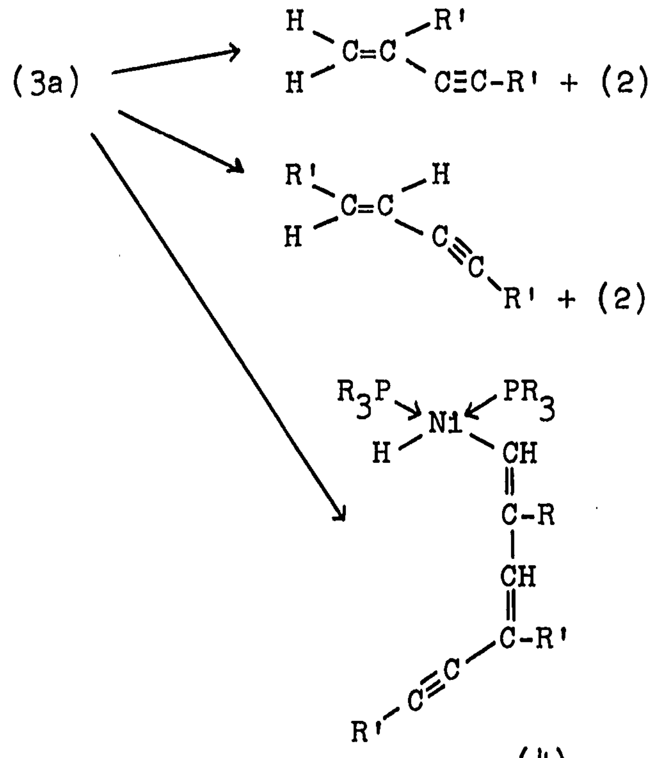
(3)

The two nickel-vinylacetylene complexes (3) resulting from insertion of an acetylene molecule can form π-complexes (3a) with another molecule of monomer.



(3a)

Again, four reactions are possible for (3a), hydrogen transfer from the acetylene to the 2,4-disubstituted vinylacetylene group to give the vinylidene dimer, regenerating (2); hydrogen transfer from the acetylene to the 1,4-disubstituted vinylacetylene to give the trans dimer and (2); cis insertion of the acetylene molecule between the nickel and the vinyl carbon atom of the disubstituted vinylacetylene complexes such that the R' group of the acetylene is adjacent to the central double bond; to the nickel atom. The latter two reactions lead to higher homolog.



(4)

(4) Forms again a π-complex with a new monomer molecule, reacts in like fashion to produce two linear trimers and (2), and the nickel tetramer complex. This sequence is repeated for polymerization. Of course, when R' = H, there is no geometric trans or cis isomer, so that only 1 dimer, 1 trimer, etc., are formed. Assuming that there is a favored conformation of (4) in which the 1 and 6 carbon atoms of the butadienyl-acetylene group can approach bonding distance, a concerted hydrogen transfer and ring closure would account for aromatic products.

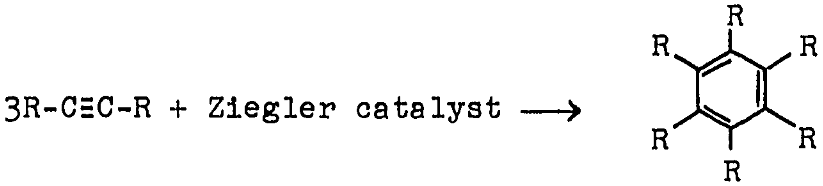
Finally, other Group VIII metallic catalysts that polymerize acetylene include rhodium chloride and palladium chloride.[56] Although copper is not a transition metal, CuO is known to polymerize acetylene at 180-350° to form cuprene.[57]

Literature on the polymerization of phenylacetylene is not so extenseive as acetylene but all the metal catalysts discussed so far can also polymerize phenylacetylene. Natta reported the polymerization of phenylacetylene by Ziegler catalyst in a Belgium Patent.[58] The polymer consists of acetone soluble and acetone insoluble fractions, at $AlEt_3:TiCl_3$ ratio of 1.9 in benzene. Later, Berlin employed the same catalyst in benzene and found that a maximum yield of polymer (96.3%) occurred at $AlEt_3:TiCl_3$ ratio of 1.1.[59] Increasing the Al:Ti ratio causes a decrease in yield and an increase in insoluble products. The molecular weight ($\overline{M}_n$. = 5,000) is higher than those formed by thermal or free radical polymerization ($\overline{M}_n$ = 800-1,200). In addition, some cyclic product, 1,3,5-triphenylbenzene was also formed together with the linear polymer. Higashiura observed that with the Ziegler catalyst $AlEt_3:TiCl_4$ in benzene the maximum yield occurred between the Al:Ti ratio of 7-10.[60] When the ratio is less than 5, the polymer is all soluble in benzene whereas if the ratio is larger than 5, it is partly insoluble. The molecular weight increases from 280 to 1,000 as the ratio increases. The cyclic trimer, 1,3,5-triphenylbenzene was formed at a Al:Ti ratio of 0.5. Bantsyrev added in the $AlEt_3$-$TiCl_3$ system, the cyclic trimer is 1,2,4-triphenylbenzene.[61] This is only formed in heptane solution, and not formed in benzene solution.

The transition metal complexes of Group VIII elements are also known catalysts. The Luttinger catalyst, diphosphine complex of nickel and hydridic reducing agent $(Bu_3P)_2NiCl_2$-$NaBH_4$, gave dimer, trimer and tetramer, most of which are the cyclic 1,3,5-triphenylbenzene and 1,2,4-triphenylbenzene.[53] Without the hydridic reducing agent, Daniels succeeded in polymerizing phenylacetylene into linear trans polyene, by a tertiary phosphine complex of nickel, $(Ph_3P)_2NiBr_2$.[54] In the case of nickel dicarbonylphosphine complexes, Meriwether found that linear trimerization is favored by the cyanoethylphosphine complex, $[(C_2H_4CN)_3P]_2Ni(CO)_2$ while cyclic trimer is favored by triphenylphosphine complex, $[Ph_3P]_2Ni(CO)_2$.[55] Ehrlich obtained a highly crystalline polyphenylacetylene (80% crystallinity by XRD pattern) with rhodium chloride-lithiumborohydride.[33] Palladium complex, $PdCl_2 \cdot (PhCN)_2$ gave a polymer together with 1,2,4-triphenylbenzene and 1,3,5-triphenylhexa-2,5-dien-1-yne.[56] Platinum-tertiary phosphine complex,[62] and ferric acetylacetonate-diisobutylaluminum hydride complex[34] are reported to give polyphenylacetylene. Of all the Group VIII metals only three elements are left out which have not been reported for the polymerization of phenylacetylene. They are ruthenium (Ru), osmium (Os), and iridium (Ir), and we can predict that they too may be catalysts for acetylene polymerization.

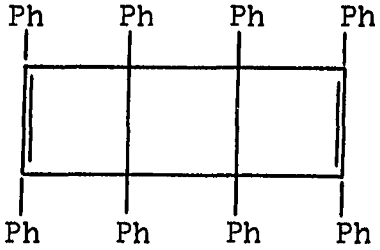
A few catalysts other than Group VIII metals have also been recorded. Among them are the cationic catalysts like BF_3, $SnCl_2$ or CF_3COOH;[63,64] metal alkyl-metal dimethylglyoximate;[65] and cupric oxide.[66]

The first polymerization of diphenylacetylene with Ziegler type catalyst was by Franzus.[67] He found that diphenylacetylene could be trimerized into hexaphenylbenzene with $(i\text{-}Bu)_3Al\text{-}TiCl_4$ at Al:Ti ratios of 1-3. Outside these limits, the yield of hexaphenylbenzene was zero, and polymerization could occur. A completely general reaction of the following type was proposed.

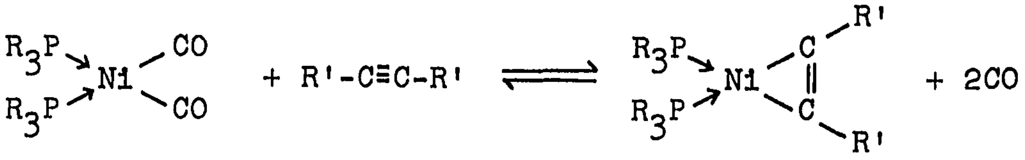


Any symmetrical dialkyl or diarylacetylene will trimerize at the proper catalyst ratio. Drefahl treated benzene solution of diphenylacetylene with $Et_3Al\text{-}TiCl_4$.[68] The major product was hexaphenylbenzene, maximum yield at a Al:Ti ratio of 2. At 1:1 ratio, he obtained 4% of a tetramer of diphenylacetylene, octaphenyltricyclooctadiene, the structure of which had been originally determined by

Freedman,[69] and Tsutsui.[70]

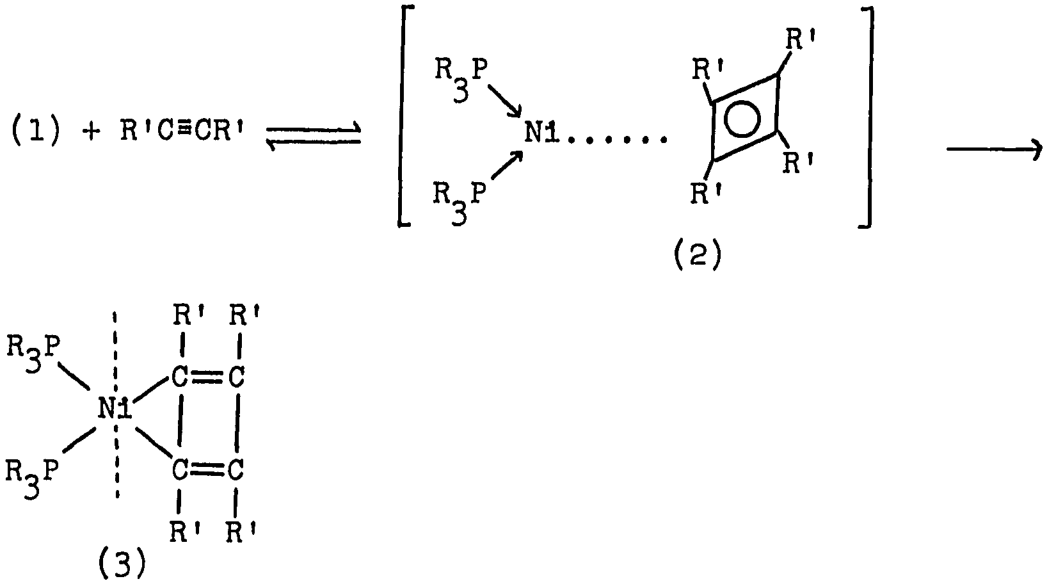


Luttinger reported that the nickel complex-hydridic reducing agent system failed to polymerize at room temperature, but at 78°, 1% of hexaphenylbenzene was recovered.[53] Meriwether suggested a mechanism for the aromatization of diphenylacetylene with the nickel dicarbonyl-diphosphine complex.[55]

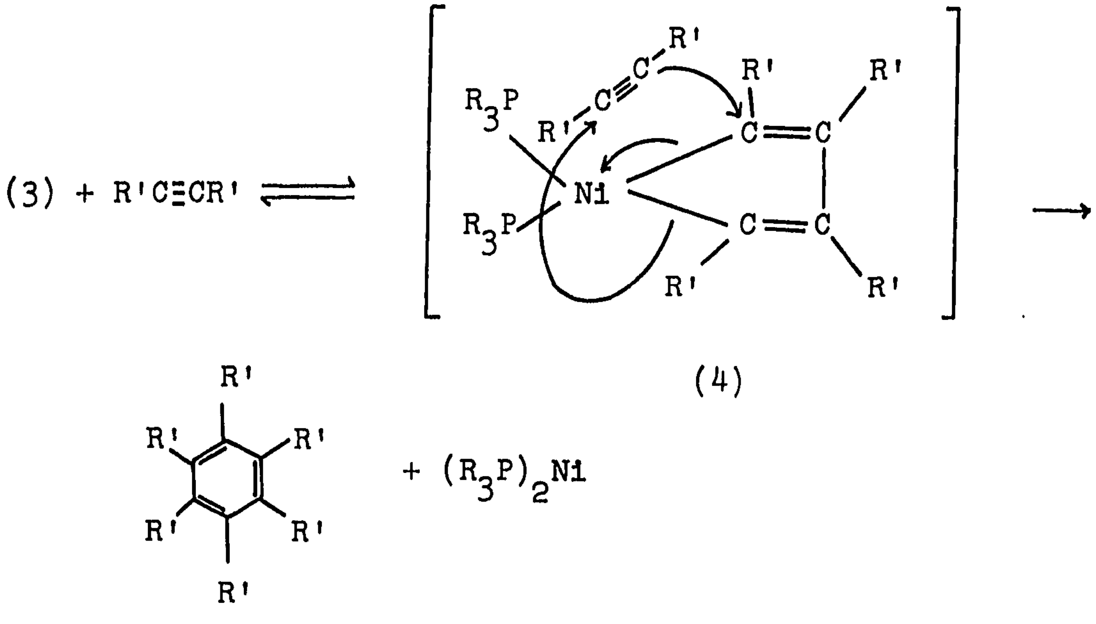


(1)

Complex (1) reacts with a second acetylene molecule (R'=phenyl) probably by way of a diphosphine-nickel-cyclobutadiene (2) to form the planar complex (3) in which nickel and the two acetylene group formed a five-membered ring.



Complex (3) has a vacant p_z orbital for coordination of a third acetylene. The resulting π-complex (4) can then collapse to form the aromatic product.



Again, this type of reaction is perfectly general for diacetylene. Maitlis cyclotrimerized diphenylacetylene into hexaphenylbenzene in the presence of bis(benzonitrile) palladium chloride. Some bis(cyclobutadiene) complex was also observed.[71]

Other catalysts have been found effective for the polymerization of diphenylacetylene. Tsutsui identified a trimer and tetramer with a Grignard reagent, phenylmagnesium bromide. Leavitt dimerized diphenylacetylene into tetraphenylbutadiene derivative and 1,2,3-triphenylnaphthalene with lithium metal.[72] Finally, some Russian workers supposedly synthesized polydiphenylacetylene with dilithio-tetraphenylbutadiene-1,3 with metal halide.[73] Although the monomer was tetraphenylbutadiene-1,3, it was related to diphenylacetylene through a dimerization in lithium. The resultant products composed a soluble and an insoluble fraction as usual.

The only recorded polymerization of diphenyldiacetylene by metal catalyst was that of Teyssie[74] in 1964. He used the Ziegler-type catalyst, $(i\text{-Bu})_3Al\text{-}TiCl_4$. Maximum yield of the polymer was observed at a Al:Ti ratio of 2.7 and further increase of the ratio decreases the yield rapidly. More polymers were formed at higher temperatures but this did not affect the molecular weight appreciably, ($\overline{M}_n = 1078 - 1250$). The polymer so obtained was treated either thermally at 400° under argon or with antimony pentachloride, and had very good heat resistance with a softening point around 480°. Both the treated and the untreated polymers had narrow electron paramagnetic resonance signal, and showed a low conductivity (10^{-14} mho/cm.). They also gave indication of photoconductivity. However, a year later, Davydov prepared polydiphenyldiacetylene with triethylaluminum and vanadyl acetylacetonate, and found no photoconductivity.[36]

Literature on the polymerization of naphthylacetylene is scarce. About the only polymerization of naphthylacetylene is that of Kambara[75] in 1967. He polymerized 1-ethynylnaphthalene with a Ziegler-type catalyst and obtained a colored product. Based on infrared measurement, he assigned a conjugated structure to the polymer.

2.3 Polymerization of Acetylenes by Other Methods

There are other types of reactions in which the triple bond of acetylene becomes a double bond by the addition of non-metallic elements other than carbon. The substances capable of addition to acetylene include hydrogen, halogen, oxygen, sulfur, nitrogen, water, hydroxyls, etc., but they do not necessarily lead to polymerization through chain processes. On the other hand, polymerization of acetylene may be initiated by purely physical means like radiation, ultrasonics, shock waves, etc.

The hydrogenation of acetylene by molecular hydrogen in the presence of catalyst gave the expected products, ethylene, ethane and some polymers.[76] Wijnen has reported a chlorine atom induced polymerization of acetylene by photolyzing phosgene.[77] Carbon monoxide, vinyl chloride, 1-chloro-1,3-butadiene, benzene and polymer are believed to form in the initial stages of the chlorine atom initiated polymerization.

Photopolymerization of acetylene, sensitized by mercury vapor, gave benzene, polymer and hydrogen as the reaction products.[78] Polymerization by alpha rays from radon[79] and beta rays from 1 Mev. Van de Graaff generator[80] have been noted in the literature. Feibush found that in the beta irradiation of acetylene by Kr-85, oxygen must be rigorously excluded in order for polymerization to occur.[81] Yashiro studied the gamma irradiation of acetylene under pressure of 5-10 kg./cm.^{2} from 10-150°, and obtained as the major product a yellow insoluble, infusible powder similar to cuprene.[82] A small amount of benzene was also detected. At low temperatures, Tabata observed in the gamma irradiation of acetylene that the rate of polymerization is proportional to the first power of dose rate and concluded that polymerization proceeds by an ionic mechanism.[83] Yanko irradiated eighteen acetylenes by Co-60 and found that the G value is between 10 to 200, indicative of a chain process.[84] Phenylacetylene was polymerized by gamma rays with a G value of 11.[85] Diphenylacetylene when subjected to compression by shock waves was reported to polymerize by a radical mechanism.[86] The yield, though small, depends on the reaction pressure and compression time. Other methods for the polymerization of diphenyldiacetylene and naphthylacetylene have not been found to date.

3. EXPERIMENTAL

3.1 Material

Diphenyldiacetylene (DPDA) was supplied by Farchan Research Laboratories. Diphenylacetylene (DPA) and phenylacetylene (PA) were supplied by Aldrich Chemical Company. 2-Acetonaphthone was supplied by Fisher Scientific Company.

Diphenyldiacetylene 50 g. was recrystallized in 750 ml. of reagent grade methanol twice. Large needle crystals, 45.1 g. was obtained, yield 90.2%, m.p. 86-87.5^o (uncorrected). Diphenylacetylene 27 g. was also crystallized in 160 ml. of methanol twice. Large plate crystals, 19.5 g. was obtained, yield 73.9%, m.p. 62-64.5^o (uncorrected). Phenylacetylene was purified by the procedure of Isfendiyaroglu.[87] Yellow phenylacetylene, 46.5 g. was distilled under vacuum with prepurified nitrogen (oxygen content $<$8 ppm.) bubbling. At 10 mm. Hg., the constant boiling fraction 44-50^o was collected, and dried over $CaCl_2$. A second distillation over $CaCl_2$ under vacuum gave 29 g. of colorless liquid, yield 62%, fraction of 50-58^o at 10 mm. Hg. This was stored under nitrogen at -15^o. 2-Acetonaphthone was used as received. Reagent grade benzene was dried over sodium metal chips, and redistilled over sodium under atmospheric pressure with protection from $CaCl_2$ tubes. Carbon tetrachloride and N,N'-dimethylformamide were spectrograde, and used without purification.

3.2 Polymerizations

3.2.1 Gamma Radiation Polymerization

A 100 ml. polymerization tube was cleansed in concentrated nitric acid and dried. To obtain an oxygen-free atmosphere in which monomers could be irradiated, a high vacuum system consisting of a 3-stage mercury diffusion pump was set up as shown in Figure 1. The system has been monitored during pump-down period to better than 10^{-6} mm. Hg. A McLeod gauge and a cold cathode gauge were used to determine the vacuum. The system was flushed with argon of analyzed purity (oxygen certified less than 1 ppm.) before the diffusion pump was turned on. The manifold allows degassing of the samples. The polymerization tube was evacuated for 10 minutes, stopcocked, and transferred into a polyethylene glove box which has been evacuated and flushed with argon gas. Diphenyldiacetylene, or diphenylacetylene, and solvent then were added, stopcocked and again connected to the high vacuum system. The mixture was degassed by freezing and thawing three times, evacuated at -78° for two hours and sealed under vacuum. The tube was irradiated at a dose rate of 0.102 - 0.035 Mrad/hr. to a total dose of 10-29 Mrads. The solvent was evaporated under vacuum, and the solids were dissolved in benzene. The benzene soluble but methanol insoluble fraction was taken as the polymer, and the molecular weight as well as the other physical properties were determined.

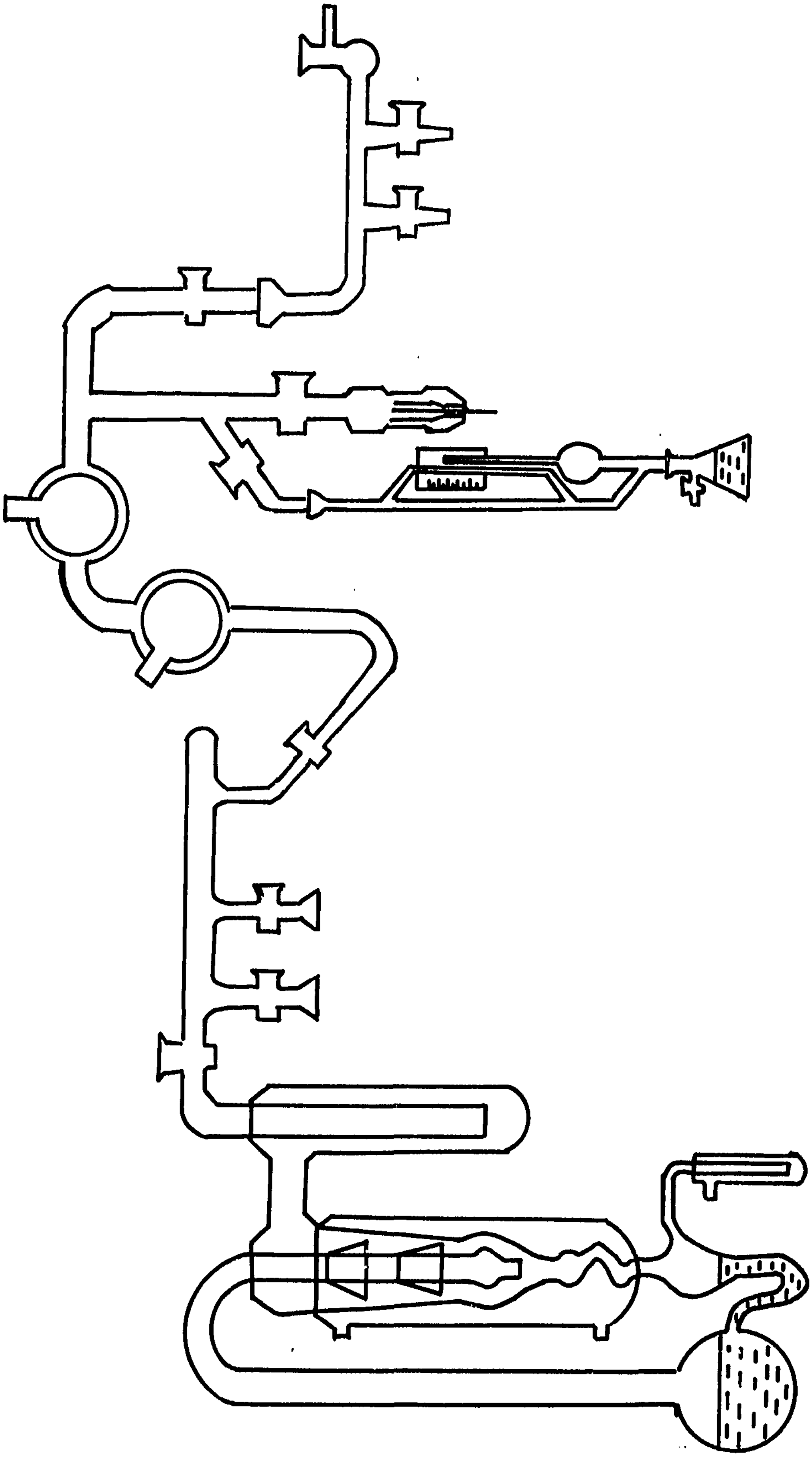


FIG. I THREE STAGE MERCURY DIFFUSION PUMP AND ACCESSORIES

3.2.2 Polymerization by Thermal or Peroxide Method

Into a 100 ml. polymerization tube, 1.4 g. of diphenyldiacetylene was introduced. Benzoyl peroxide (0.5% based on weight of monomer) was then added when necessary. Benzene, 1.5 ml. was pipetted into the polymerization tube which was then connected to the vacuum manifold. The system was flushed with prepurified nitrogen three times at -78°, subjected to three cycles of freezing and thawing, and finally evacuated for two hours at -78° before sealing under vacuum. The tube was submerged into a constant oil temperature bath, controlled to $\pm 0.5^{\circ}$ throughout the range of $120-140^{\circ}$. At the end of the polymerization period, the tube was cooled in running tap water and kept at -15°, otherwise it was at once broken open in the polyethylene glove box under nitrogen atmosphere. The content was poured into 150 ml. of methanol, filtered, redissolved in a minimum amount of benzene, and precipitated dropwise into 150 ml. of methanol. After filtering, the polymer was dried in a vacuum oven at 50° for 16 hours. It should be emphasized that throughout the experiment, all handling was under dry nitrogen atmosphere. The percent conversion was determined gravimetrically. When the percent conversion was plotted against reaction time, there was usually an induction period. The initial rate of polymerization was taken as the initial slope on the time-conversion curve. If the final product is all soluble in methanol, as with the monomer, it is assumed that no polymerization has taken place. In the study of the effect of concentration of the monomer on the rate of polymerization, the amount of benzene added is adjusted to the proper concentrations, other conditions being the same.

3.2.3 Polymerization by Ziegler-Type Catalyst

A 5-neck flask, fitted with a thermometer, a dropping funnel, a nitrogen capillary inlet, a rubber cap, and a condenser protected with a calcium chloride tube at the end, was subjected to a vacuum with stirring by a magnetic stirrer. The system was flamed with an oxygen burner to get rid of moisture for about 10 minutes. It was then let cool with nitrogen slowly bubbling through. Benzene, 30 ml. was quickly introduced, and nitrogen was allowed to bubble at least for one half-hour period before titanium tetrachloride was injected through the rubber cap by a gas-tight syringe. Aluminum trialkyl was next injected. This order was suggested by Kennedy rather than aluminum and then titanium.[88] The initial and final weights of the catalyst were determined by an analytical balance to the nearest milligram. Monomer, 2 g. dissolved in 20 ml. of benzene was added dropwise through the funnel, after which it was heated to reflux for 1 hour. Excess methanol was added, and the mixture was filtered through a sintered glass filter. HCl, 5% in methanol was used as the washing solution to remove any remaining catalyst. The solid was dissolved in benzene and precipitated twice in excess methanol. In diphenylacetylene, two fractions were found, one benzene soluble and one benzene insoluble. They were separated and the polymer was dried in a vacuum oven. For phenylacetylene, the isolation was done according to Berlin,[59] except under nitrogen environment in the present study. After monomer addition, the mixture was heated to reflux and cooled. Fifty ml. of 10% HCl in methanol was added, and the benzene layer was washed with deionized water three times to remove any chloride ion. The benzene layer was precipitated in methanol twice and the polymer was dried in the vacuum oven as usual and stored under nitrogen.

3.2.4 Synthesis of 2-Ethynylnaphthalene

The synthesis was done after Robin's procedure.[89] 2-Acetonaphthone was treated with phosphorus pentachloride and then dehydrohalogenated with potassium metal and alcohol. The monomer obtained this way was not pure. Infrared spectrum showed in addition to the expected $C \equiv C - H$ and $C \equiv C$ stretchings, an aliphatic $C - H$ stretching vibration at 2800 - 2950 $cm.^{-1}$ Elemental analysis was also in poor agreement with the calculated composition:

Anal. Calcd. for $C_{12}H_8$: C, 94.73; H, 5.26
Found: C, 80.36; H, 5.41

The procedure was modified. Potassium hydroxide and absolute ethanol were used for the dehydrohalogenation step. Both the infrared spectrum and the elemental analysis agree with the monomer structure, (see Section 4.1).

The Modified Procedure - Into a 3-neck flask fitted with a thermometer, a dropping funnel and a condenser, 94 g. of phosphorus pentachloride (0.45 mole) was introduced under a nitrogen atmosphere in a glove box. 2-Acetonaphthone (68 g., 0.40 mole) was dissolved in 100 ml. of benzene and added dropwise with magnetic stirring. The temperature was kept below 30° by occasional ice cooling. After addition was completed in about one hour, it was allowed to stand overnight. The mixture was vacuum distilled, collecting the fraction between 34-40° at 1 mm. Hg. Yellow solid, 52 g. was obtained, and 27 g. of this solid is added to 40.5 g. of potassium hydroxide in 154 ml. of absolute ethanol. The mixture was heated at 90° in an oil bath for 5 hours at the end of which 100 ml. of water was added, and the system was extracted with ether three times. The ether extract was dried over $CaCl_2$. After filtering, the ether was first distilled off, and the residue was vacuum distilled at 0.75 mm. Hg., collecting the fraction 80-96°. 2-Ethynylnaphthalene, 8.4 g. was obtained, yield 10.7%. It was vacuum distilled again just before use. Elemental analysis shows good agreement between the calculated and found values.

Anal. Calcd. for $C_{12}H_8$: C, 94.73; H, 5.26
Found: C, 94.46; H, 5.12

3.2.5 Preparation of Charge-Transfer Complexes

The procedure used is that of Higgins.[90] About 0.4 g. of the polymer (donor) was dissolved in 5 ml. of benzene in a 50-ml. flask fitted with a nitrogen capillary inlet and a condenser with $CaCl_2$ tube. Resublimated iodine crystals, 0.6 g. was then added. The mixture was gently heated at 55° for three hours with nitrogen bubbling. After the mixture was cooled, it was freeze-dried into fluffy solids. n-Hexane, 30 ml. was added to wash off the unreacted iodine crystals, followed by washing with methanol and n-hexane again until on the sintered glass filter, no yellow color appeared in the filtrate. The complex was dried in a vacuum oven at 40° for 16 hours and stored under nitrogen, protected from light by totally wrapping it in aluminum foil. When the acceptor was not iodine, as for example, antimony trichloride, niobiumpentachloride, etc., a saturated solution of the acceptor was used instead of pure crystals. The mixture was heated at 55° as above.

3.3 Measurements

3.3.1 Molecular Weight

The number average molecular weight was measured by cryoscopic method. A 2% solution of polymer in benzene was introduced into a test tube fitted with a Beckman thermometer and a stirring coil. The thermometer was graduated in 0.01 of a degree. The test tube was jacketed into a large tube as a means of insulation. The whole system was submerged into an ice-salt bath, the temperature of which was constant at -21°. The temperature was recorded as a function of time with stirring. The stopwatch was graduated in 0.01 of a second. A typical cooling curve is shown in Figure 2. The freezing point was read off by extrapolating to where the two curves intersect. The freezing point was also calculated by an Olivetti electronic desk computer with the least square program for a straight line, $y=ax+b$. The two curves give two equations which are solved simultaneously to get y the freezing temperature. Agreement between the graphical and the least square methods is very good. The difference in freezing point ΔT was obtained by subtraction and the molecular weight was calculated by the expression.

$$\mathrm{MW} = \frac{\text{Sample (g.)} \times 5100}{\text{Benzene (g.)} \times \Delta T\ (^{\circ}\mathrm{C.})}$$

Since T can be read to 0.01° and ΔT is of the magnitude of 0.1°, the molecular weight should be accurate to ±10%. Some molecular weight was measured osmometrically by Schwarzkopf Analytical Laboratory with a claimed accuracy of ±15%. In the molecular weight range dealt here, the agreement between these two methods was fair. For example, the cryoscopic molecular weight of a thermal polymer of diphenyldiacetylene was determined to be 913, whereas the

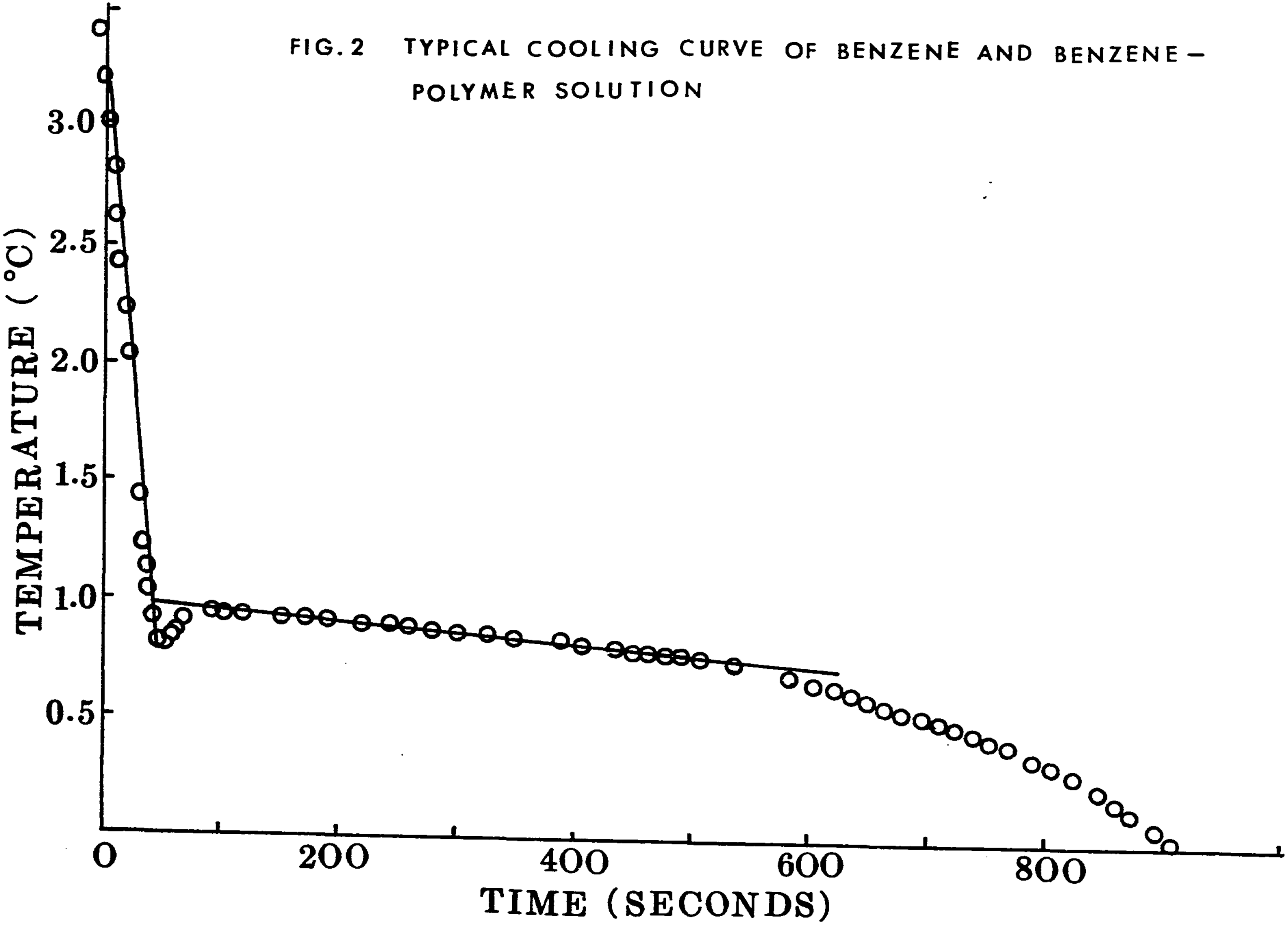


FIG. 2 TYPICAL COOLING CURVE OF BENZENE AND BENZENE — POLYMER SOLUTION

osmometric molecular weight of the same sample was determined to be 721. The lower figure of 913 is 822 and the higher figure of 721 is 829 so that the two values are within the experimental error. It seems then the osmometric molecular weight is lower than the cryoscopic molecular weight. The molecular weights reported in the following tables are indicated (OS) for osmometric and (CR) for cryoscopic.

3.3.2 Spectral Measurements

Infrared spectra were recorded either as a KBr pellet or in solution with a Perkin-Elmer IR 21 or Perkin-Elmer 700. Raman spectra were taken with a saturated solution of the sample in a capillary tube by Spec 1401 double beam spectrometer with a He-Ne laser, Spectra Physics Model 125. The spectrum was obtained by scanning the region of interest, from 2100 to 2300 cm.$^{-1}$ where the $C \equiv C$ bond stretches.

NMR spectra were recorded in carbon tetrachloride solution with a Varian 60 Mhz nuclear magnetic resonance spectrometer. A sample solution of 10-20% was made and was scanned with a sweep width of 1000 Hz. After being sure that nothing absorbs higher than 500 Hz, the normal NMR spectrum of 500 Hz sweep width was taken at room temperature. A sealed tube of tetramethylsilane was used as the external standard for $\tau = 10$ ppm.

Ultraviolet and visible spectra were taken with a Cary 14 spectrophotometer. The concentration had to be adjusted to fit the recorder scale by proper dilution, about 10^{-6} M.

Electron paramagnetic resonance (EPR) spectra were measured with a Varian V4502-15 spectrometer equipped with a Fieldial magnetic field regulator, operating in a high power mode. The three quantities measured are the position of the lines, the shape of the lines and the intensity of the lines.

The position of the line where the resonance occurs can be read off from the spectrum when it is compared to the resonance line of a standard which has been measured in an absolute way. In the present case, the strong pitch in potassium chloride as supplied by the Varian Associates was used as a standard (EPR sample 90445-01). The g value can then be calculated from the equation

$$h \nu = gBH$$

where h is Planck's constant, ν the resonance frequency, B the magnetic moment of the electron or the Bohr magneton, H the magnetic field where resonance occurs and g is the spectroscopic splitting factor or the Lande factor, a measure of the contribution of the spin and orbital motion of the electron to its total angular momentum. If g_s and H_s of the standard is known, the g_u value of the unknown sample can be calculated if H_u is known by the expression

$$g_u H_u = g_s H_s$$

The lines shapes are of two kinds, a Lorentzian or a Gaussian line. The line shape can provide many useful information but its measurement requires the line width also to be known. The line width ΔH is just the distance from the peak maximum to the peak minimum along the time or x axis. If a is one-half ΔH, then a Lorentzian and a Gaussian line[91] can be written as

$$f(x) = \frac{(8/3)a}{1 - \dfrac{x^2}{3a^2}} \qquad \text{(Lorentzian)}$$

$$f(x) = 1.65\, a\, e^{-x^2}/2a^2 \qquad \text{(Gaussian)}$$

The determination of the line shape of an experimental curve then involves drawing a baseline, finding a, and dividing the x axis in units of a, and comparing the values for a Lorentzian or Gaussian line in a table. This is illustrated in Figure 3 which shows the EPR curves of a polymer of phenylacetylene prepared by thermally heating at 130° and by Ziegler catalyst initiation. Comparison with Table 2 indicates that both lines are Gaussian in shape.

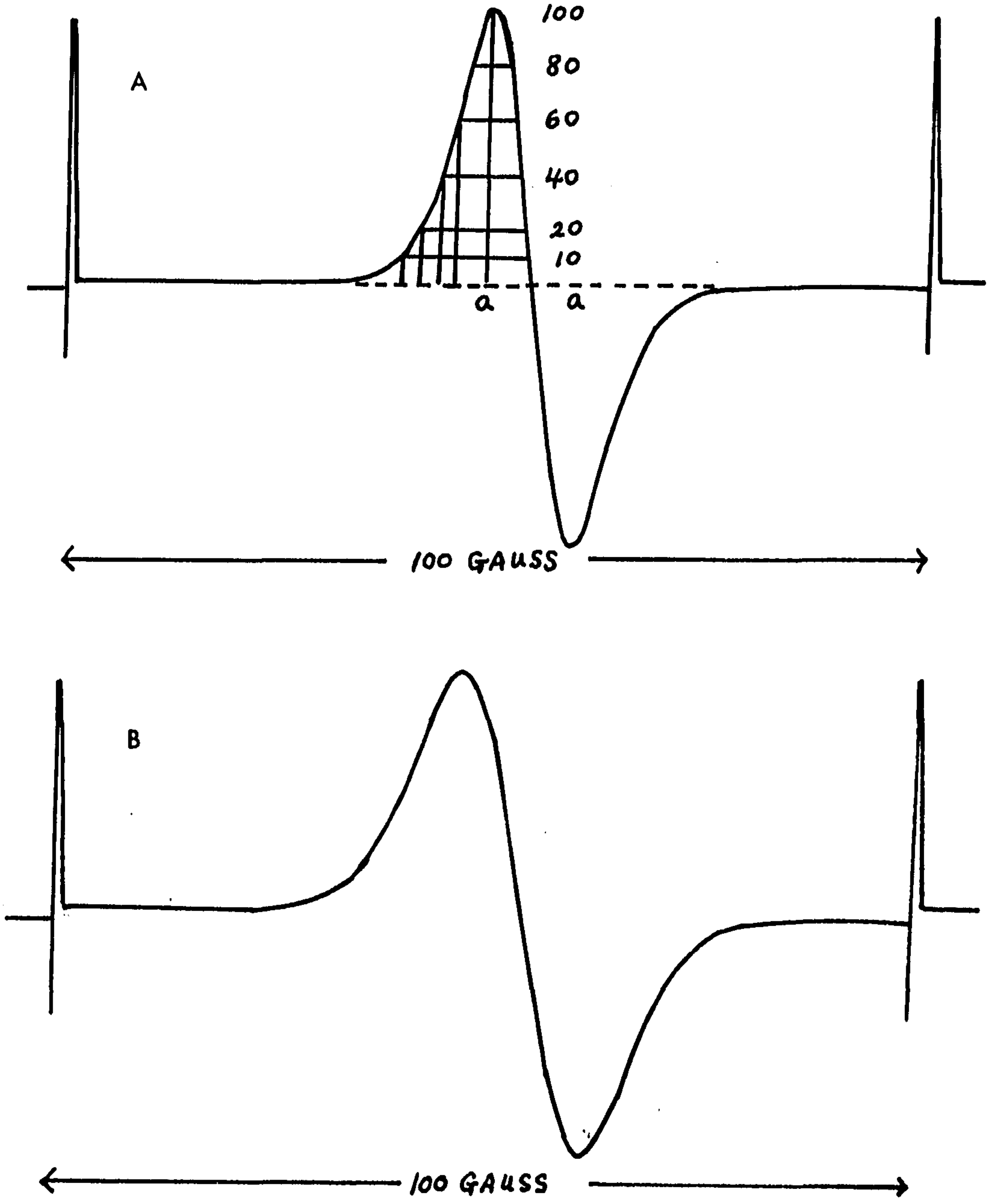


FIG.3 EPR SPECTRA OF POLYPHENYLACETYLENES
A. CATALYST
B. THERMAL

Table 2 Determination of Line Shapes by Comparison of Calculated Values

Height of Curve (% Maximum)	Lorentzian Position (a)	Gaussian Position (a)	Experimental 130° (a)	Experimental Catalyst (a)
100	1.00	1.0	1.0	1.0
80	1.65	1.5	1.5	1.5
60	2.10	1.8	1.8	1.8
40	2.75	2.1	2.2	2.2
20	3.80	2.5	2.6	2.5
10	5.00	2.8	3.0	3.1

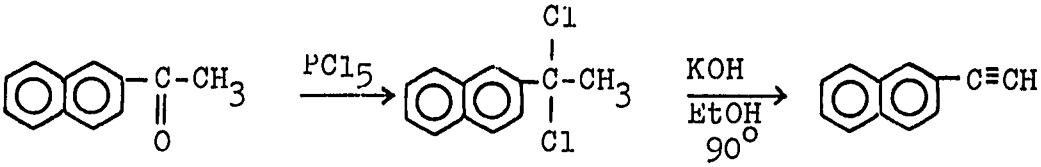
The most difficult job is to measure the absolute values of the integrated line intensities or the spin concentration of a sample. Here, we made use of the comparison method. Since the spin concentrations of the strong pitch in KCl has been determined by Varian to be 3×10^{15} spins per centimeter of sample tube, a comparison of the area under the curve affords the spin concentration of the unknown sample to be calculated provided that the line width and the spin concentration of the unknown are close to that of the standard. This method of comparing the area under the curve to calculate spin concentration is after that of Hatano.[92]

Differential thermal analysis was performed with a DuPont Differential Thermal Analyzer. One set of experiments involves introduction of the sample into a small flat-bottom glass tube, and sealed it in air. The other set involves introduction of the sample into a small aluminum cup which has a cover under nitrogen, transferring it to a hand press, and sealed. Fine glass beads were used as a reference. The thermogram was obtained under nitrogen atmosphere.

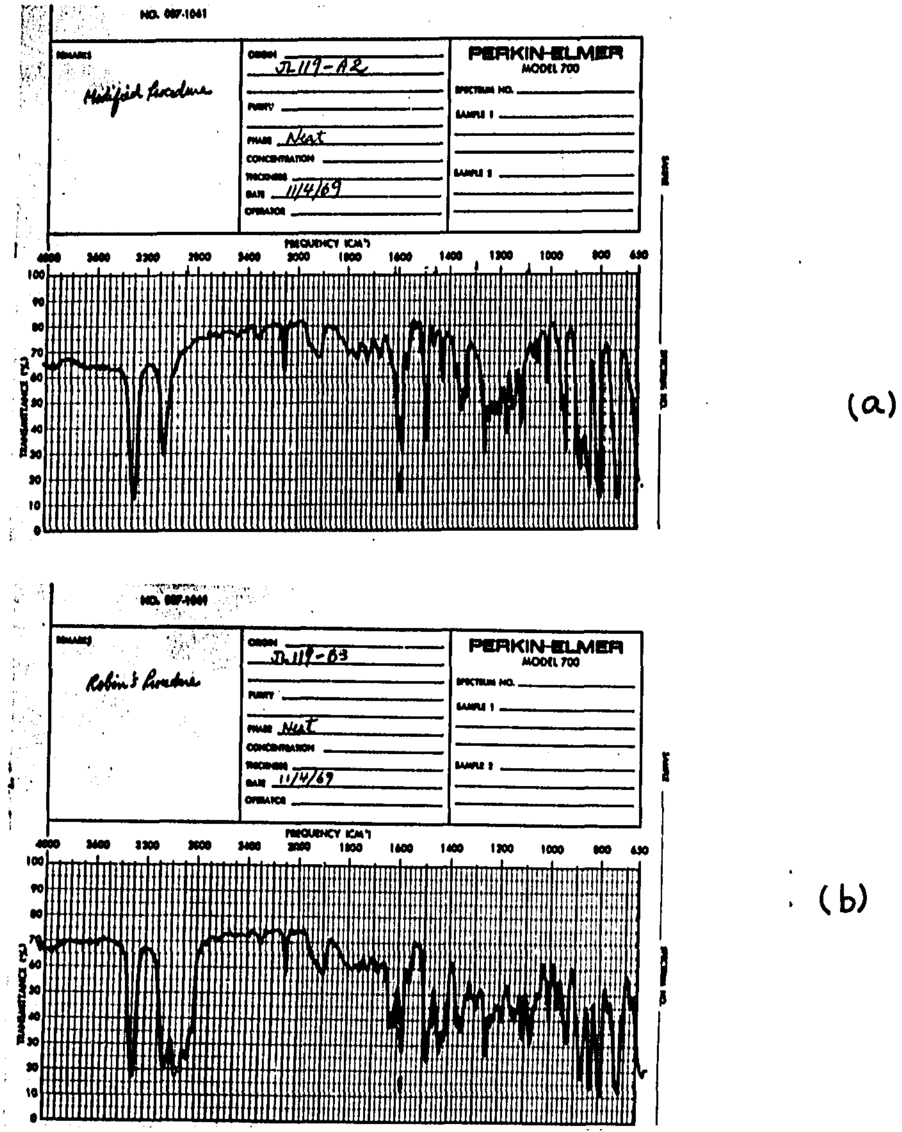
4. RESULTS AND DISCUSSION

4.1 Synthesis of Monomer, 2-Ethynylnaphthalene

The rationale for using a naphthylacetylene arises from the theoretical calculation that the naphthalene group may function as the polarizable side chain in Little's superconductor model.[93,94] As such, 2-ethynylnaphthalene was not commercially available. Its synthesis was first reported by Robin.[89] However, we found it necessary to modify the dehydrohalogenation procedure to get pure monomer. The synthesis involves reaction of 2-acetonaphthone with phosphorus pentachloride, then treating the chloro-derivative with potassium hydroxide in ethanol according to the equation.



The infrared spectra of 2-ethynylnaphthalene by (a) our modified procedure and by (b) Robin's method are given in Figure 4. In both cases, the appearance of the bands at 3300 and 2100 cm.$^{-1}$ indicates that the group C≡C-H is present. The disappearance of the 1680 cm.$^{-1}$ band due to the carbonyl group of the starting material indicates reaction has taken place. An obvious difference is the bands at 2860-2950 cm.$^{-1}$ in (b) suggesting aliphatic CH stretchings that should not be present in the pure monomer. The assignments are taken from a standard reference.[95]



NO. 007-1061

REMARKS Modified Procedure

ORIGIN JL119-A2

PURITY

PHASE Neat

CONCENTRATION

THICKNESS

DATE 11/4/69

OPERATOR

SPECTRUM NO.

SAMPLE 1

SAMPLE 2

NO. 007-1061

REMARKS Robin's Procedure

ORIGIN JL119-B3

PURITY

PHASE Neat

CONCENTRATION

THICKNESS

DATE 11/4/69

OPERATOR

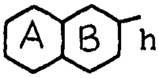
SPECTRUM NO.

SAMPLE 1

SAMPLE 2

FIG. 4 INFRARED SPECTRA OF 2-ETHYNYLNAPHTHALENE

3300 cm.$^{-1}$	≡C-H stretching
3050	aromatic C-H stretching
2100	C≡C stretching
200-1660	absorption of ortho and 1,2,4-trisubstituted phenyl
1600-1460	phenyl nucleus
1225-950	in plane bending of aromatic C-H
880	1 isolated H in phenyl out-of-plane bending
840,800	2 adjacent H
730	4 adjacent H

If 

has A,B, ring, there are 1 and 2 adjacent hydrogens in B ring and 4 adjacent hydrogens in the A ring. The major bands can be explained satisfactorily except the bands at 1360 and 1260 cm.$^{-1}$ which may be overtones of the 730-650 cm.$^{-1}$ bands. The NMR spectrum of the pure monomer has two absorptions, one broad peak centering around 2.6 τ corresponding to naphthyl protons and aromatic protons, and one small band at 7.1 τ corresponding to the terminal acetylenic protons.[96] As expected, there is no spin-spin splitting for the acetylenic proton, while it is very complex for the aromatic region, the splitting of which cannot be analyzed in a simple way. It is important the protons all fall into the chemical shifts expected, and other protons not consistent with the pure monomer are absent. Finally, the calculated composition,

Anal. Calcd. for $C_{12}H_8$: C, 94.73; H, 5.26

Found: C, 94.46; H, 5.12

agrees very well with the composition found by elemental analysis.

4.2 Polymerizations

In order to obtain polymers different from those reported in the literature, great care was exercised in preparing and isolating the polymers under inert and dry atmosphere for which the polyenes are known to be sensitive. The resultant polymers were also stored under nitrogen and protected from light by covering with aluminum foil. Three techniques of polymerization were evaluated. The Ziegler-type catalyst is known to give stereospecific vinyl polymers. Natta,[47] and Watson,[49] have described the Ziegler-type catalysts as effective for stereospecific polymerization of acetylene and its derivatives. The thermal polymerization should give polymer structures free from the contaminations by metallic catalysts and oxygen end groups from peroxides. Finally, polymerization by ionizing radiations could yield polymers also free from contaminations, and high-temperature side reactions since the irradiation can be done at low temperatures.

4.2.1 Polymerization of Diphenyldiacetylene

Polymerization of diphenyldiacetylene by the Ziegler-type catalyst under inert and dry atmosphere gave polymers consistently higher in molecular weight than those obtained by Teyssie.[74] Thermal polymerization in the absence of any catalyst is a second order reaction. From the kinetic dependence of the molecular weights on the monomer concentrations, it was concluded that mechanistically polymerization involves a bimolecular initiation step and a bimolecular termination step. Kinetic studies show that benzoyl peroxide added in the thermal polymerization does not function as an initiator. Gamma irradiation of diphenyldiacetylene gave only dimers at best.

a. Ziegler-Type Catalyst - Results of polymerizing diphenyldiacetylene by triisobutylaluminum-titanium tetrachloride are given in Table 3, and triethylaluminum-titanium tetrachloride in Table 4. As indicated in Table 3, the yield of the polymer depends on the molar ratio of the organometallic to the transition metal halide. Keeping the latter constant, and increasing the amount of the former, the polymer conversion increases up to a maximum and then falls off on further increase. Such an optimum ratio of organometallic to transition metal is quite characteristic of the Ziegler-type catalyst system,[97] which is related to the optimum number of active sites on the surfaces of the complex. This is shown in Figure 5. The optimum ratio is around 3.2. Up to this ratio, increasing the total concentration of the catalysts increases the yield of the polymer. In the triethylaluminum-$TiCl_4$ system, as shown in Table 4, the total volume of catalysts added is held constant. Changing the volume ratio and, hence, also changing the molar ratio of Al:Ti similarly brings about an optimum yield of polymer. The optimum ratio occurs around 2.5 from Figure 6.

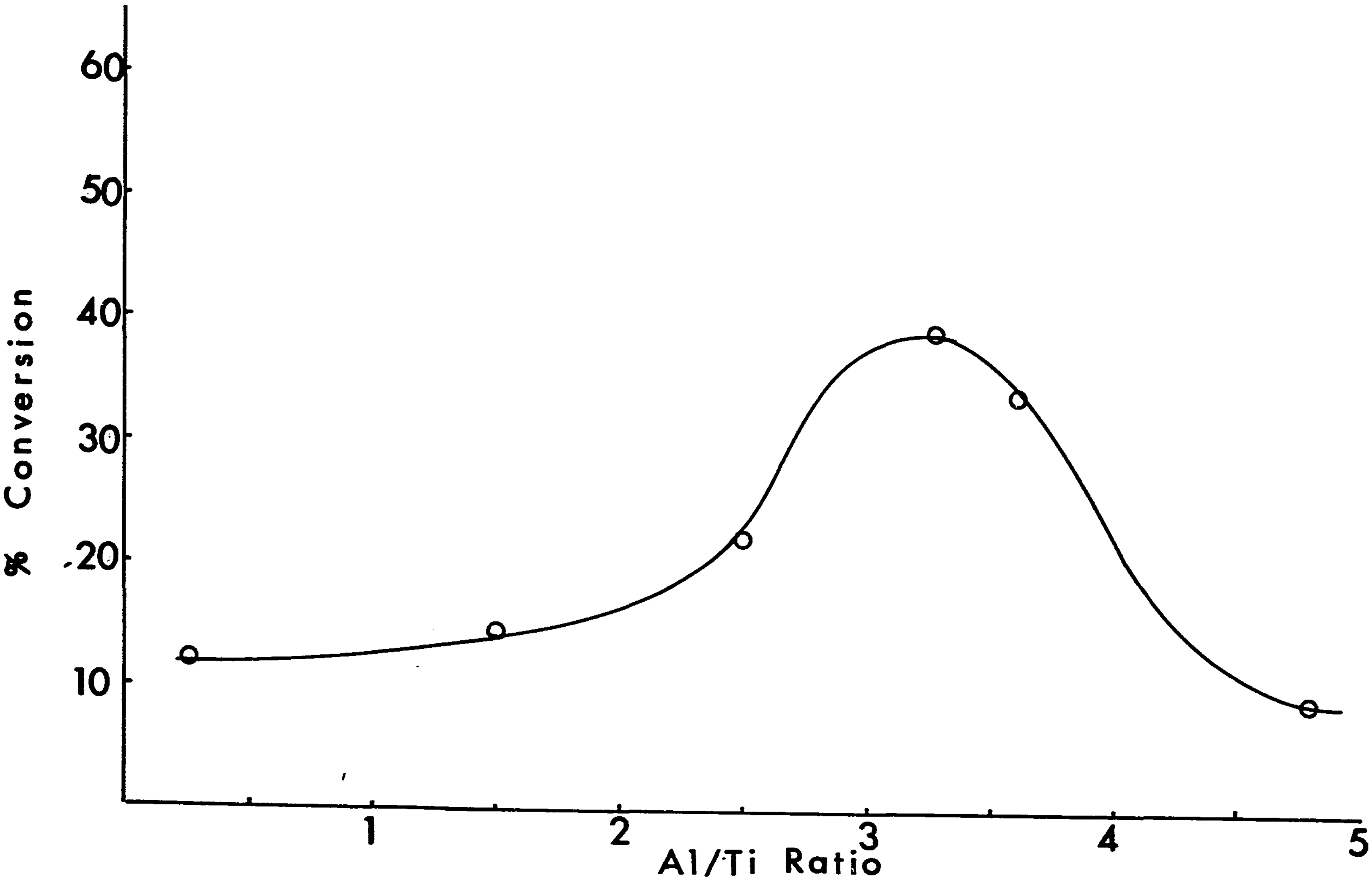
Table 3 Polymerization of Diphenyldiacetylene by $Al(i\text{-}Bu)_3$-$TiCl_4$

Expt. No.	Monomer (mole/l.)	$TiCl_4$ (mole/l.)	$Al(i\text{-}Bu)_3$ (mole/l.)	Molar Ratio (Al/Ti)	Reaction Temp. (°C.)	Polymer Yield (%)	$\overline{M}_n$(OS)
53	0.25	2.8×10^{-2}	7.0×10^{-3}	0.25	25° initial, then reflux	12.1	
61	0.25	2.4×10^{-2}	8.6×10^{-2}	3.6	" "	33.1	
116	0.25	2.8×10^{-2}	6.9×10^{-2}	2.5	" "	22.0	1627
136	0.25	2.8×10^{-2}	9.3×10^{-2}	3.3	" "	38.8	
138	0.25	2.4×10^{-2}	11.5×10^{-2}	4.8	" "	8.7	3067
141	0.25	2.5×10^{-2}	2.5×10^{-2}	1.0	" "	14.6	

Table 4 Polymerization of Diphenyldiacetylene by $AlEt_3$-$TiCl_4$. Initial Reaction Temperature 25°, then Reflux

Expt. No.	Monomer (mole/l.)	$TiCl_4$ (mole/l.)	$AlEt_3$ (mole/l.)	Molar Ratio (Al/Ti)	Volume Ratio (Al/Ti)	Polymer Yield (%)	$\overline{M}_n$ (CR)	Softening Temp. (°C.)
18-1b	0.10	2.8×10^{-2}	7.7×10^{-2}	2.83	3.0	42.3	-	280-290
18-2b	0.10	2.8×10^{-2}	7.7×10^{-2}	2.83	3.0	42.5	1255	280-290
18-3b	0.10	5.4×10^{-2}	5.1×10^{-2}	0.94	1.0	14.1	1454	270-290
18-4b	0.10	8.4×10^{-2}	2.6×10^{-2}	0.31	0.33	22.1	2000	285-300
18-5b	0.10	2.8×10^{-2}	7.7×10^{-2}	2.83	3.0	55.1	2278	270-280
18-6b	0.10	1.8×10^{-2}	8.5×10^{-2}	4.61	5.0	55.9	816	290-300
143	0.10	0.8×10^{-2}	7.9×10^{-2}	10.58	10.0	18.2	-	280-290

FIG. 5 INFLUENCE OF Al/Ti RATIO ON THE POLYMERIZATION OF DIPHENYLDIACETYLENE



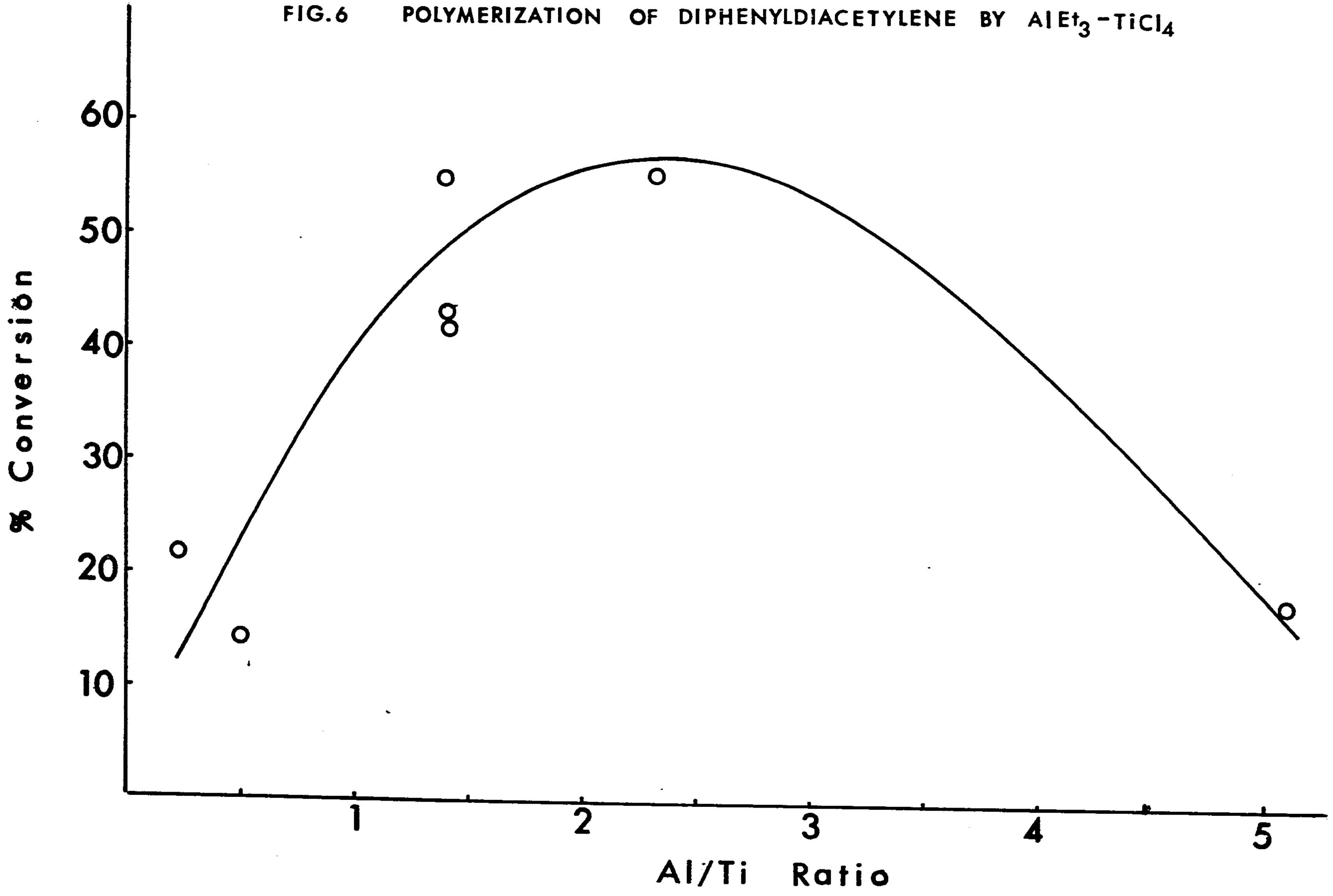
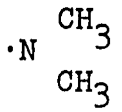


FIG.6 POLYMERIZATION OF DIPHENYLDIACETYLENE BY $AlEt_3-TiCl_4$

Teyssie,[74] who first studied the polymerization of diphenyldiacetylene, reported an optimum yield at a ratio of Al:Ti around 2.7. However, our polymers consistently show a higher molecular weight than his. For example, one of the highest number average molecular weight in our experiment is 3067, corresponding to a number average degree of polymerization ($\overline{DP}_n$) of 15. The highest number average molecular weight found by Teyssie was 1270, with a $\overline{DP}_n = 6$. The higher molecular weight of the polymer can be explained by the careful exclusion of oxygen and moisture, both during and after polymerization, the recovery and the storage under nitrogen. Duncan and Forbes have presented evidence that polyacetylenes degrade rapidly in oxygen and only by rigorously excluding oxygen during the polymerization and recovery of the polymer can oxidative degradation be avoided.[98]

b. Thermal Polymerization - In his paper about the first polymerization of diphenyldiacetylene, Teyssie reported that Ziegler type catalysts are the only catalysts active enough to polymerize diphenyldiacetylene, and radical type catalysts like azobisisobutyronitrile or anionic catalysts like biphenyl sodium did not polymerize diphenyldiacetylene. It has been shown in this study that diphenyldiacetylene can be polymerized by heat alone or by heat together with a radical catalyst like benzoyl peroxide. Because thermal polymers are free from catalyst contaminants, they are valuable in the study of their semiconducting properties or superconductor models. Preliminary experiments of polymerizing diphenyldiacetylene by only heat indicated it to be a possibility. Results of the experiments in N,N'-dimethylformamide (DMF) are listed in Table 5.

It seems that there is no thermal polymerization below 107°. Furthermore, it seems that the molecular weight decreases as the temperature increases, an effect usually observed in vinyl polymerization.[99] It is suspected that the solvent N,N'-dimethylformamide could decompose into  $\cdot N\begin{matrix}CH_3\\CH_3\end{matrix}$ or $CH_3\cdot$ radicals, but elemental analysis failed to show any nitrogen present in the polymer. On the other hand, there was no carbonyl absorption from infrared spectra. The only initiation must come from the monomer itself.

To avoid the complications of a solvent that may decompose, the rate of thermal polymerization of diphenyldiacetylene was done in benzene. Results are given in Table 6.

The percent polymer conversion increases as the time increases and levels off at long reaction time as clearly indicated at 140°. It also increases as the temperature of polymerization increases. The conversion-time relationship curves are shown in Figure 7. There is an induction period the length of which depends on the polymerization temperature. Increasing the temperature

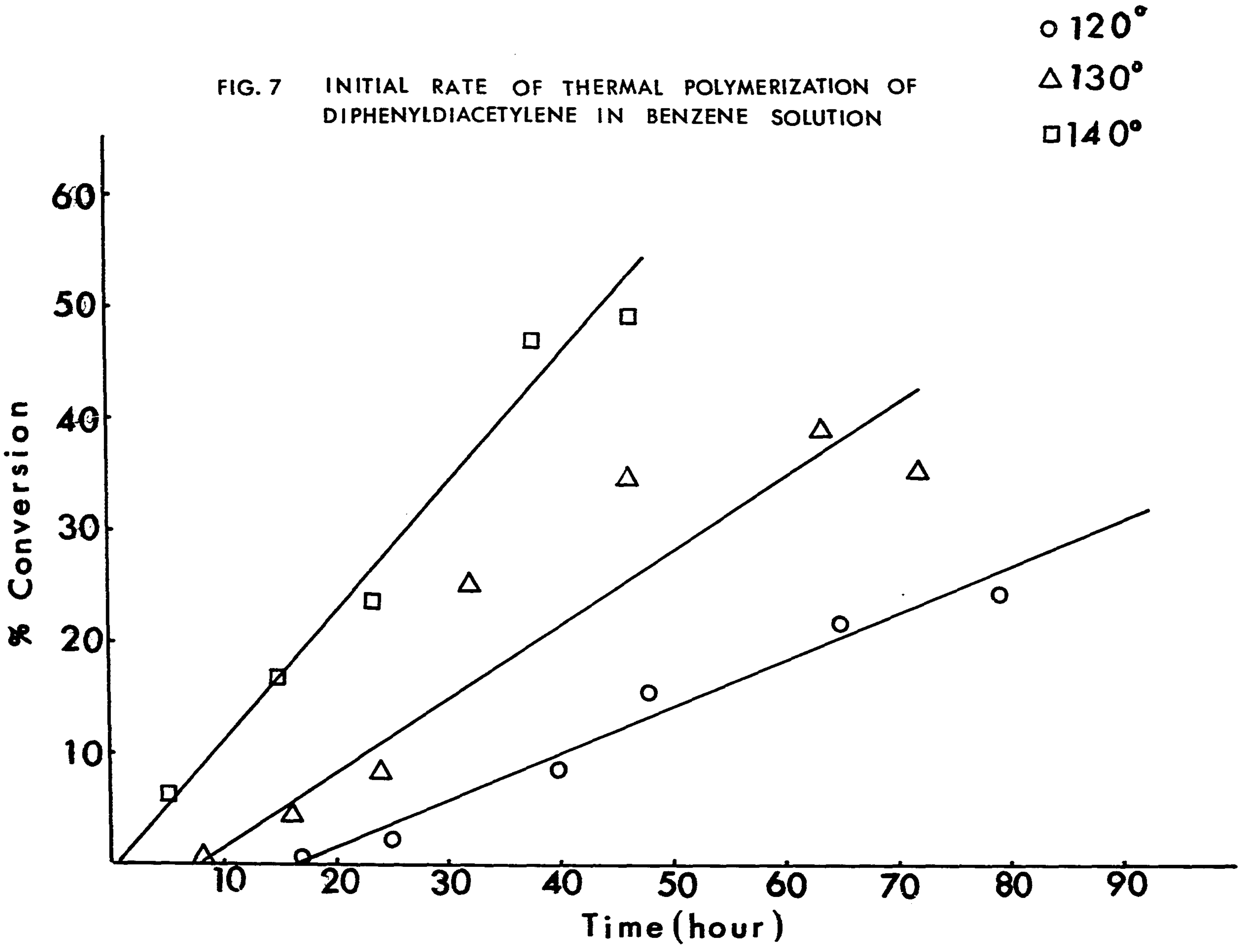
Table 5 Thermal Polymerization of Diphenyldiacetylene in N,N'-dimethylformamide

Expt. No.	Monomer (mole/l.)	Temperature (^{o}C.)	Reaction Time (hrs.)	Polymer Yield (%)	$\overline{M}_n$ (OS)	Percent Nitrogen in Polymer
46	9.85	80	94.5	0	-	-
20	9.85	100	8.5	0	-	-
48	9.85	107	123	0.92	1286	0
44	9.85	120	94.5	10.6	924	0
69	9.85	140	67.8	22.9	445	0
38	9.85	150	15.3	6.3	-	-

Table 6 Rate Studies of Thermal Polymerization of Diphenyldiacetylene in Benzene

Expt. No.	Temp. (°C.)	Monomer (mole/l.)	Reaction Time (hrs.)	Polymer Yield (%)	$\overline{M}_n$(OS)
97	120	4.62	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
137	130	4.62	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 (CR)
90	140	4.62	5.0	6.43	
			15.0	16.54	1410
			23.7	23.42	1240
			38.0	46.88	632
			46.5	48.84	1268
			89.2	60.74	1493
			117.0	60.64	

FIG. 7 INITIAL RATE OF THERMAL POLYMERIZATION OF DIPHENYLDIACETYLENE IN BENZENE SOLUTION



shortens the induction period. The initial part of the curves are linear so that the initial slope of the curve m gives the initial rate of polymerization V. The slope and the rate of polymerization, calculated by the least square method are given in Table 7.

Table 7 Initial Rate of Thermal Polymerization of Diphenyldiacetylene in Benzene

Temp. (°C.)	$^1/T$ (°K)	m Slope of Curve (%-hr.$^{-1}$)	V Rate of Polymerization (mole/l.-sec.)	Log V
120	2.55×10^{-3}	0.416	5.34×10^{-4}	-3.2715
130	2.48×10^{-3}	0.755	9.69×10^{-4}	-3.0137
140	2.42×10^{-3}	1.099	14.10×10^{-4}	-2.8508

The order of thermal polymerization at 140° was determined by varying the concentrations of diphenyldiacetylene according to the following equation.

$$\text{Rate of Polymerization} = V = k\,[\text{DPDA}]^{n}$$

Results are given in Table 8, where both the temperature and reaction time parameters were kept constant.

If we plot log $[M]$ versus log V, we should get a straight line with the slope equal to the order of reaction, and the intercept equal to reaction rate constant k. Such a plot is illustrated in Figure 8. The slope being 1.92 and the intercept 5.96×10^{-6}. The uncatalyzed thermal polymerization of diphenyldiacetylene then depends approximately on the second power of the monomer concentration. It is known that the thermal

Table 8 Studies on the Order of Reaction of Diphenyldiacetylene Thermal Polymerization

Temp. (°C.)	Time (hrs.)	Monomer [M] (mole/l.)	Polymer Conversion (%)	V Rate of Polymerization (mole/l.-sec.)	Log V	$\bar{M}_n$ (OS)
140	15	2.27	7.76	$3.26\text{x}10^{-5}$	-4.4867	1740
140	15	4.62	16.54	$14.15\text{x}10^{-5}$	-3.8483	1410
140	15	5.90	16.60	$18.14\text{x}10^{-5}$	-3.7414	1450
140	15	9.67	29.35	$52.48\text{x}10^{-5}$	-3.2800	1303

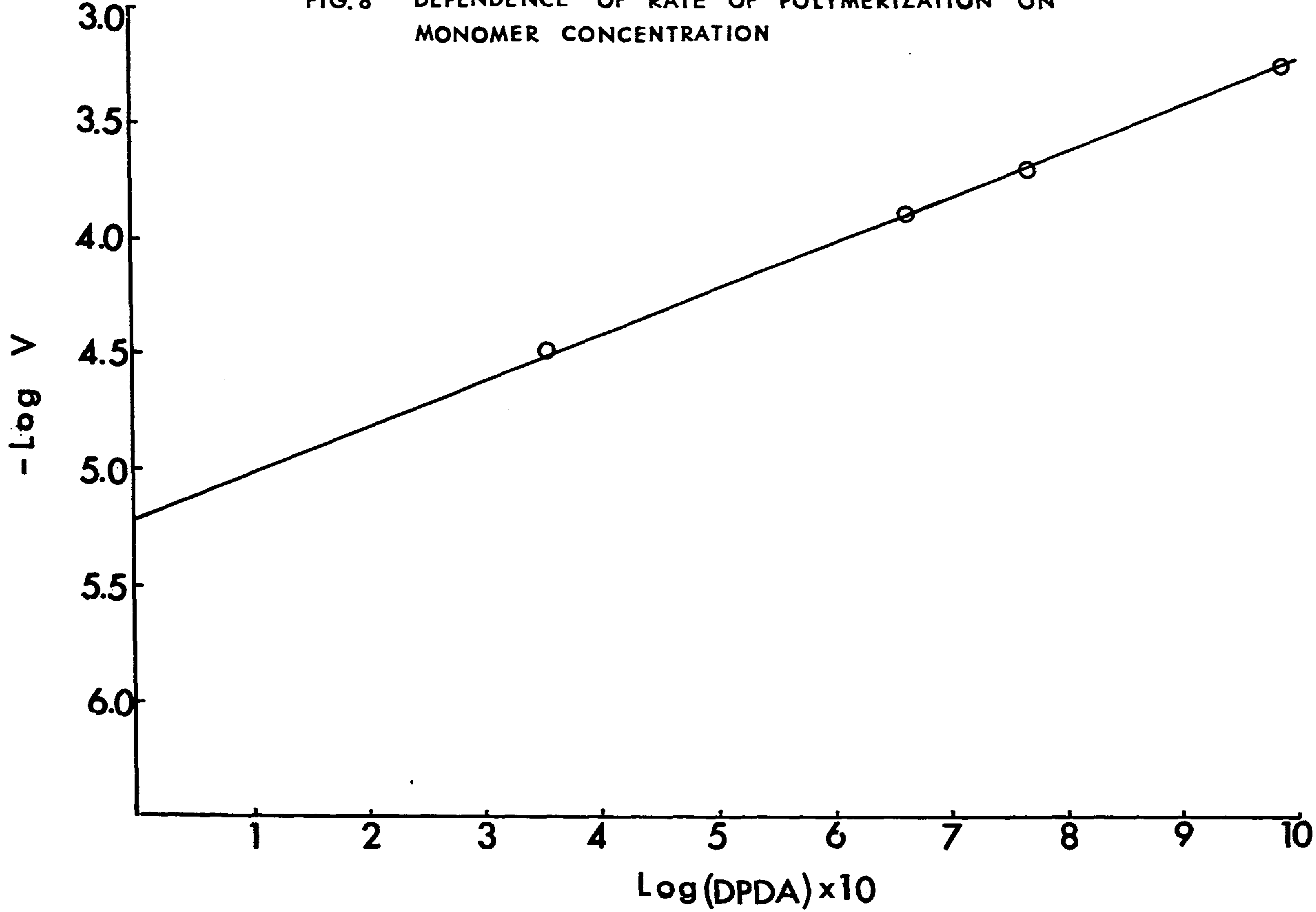


FIG. 8 DEPENDENCE OF RATE OF POLYMERIZATION ON MONOMER CONCENTRATION

polymerization of styrene was proportional to the second to third power of monomer concentration, but the mechanism is not yet clearly understood.[99] A kinetic analysis of the reaction mechanism of thermal polymerization of diphenyldiacetylene shows that the dependence of the rate of polymerization on the second power of monomer concentration is consistent with a bimolecular initiation and a bimolecular termination mechanism. The molecular weight of the polymer should be independent of monomer concentration. Flory has shown that in thermal polymerization, chain initiation cannot be first order in the absence of catalyst, but can be either second or third order.[100] For thermal polymerization involving a bimolecular initiation but unimolecular termination, the polymerization rate should depend on the third power of monomer concentration and the molecular weight depends on the first power of monomer. A termolecular initiation with bimolecular termination should give a rate dependence on the five-halves power of monomer concentration and the molecular weight depends inversely on the square root of monomer concentration. A termolecular initiation with a unimolecular termination should give a rate dependence on the fourth power of monomer, and the molecular weight depends on the first power of monomer (see Appendix). Since the rate of thermal polymerization of diphenyldiacetylene depends on the second power of monomer concentration and the molecular weight of the polymer appears to be independent of monomer concentration, we conclude that the polymerization involves a bimolecular initiation and bimolecular termination.

The apparent activation energy of the thermal polymerization of diphenyldiacetylene was obtained from the slope of a plot of the logarithm of the rate of polymerization V against $^1/T$. The plot is shown in Figure 9. The apparent activation energy is 6.4 Kcal/mole. The value is quite low as compared to that of styrene, 22.1 Kcal/mole, but low apparent activation energy has been reported in the literature. Flory has obtained an apparent activation energy for the thermal polymerization of methyl methacrylate of 10.3 Kcal/mole.[100]

c. Peroxide Catalysts - Preliminary results using various peroxides in different solvents for the polymerization of diphenyldiacetylene are listed in Table 9.

The three peroxides used have very different half-lives. From the half-life-temperature curve,[101] t-butyl hydroperoxide has a half-life of 1 hour, cumene hydroperoxide 55 hours, and benzoyl peroxide less than one minute at 140°. However, it seems a bit surprising that all three have approximately the same percent conversion. The molecular weight data suggested a dimer to tetramer. There seems to have been some solvent effect on the rate of polymerization. In a good solvent like toluene, the yield is 62.8%, while in a poor solvent like

FIG. 9 APPARENT ENERGY OF ACTIVATION FOR THE THERMAL POLYMERIZATION OF DIPHENYLDIACETYLENE

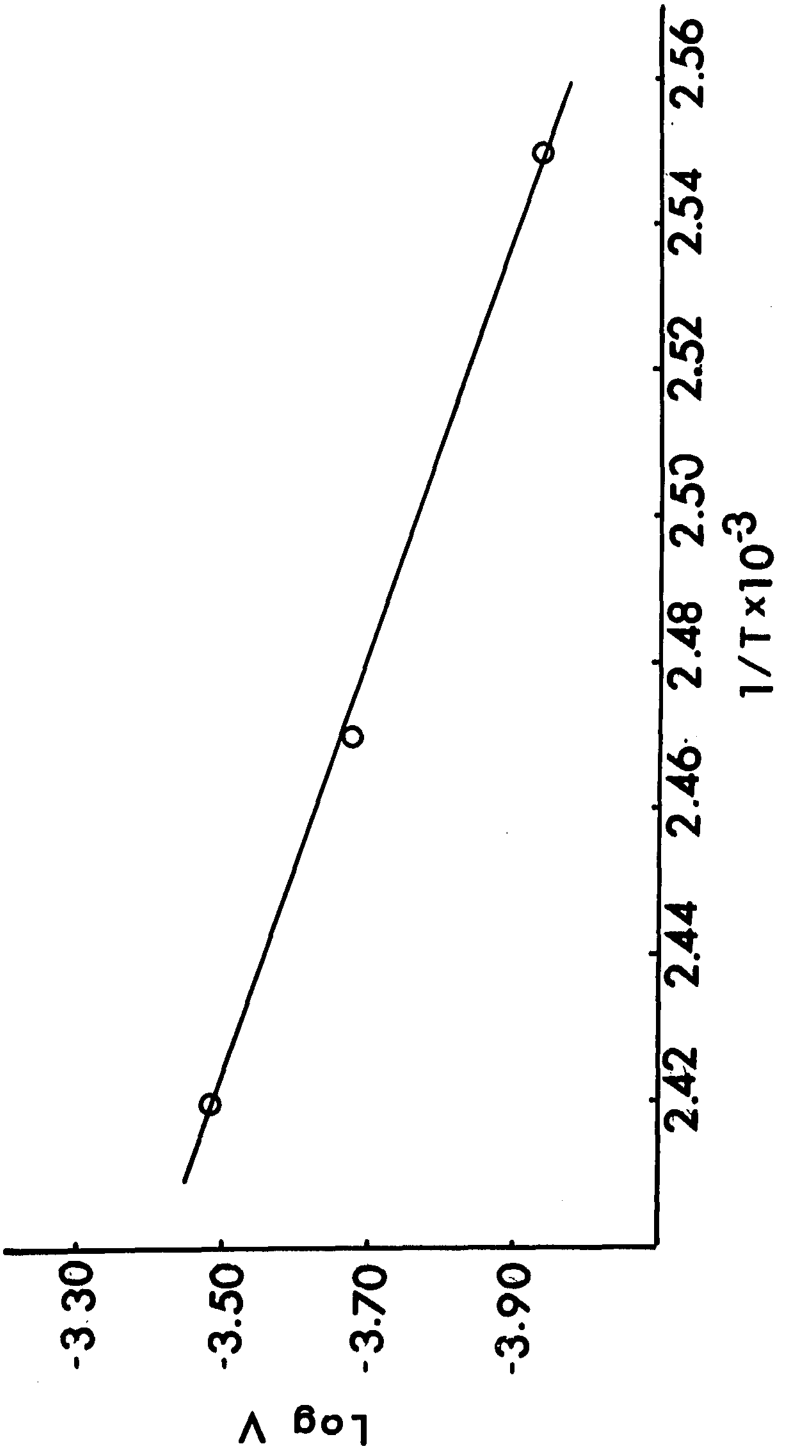


Table 9 Peroxide Initiated Polymerization of Diphenyldiacetylene at 140°

Solvent	Initiator	Initiator Conc. (mole/l.)	Monomer Conc. (mole/l.)	Time (hrs.)	Yield (%)	$\overline{M}_n$(CR)
Toluene	t-butyl hydroperoxide	0.35	4.62	50.2	59.1	600
Toluene	cumene hydroperoxide	0.28	4.62	50.2	59.2	573
Toluene	benzoyl peroxide	0.051	4.62	67.7	62.8	798
Methanol	benzoyl peroxide	0.047	4.62	67.7	25.3	
DMF	benzoyl peroxide	0.044	4.62	43.0	50.5	

methanol the yield is 25.3%. In a good solvent where the polymer is soluble, the chain radical can keep on propagating by added with the monomer whereas in a poor solvent, the chain radical precipitates out from the solution, and kept away from the monomer. N,N'-dimethylformamide seems also to be a good solvent.

Rate studies of the polymerization of diphenyldiacetylene were performed at three different temperatures with benzene as the solvent. Benzoyl peroxide, 0.5%, based on the weight of the monomer was used. Results are given in Table 10. The percent polymer conversion increases with time and temperature. Figure 10 shows such a relationship. Again, there is an induction period which is unexpected for benzoyl peroxide at this temperature. The curves are very similar to the curves of thermal polymerization. Such an induction period would suggest that perhaps thermal polymerization still predominates in spite of the added peroxide. The initial part of the curve is linear, the slope of which gives the initial rate of polymerization. The rates are given in Table 11 from which the apparent activation energy of polymerization is calculated. The Arrhenius plot is depicted in Figure 11. The apparent activation energy is 10.36 Kcal/mole, somewhat higher than that of uncatalyzed thermal polymerization.

Table 10 Rate Studies of Diphenyldiacetylene in Benzene with 0.5% Benzoyl Peroxide

Temp. (°C.)	Monomer (mole/l.)	Benzoyl Peroxide (mole/l.)	Reaction Time (hrs.)	Polymer Yield (%)	$\overline{M}_n$ (OS)
120	4.62	0.21	11.20	0	
	4.62	0.21	27.80	1.09	
	4.62	0.21	50.50	8.66	
	4.62	0.21	64.00	11.01	
	4.62	0.21	89.00	25.01	660
130	4.62	0.21	5.60	0	
	4.62	0.21	15.25	9.15	
	4.62	0.21	27.33	21.96	
	4.62	0.21	46.75	38.13	639.2
	4.62	0.21	70.75	47.92	808
140	4.62	0.21	1.00	0	
	4.62	0.21	2.00	0	
	4.62	0.21	4.00	0	
	4.62	0.21	7.75	1.18	
	4.62	0.21	13.00	9.07	
	4.62	0.21	16.00	22.41	
	4.62	0.21	21.33	14.54	1870
	4.62	0.21	26.45	35.27	
	4.62	0.21	32.00	47.22	

FIG. 10 POLYMERIZATION OF DIPHENYLDIACETYLENE WITH 0.5 % BENZOYL PEROXIDE IN BENZENE

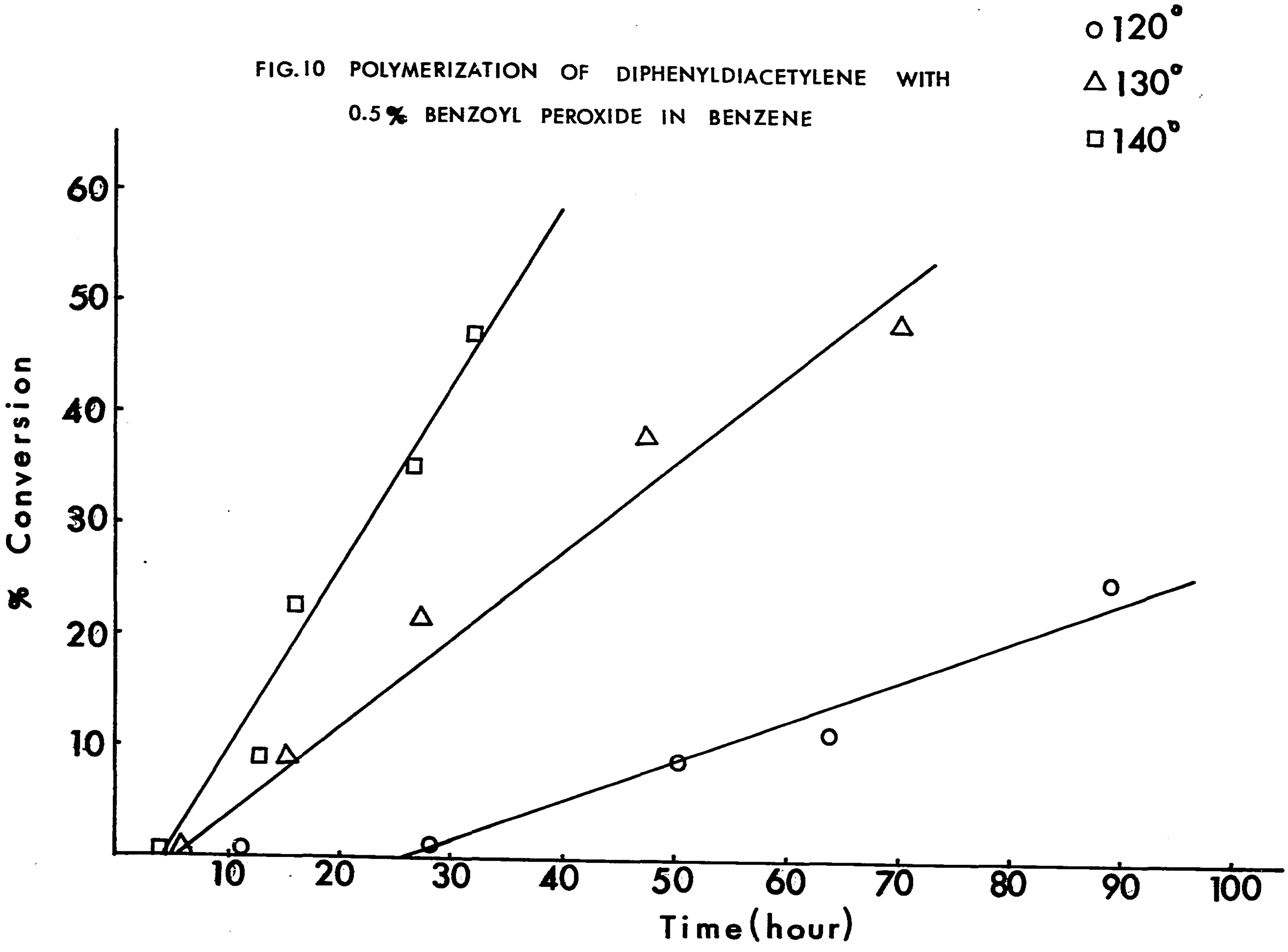


Table 11 Initial Rate of Polymerization of Diphenyldiacetylene in 0.5% Benzoyl Peroxide

Temp. (°C.)	1/T (°K)	m Slope of Curve (%-hr.$^{-1}$)	V Rate of Polymerization (mole/l.-sec.)	Log V
120	2.55×10^{-3}	0.382	4.90×10^{-4}	-3.3098
130	2.48×10^{-3}	0.932	11.9×10^{-4}	-2.9245
140	2.42×10^{-3}	1.800	23.1×10^{-4}	-2.6364

The kinetic order of the benzoyl peroxide initiated polymerization could not be determined with good accuracy; the points were quite scattered in the Log V versus Log M curve, and the slope which gives the order of the reaction is approximately 3.18 or third order. Definitely, the benzoyl peroxide was not functioning as a catalyst in the present system for which the rate would be expected to depend on the first power of the monomer concentration.

d. Gamma Radiation - Diphenyldiacetylene was irradiated in the crystalline state, in benzene solution, and in DMF solution which was frozen into a solid at -78°. Preliminary results are shown in Table 12. Both the melting point and molecular weight indicated the irradiated product to be a monomer or at most a dimer. This approach was not pursued further.

4.2.2 Polymerization of Diphenylacetylene

The same three techniques for the polymerization of diphenyldiacetylene were applied to diphenylacetylene.

FIG.11 ARRHENIUS PLOT OF DIPHENYLDIACETYLENE POLYMERIZATION IN 0.5% BENZOYL PEROXIDE

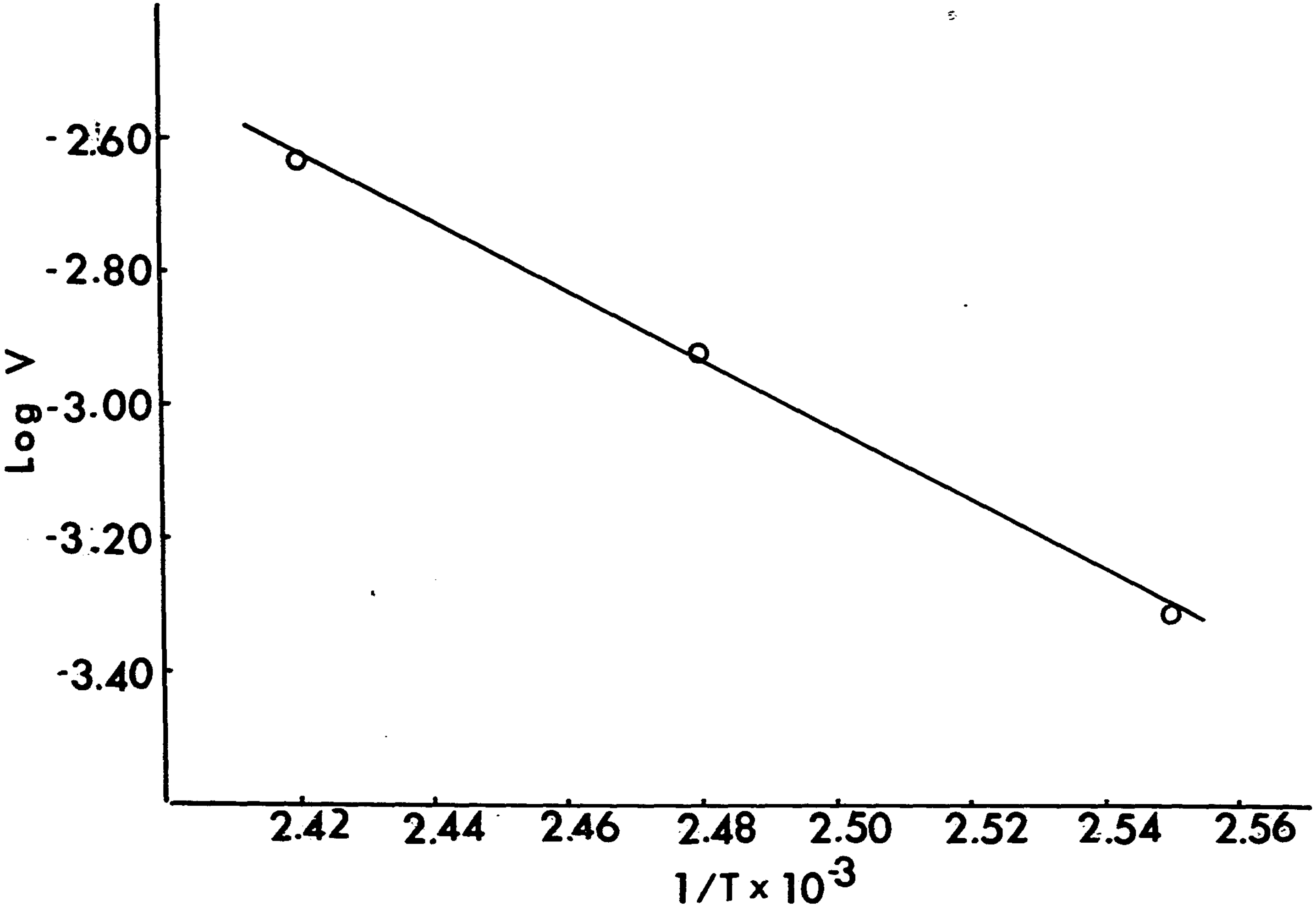


Table 12 Gamma Irradiation of Diphenyldiacetylene

Solvent	Monomer (mole/l.)	Radiation Temp. (°C.)	Dose Rate (Mrad/hr.)	Total Dose (Mrads)	Polymer Yield (%)	$\overline{M}_n$ (CR)	Melting Point (°C.)
Benzene	0.37	25	0.0148	4.44	53.0	225,336	87.5-89.5
DMF	4.95	-78	0.0148	1.79	MeOH soluble		86.0-88.0
None	-	25	0.0148	1.79	MeOH soluble		86.0-88.0

The results are quite different. In spite of preparing and isolating the polymer under carefully dry and inert atmosphere, the polymers obtained by Ziegler type catalyst give a high melting and colorless product, the infrared spectrum of which was identical to that of hexaphenylbenzene. The polymerization was then cyclotrimerization. There was no thermal or peroxide initiated polymerization of diphenylacetylene. Gamma irradiation gave only a dimer in very low yield.

a. Ziegler-Type Catalyst - Results of polymerizing diphenylacetylene by triethylaluminum-$TiCl_4$ in benzene are given in Table 13. From Figure 12, it can be seen that there is an optimum Al:Ti ratio that gives a maximum yield of product which consists of two fractions, one benzene soluble fraction and one benzene insoluble fraction. Molecular weight measurement on the soluble fraction roughly indicates them to be a trimer to pentamer. They all have very high melting points. As compared to polydiphenyldiacetylene, the polydiphenylacetylene has a lower molecular weight, higher melting point and absence of color, a fact together with infrared spectra suggests it to be a cyclic compound.

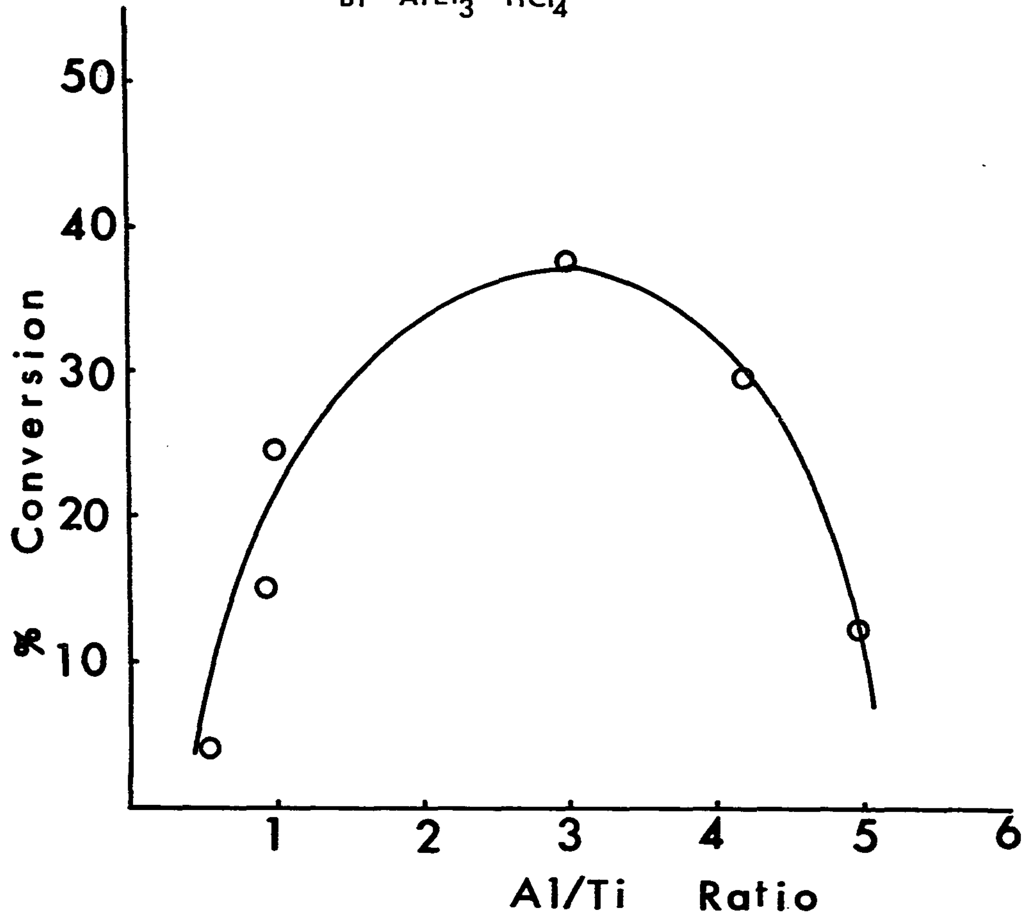
b. Thermal and Peroxide Initiation - In contrast to diphenyldiacetylene, diphenylacetylene did not give any polymer under the same conditions for both uncatalyzed thermal and peroxide initiated polymerizations. The resulting product is always soluble in methanol, and

Table 13 Polymerization of Diphenylacetylene by Ziegler-Type Catalyst, $AlEt_3$-$TiCl_4$. Initial Temperature 25°, then Reflux

Expt. No.	Monomer (mole/l.)	$TiCl_4$ (mole/l.)	$AlEt_3$ (mole/l.)	Volume Ratio (Al/Ti)	Molar Ratio (Al/Ti)	Polymer Yield (%)	$\overline{M}_n$ (CR)	Softening Temp. (°C.)
18-1a	0.23	$9.0x10^{-2}$	$8.6x10^{-2}$	1	0.96	22.0		>450
						2.6*	597	>450
18-2a	0.23	$7.2x10^{-2}$	$6.9x10^{-2}$	1	0.96	13.3		>450
						1.7*	466	>450
18-3a	0.23	$6.3x10^{-2}$	$3.6x10^{-2}$	0.5	0.56	3.6*	-	>450
18-4a	0.23	$2.7x10^{-2}$	$11.4x10^{-2}$	4.3	4.19	26.6		>450
						3.0*	-	>450
18-5a	0.23	$3.6x10^{-2}$	$11.0x10^{-2}$	3.2	3.03	34.2		>450
						3.3*	859	>450
122	0.17	$0.9x10^{-2}$	$4.5x10^{-2}$	9.0	4.91	10.9		>450
						1.3*	-	>450

*Benzene-soluble fraction

FIG.12 POLYMERIZATION OF DIPHENYLACETYLENE BY $AlEt_3-TiCl_4$



colorless. Melting point and spectra identify it to be the monomer.

c. Gamma Radiation - Diphenylacetylene was irradiated in the crystalline state, in benzene solution and in frozen benzene solution at -78°. Results are shown in Table 14. Gamma radiation of diphenylacetylene gave very little product less than 0.2% of methanol insoluble fraction, the molecular weight of which is a dimer. Both the melting point and ultraviolet spectra are similar to that of the diphenylacetylene monomer. In this respect, the gamma radiation behavior of diphenylacetylene closely resembles the ultraviolet counterpart. Buchi has found dimerization occurring upon UV irradiation of diphenylacetylene in low yield.[102]

4.2.3 Polymerization of Phenylacetylene

Polymerizations of phenylacetylene were carried out by Ziegler catalyst and thermal methods. Polymer yield obtained with the Ziegler catalyst was comparatively lower than diphenyldiacetylene and diphenylacetylene, and with the increase of Al:Ti ratio, a red insoluble fraction appears. No insoluble fraction was observed in thermal polymerization. The thermally initiated polyphenylacetylene has a higher degree of polymerization than the other acetylenic polymers, having a degree of polymerization of 27. This can be explained by the free valence index (Section 4.3.1) calculated from the bond order and steric effect since phenylacetylene has a larger free

Table 14 Gamma Radiation of Diphenylacetylene

Solvent	Monomer (mole/l.)	Temp. (°C.)	Dose Rate (Mrad/hr.)	Total Dose (Mrads)	Product Yield (%)	$\overline{M}_n$ (CR)	Melting Point (°C.)
Benzene	0.50	25	0.0175	5.23	0.2	-	-
Benzene	0.62	25	0.0363	10.31	trace	356	-
None	-	25	0.0213	8.95	0.1	356	-
Benzene	0.62	-78	0.0136	5.73	trace	-	-
Benzene	0.71	25	0.102	29.2	"	-	57-59
Heptane	0.62	25	0.102	29.2	"	-	55-59
Heptane	0.62	25	0.036	10.3	"	-	58-59

valence, and is less crowded sterically.

a. Ziegler-Type Catalyst - Results of polymerizing phenylacetylene are given in Table 15. Again, the trend of having an optimum Al:Ti ratio in the percent polymer conversion-catalyst composition curve is evident in Figure 13. The maximum yield is only 21.1% at a ratio of Al:Ti = 1.7.

However, it was observed that increasing the Al:Ti ratio beyond its optimum range causes a red insoluble fraction to appear in the product, and the yield of polymer decreases. We were unable to verify the results of Berlin,[59] even under our strictly inert conditions, who reports that the optimum Al:Ti ratio of one, the polymer yield was 96.3% with a molecular weight of 5000. This was one of the highest molecular weights so far obtained for arylacetylenes. Most published values are much lower,[103] about 280-1000 for phenylacetylene.[60]

b. Thermal Polymerization - Results of thermal polymerization of phenylacetylene in benzene are given in Table 16 and are illustrated in Figure 14. There is an induction period which varies with the temperature of polymerization. The higher the temperature, the shorter is the induction period. The percent of polymer conversion increases linearly with time up to 80 hours, and also increases with temperature. The initial slope of the curves calculated by the least square method is given in Table 17 from which the apparent energy of activation of

Table 15 Polymerization of Phenylacetylene by $Al(i\text{-}Bu)_3\text{-}TiCl_4$.
Initial Temperature 25°, then Reflux

Expt. No.	Monomer (mole/l.)	$TiCl_4$ (mole/l.)	$Al(i\text{-}Bu)_3$ (mole/l.)	Molar Ratio (Al/Ti)	Polymer Yield (%)	$\overline{M}_n$ (OS)
42	0.975	$1.8x10^{-2}$	$3.1x10^{-2}$	1.7	21.1	622
50	0.975	$1.7x10^{-2}$	$2.4x10^{-2}$	1.4	17.4	
117	0.975	$1.7x10^{-2}$	$1.4x10^{-2}$	0.82	7.60	1507
139	0.975	$1.5x10^{-2}$	$5.2x10^{-2}$	3.5	14.29 1.51*	1770
140	0.975	$1.7x10^{-2}$	$8.9x10^{-2}$	5.2	11.94 9.84*	

* Benzene-insoluble fraction

FIG.13 POLYMERIZATION OF PHENYLACETYLENE BY $Al(i\text{-}Bu)_3\text{-}TiCl_4$

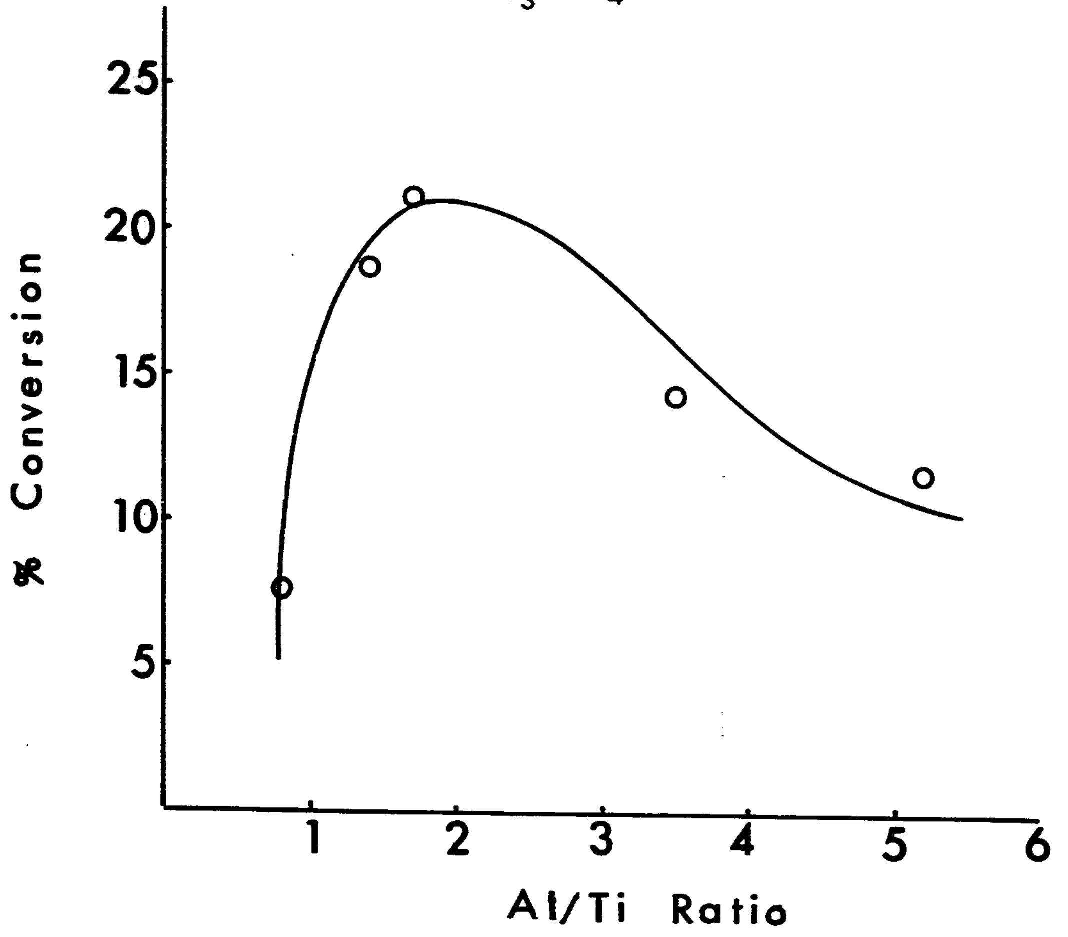


Table 16 Thermal Polymerization of Phenylacetylene

Expt. No.	Temperature (°C.)	Monomer (mole/l.)	Reaction Time (hrs.)	Polymer Yield (%)	$\bar{M}_n$ (OS)
99	120	2.75	20.00	0.60	
	120	2.75	40.00	1.79	1860
	120	2.75	55.00	2.49	
	120	2.75	64.55	4.09	
	120	2.75	89.00	7.86	
103	130	2.75	10.50	0	
	130	2.75	25.00	5.89	
	130	2.75	37.50	5.03	
	130	2.75	50.50	11.66	
	130	2.75	72.00	15.20	1080
	130	2.75	85.50	16.21	
107	140	2.75	10.00	2.01	
	140	2.75	30.00	13.04	2747
	140	2.75	50.00	25.48	
	140	2.75	81.00	41.84	

Table 17 Initial Rates of Thermal Polymerization of Phenylacetylene

Temperature (°C.)	1/T (°K)	m Slope of Curve (%-hr.$^{-1}$)	V Rate of Polymerization (mole/l.-sec.)	Log V
120	2.55×10^{-3}	0.0724	5.53×10^{-5}	-4.2573
130	2.48×10^{-3}	0.211	1.61×10^{-4}	-3.7927
140	2.42×10^{-3}	0.521	3.98×10^{-4}	-3.4001

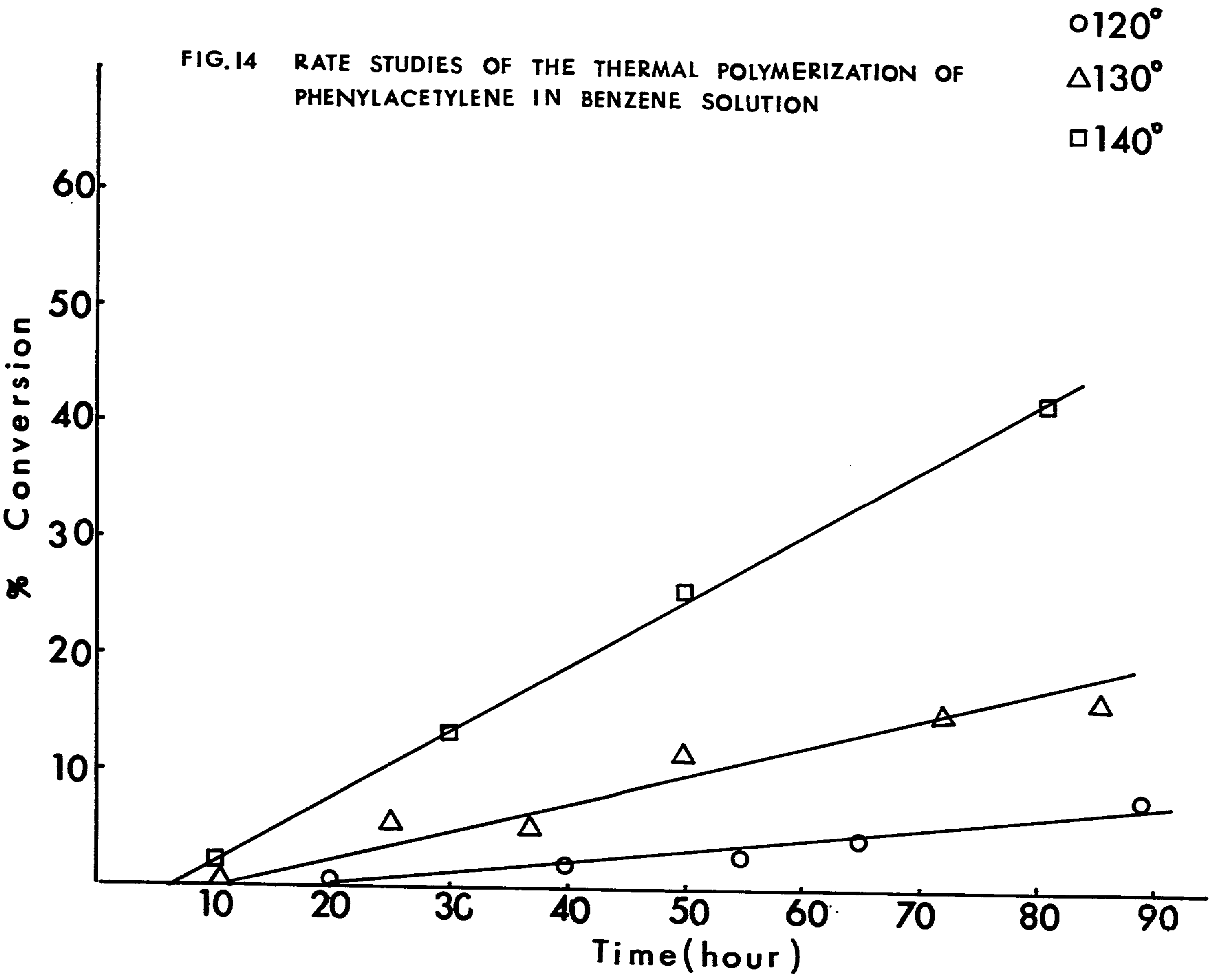


FIG.14 RATE STUDIES OF THE THERMAL POLYMERIZATION OF PHENYLACETYLENE IN BENZENE SOLUTION

the thermal polymerization of phenylacetylene is calculated to be 13.09 Kcal/mole. The Arrhenius plot is depicted in Figure 15.

4.2.4 Polymerization of 2-Ethynylnaphthalene

Polymerization of 2-ethynylnaphthalene was carried out with Ziegler-type catalyst. Results are listed in Table 18. This is the first reported polymerization of the monomer 2-ethynylnaphthalene in the literature. Under our experimental conditions to exclude air, oxygen, moisture, the yield of the new polymer depends on the molar ratio of the organometallic to the transition metal halide. The maximum yield, 44.1% was obtained with an Al:Ti ratio of 2.8. The conversion-catalyst composition curve is given in Figure 16. Also shown are the number average molecular weight determined osmometrically. Coincidentally, the molecular weight appears to depend on the catalyst composition. The highest molecular weight, 2091 happens to occur at a catalyst ratio where the polymer yield was a maximum. Decreasing the Al:Ti ratio to 0.9 gave only 4.9% polymer the molecular weight of which was only 495. Increasing the ratio to 4.9 reduces the polymer yield to 31.0% the molecular weight of which was intermediate, 1050. The color of the polymer ranges from red to brown.

Summary: Diphenyldiacetylene was polymerized by Ziegler-type catalyst. With careful control of air, oxygen and moisture during polymerization and after

FIG.15 ARRHENIUS PLOT OF THERMAL POLYMERIZATION OF PHENYLACETYLENE IN BENZENE

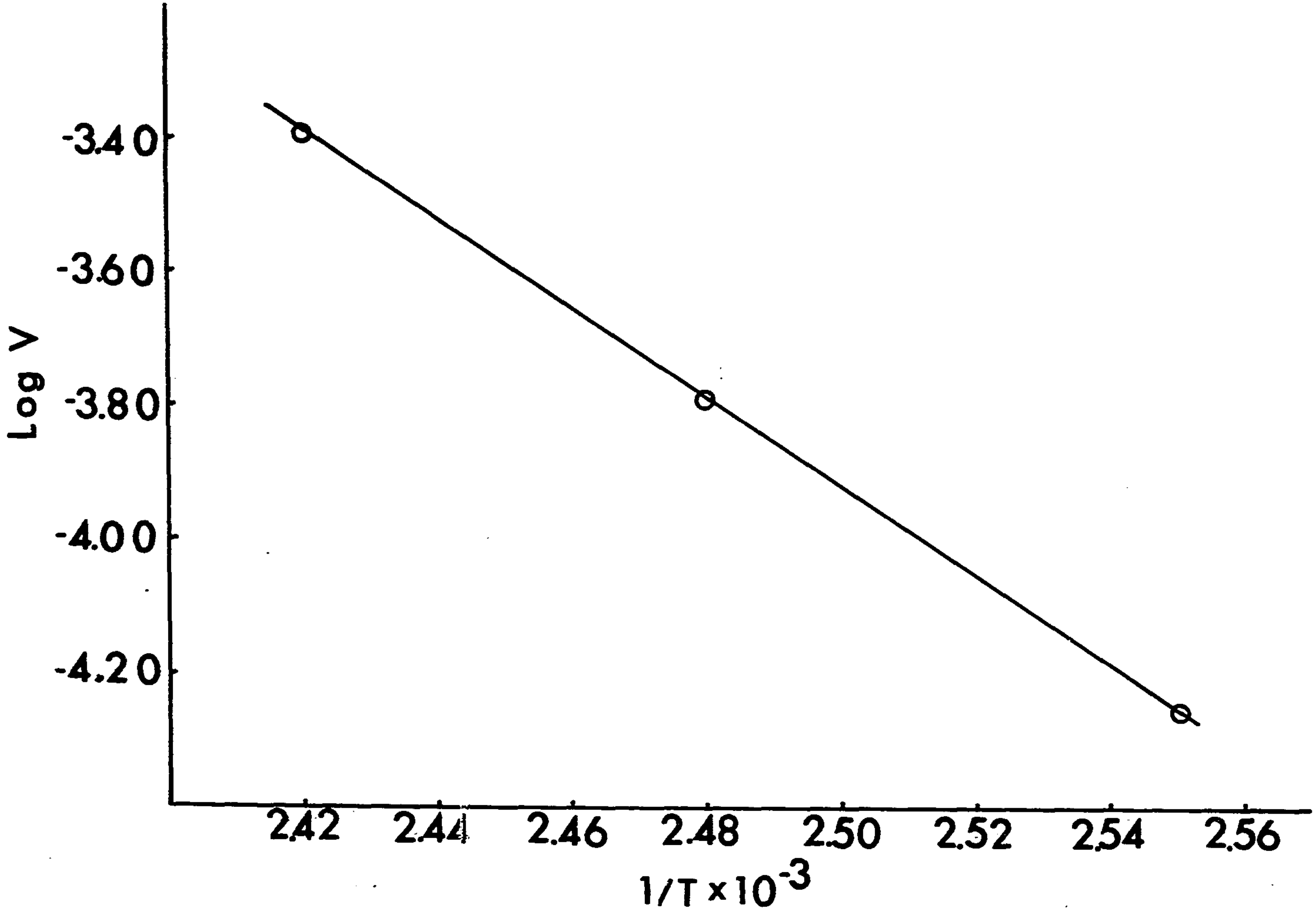
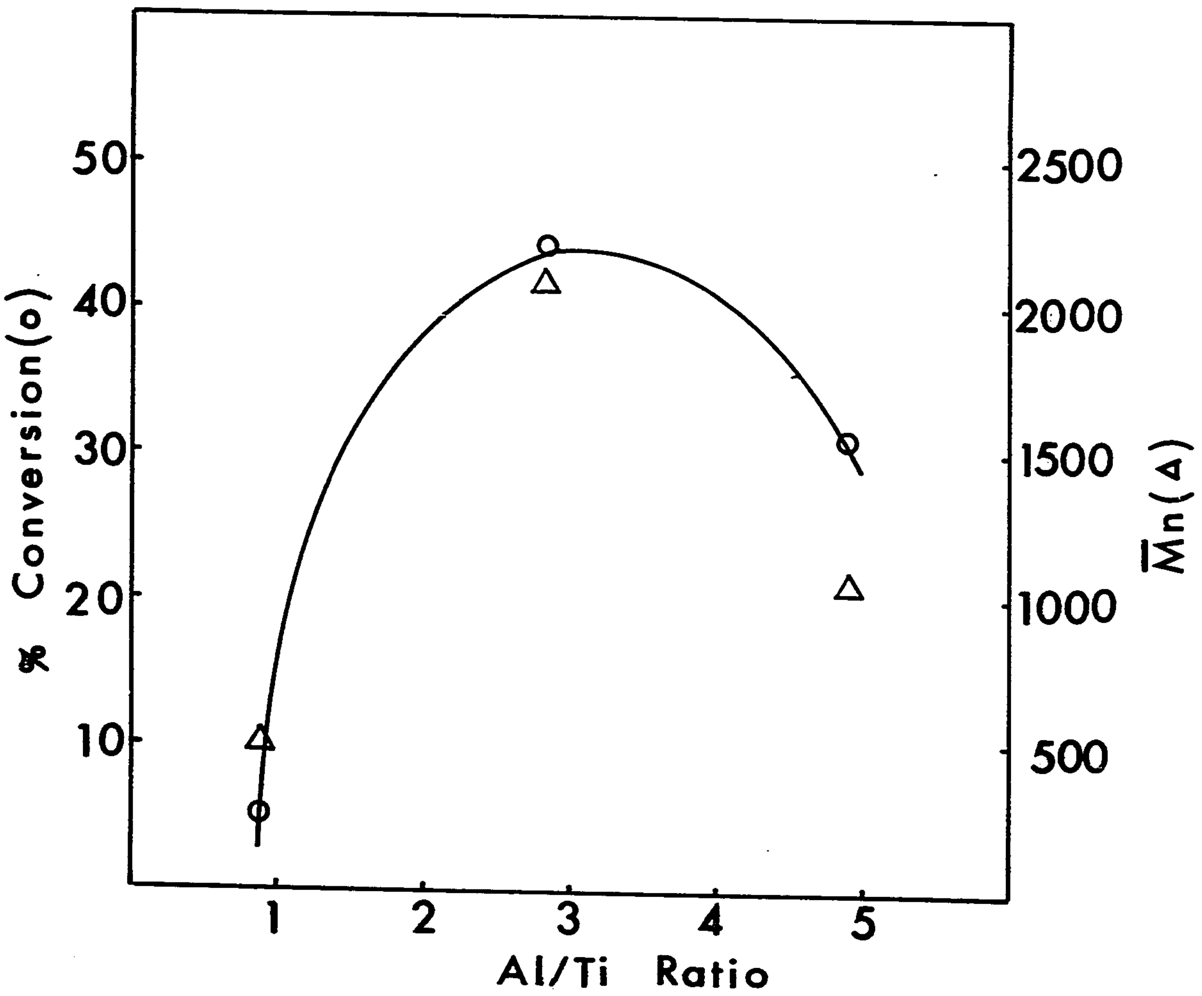


Table 18 Polymerization of 2-Ethynylnaphthalene by $Al(i\text{-}Bu)_3$-$TiCl_4$. Initial Temperature 25°, then Reflux

Expt. No.	Monomer (mole/l.)	$TiCl_4$ (mole/l.)	$Al(i\text{-}Bu)_3$ (mole/l.)	Molar Ratio (Al/Ti)	Polymer Yield (%)	$\overline{M}_n$ (OS)
127	0.125	$2.4\text{x}10^{-2}$	$6.1\text{x}10^{-2}$	2.8	44.08	2091
132	0.125	$2.4\text{x}10^{-2}$	$2.1\text{x}10^{-2}$	0.88	4.85	495
134	0.125	$2.1\text{x}10^{-2}$	$10.1\text{x}10^{-2}$	4.9	31.01	1050

FIG.16 POLYMERIZATION OF 2-ETHYNYLNAPHTHALENE BY $Al(i\text{-}Bu)_3\text{-}TiCl_4$



polymer recovery, the resultant polymers consistently show a higher molecular weight than those reported in the literature. Thermal polymerization of diphenyldiacetylene in the absence of catalyst is also successful, contrary to the literature finding. It is a second order reaction, with the rate varying as the square of monomer concentration. This together with the fact that the molecular weight of the polymer is independent of the monomer concentration, is interpreted as involving a bimolecular initiation and a bimolecular termination step during polymerization. Gamma irradiation of diphenyldiacetylene gave a dimer only.

Diphenylacetylene was polymerized by Ziegler-type catalyst into possibly a cyclic trimer. There was no thermal polymerization up to 140°. Gamma irradiation also yields a dimer in very low yield.

Phenylacetylene was polymerized by the Ziegler-type catalyst under careful conditions. The molecular weight is higher than generally reported, with the exception of Berlin's result. Thermal polymerization is also successful. At 140°, a degree of polymerization of 27 was obtained.

2-Ethynylnaphthalene was polymerized for the first time in the present studies. Its molecular weight also falls into the same pattern for arylacetylene $\sim 10^3$ range.

4.3 Characterizations

The monomers are characterized by their physical and chemical properties. The polymers are characterized by their molecular weights, melting points, and spectral properties. The conjugated double bond system was supported by chemical color formation with antimony trichloride, ultraviolet and infrared spectra.

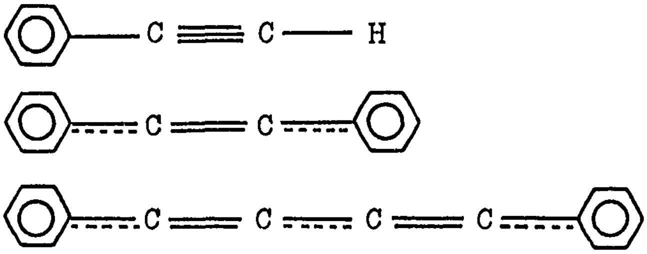
4.3.1 Characterization of the Monomers

The properties of the monomers are listed in Table 19. Diphenyldiacetylene and diphenylacetylene are colorless, crystalline solids. Phenylacetylene is a colorless liquid, but becomes yellow on standing. 2-Ethynylnaphthalene is a colorless liquid. There is a good relationship between the amount of conjugation in the molecule and their ultraviolet, infrared and nuclear magnetic resonance spectra. From Table 19 there is a bathochromic shift to longer wave length (λ max.) in the UV and a decrease in chemical shift (τ value) in the NMR spectra as we go from phenylacetylene, diphenylacetylene to diphenyldiacetylene. The bathochromic shift is expected. The longer the conjugated double bond system, the more is the delocalization of the π-electrons so that the energy required for the $\pi \longrightarrow \pi^*$ transition is less, resulting in a shift of absorption towards longer wave lengths. The decrease in chemical shift can be explained by the diamagnetic shielding of a triple bond. Whereas the π-electrons of a double bond have the electron

Table 19 Properties of the Monomers

	Phenyl-acetylene	Diphenyl-acetylene	Diphenyl-diacetylene	2-Ethynyl-naphthalene
Molecular weight	102.13	178.22	202.26	152.20
Crystalline form, color	colorless liquid	colorless plates	colorless needles	colorless liquid
Melting Point, °C.	-40 to -48	62 - 64.5	86 - 87.5	80-96 at 0.75 mm.
Boiling Point, °C.	143	-	-	-
Group classification	C_2v	D_{2h} or C_2v	D_{2h} or C_2v	C_2v
UV (group of bands)	220-250 mu	270-305 mu	280-340 mu	277-298 mu
IR ($C\equiv C$)	2100 cm.$^{-1}$	-	2150, 2215 cm.$^{-1}$	2100 cm.$^{-1}$
Raman ($C\equiv C$)	2109 cm.$^{-1}$	2220 cm.$^{-1}$	2219 cm.$^{-1}$	
NMR (phenyl protons)	3.3 τ	2.8 τ	2.6 τ	2.6 τ
EPR signal	None	None	None	None

distribution above and below the σ bond, the π-electrons of a triple bond so coalesce to give the electron distribution cylindrically symmetric about the σ bond. When the acetylenic bond is oriented parallel to the applied magnetic field, the electronic circulations within the cylindrical π-electron cloud induces a diamagnetic shielding at the protons connected to the acetylenic bond. Thus, acetylenic protons are brought into resonance at higher magnetic field (more shielding and higher τ values), than vinyl and aromatic protons, approaching the protons of alkanes. Since phenylacetylene has only one triple bond, the phenyl protons are more shielded. The phenyl protons of diphenylacetylene, and diphenyldiacetylene are less shielded because the acetylenic bond has less triple bond character due to resonance of the conjugated system as below.



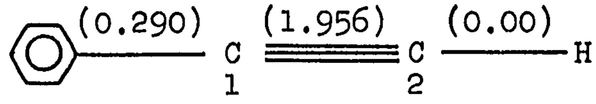
For the infrared and Raman spectra, although diphenylacetylene and diphenyldiacetylene have less triple bond character so that the $C \equiv C$ stretch should shift to lower frequency, the substituents at the triple bond exert an important effect. Thus, the $C \equiv C$ stretch of terminal acetylenes absorbs at a lower frequency

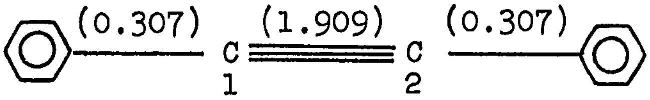
(2140-2100 cm.$^{-1}$, medium) than non-terminal acetylenes (2260-2190 cm.$^{-1}$, weak).[95] The spectral properties are what might be expected.

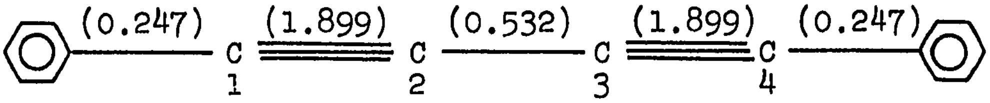
Finally, the free valence index F_i was calculated from the available bond order data as to provide some insight into the reactivity of the carbon atoms in the triple bond towards neutral molecules and free radicals. Coulson defines the free valence index from atom i as follows.[104]

$$F_i = \text{maximum Bonding power} - \sum p_{i_j}$$

where $\sum p_{i_j}$ is the sum of the bond orders of all bonds for the ith atom, and the theoretical maximum bonding power is shown to be 4.732. The mobile π bond order (in brackets) for phenylacetylene, diphenylacetylene and diphenyldiacetylene are given below.[105,106]







Phenylacetylene $F_1 = 4.732-[1+1+0.290+1.956]=0.486$

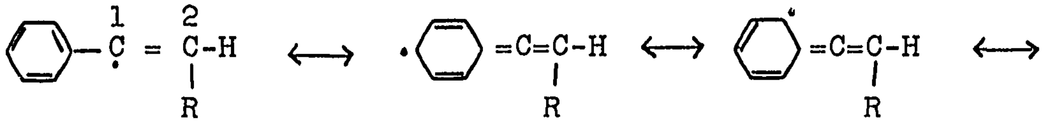
$F_2 = 4.732-[1+1+\ 0\ +1.956]=0.776$

Diphenylacetylene $F_1=F_2=4.732-[1+1+0.307+1.909]=0.516$

Diphenyldiacetylene $F_1=F_4=4.732-[1+1+0.247+1.899]=0.586$

$F_2=F_3=4.732-[1+1+0.532+1.899]=0.301$

The larger the value of F_i, the more reactive is the i^{th} atom since they are not much bonded compared to the maximum. We see at once that carbon 2 in phenylacetylene is more reactive than carbon 1; carbons 1 and 2 are identically reactive for diphenylacetylene; and carbons 1 and 4 are more reactive than carbons 2 and 3 in diphenyldiacetylene. The physical reason is consistent with the chemical reactivity since attack on carbon 2 of phenylacetylene by a radical R· gives a resonance stabilized structure whereas attack on carbon 2 does not give such a resonance stabilized structure. The same is true for diphenyldiacetylene.

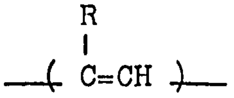


4.3.2 Characterization of the Polymers

That the polymers of diphenyldiacetylene, phenylacetylene and 2-ethynylnaphthalene are conjugated polyenes was confirmed by the color test with antimony trichloride in chloroform.[59,107] The same color test has been used for testing vitamin A and β-carotenoids,[108] which are known to contain a conjugated double bond system. The monomers do not give any coloration. Moreover, the infrared band at 1600 cm.$^{-1}$ has been assigned to indicate fully conjugated double bonds, while the band at 1665 cm.$^{-1}$ assigned to isolated double bonds.[55,98] Although all our monomers also show a weak band at 1600 cm.$^{-1}$, this band increases in intensity after polymerization, suggesting that the length of conjugated double bond system increases. If we now compare the 1600 cm.$^{-1}$ band intensity with another band that has not been assigned with conjugation, a semiquantitative estimate of conjugation can be calculated. For instance, the ratio of absorption intensities of the band 1595 cm.$^{-1}$ to 1459 cm.$^{-1}$ in the phenylacetylene monomer ($^{A}1595$/A1495) was 0.466. After it was polymerized to a molecular weight of 1507, the ratio has increased to 0.720. The ratio decreases to 0.635 in a polymer with a molecular weight of 1080, indicating a decrease in the length of conjugation. The use of intensity comparison against an internal standard in infrared spectroscopy has been documented.[109,110] Finally, the electron paramagnetic resonance measurements establishing that the polymers are all paramagnetic whereas the monomer does not seem to support a chain of conjugated double bonds which could stabilize free radicals.

4.3.2.1 Molecular Weights and Stereochemistry of the Polymers

The molecular weights have been listed in the tables given for the polymerizations. The ranges of the molecular weights of the polymers are summarized in Table 20. Apparently, there is no direct relationship between the molecular weight and the amount or the ratio of the Ziegler-type catalyst. This is also true in the thermal polymerization. Gamma radiation yields a dimer for diphenylacetylene and diphenyldiacetylene. A characteristic feature is that they all are comparatively low molecular weight materials as compared to their vinyl counterparts. The reason probably is threefold, steric factor, loss of activity of the propagating species by resonance stabilization and cyclization. Steric factors governing the stereoisomerism of the molecular chain (chain configuration) are important in polymerization. The basic unit in the polyacetylenes is the group

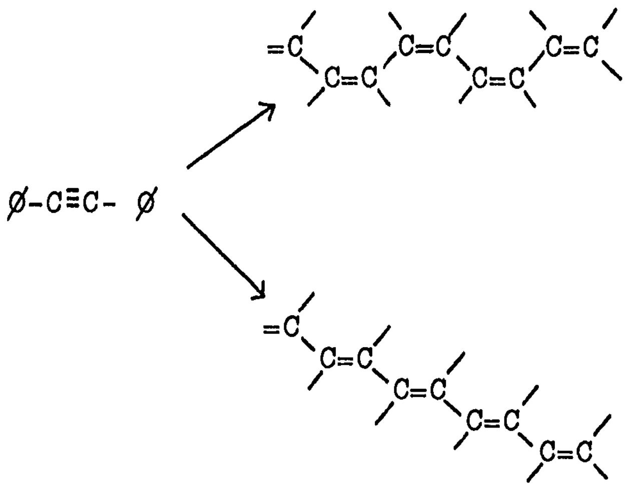


$-\!\left(\overset{\overset{R}{|}}{C}{=}CH\right)\!-$ in which R can be a hydrogen or an aryl group. The repeating unit can be joined either head-to-head, tail-to-tail or head-to-tail. The configuration about each double bond can be either cis or trans. It is known that polyolefins produced by the Ziegler-type catalyst possess a structure in which the monomer units are joined head-to-tail.[111] By analogy, it is reasonable to assume that the polyalkynes may also possess a head-to-tail structure. The steric configuration of a polymer chain

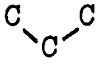
Table 20 Ranges of Molecular Weight of the Polymers

	Ziegler Catalyst	Thermal	Peroxide Catalyst	Gamma Radiation
Diphenyldiacetylene	816-3067	632-1740	640-1870	225-336
Diphenylacetylene	466-859	-	-	356
Phenylacetylene	622-1770	1080-2747	-	-
2-Ethynylnaphthalene	459-2091	-	-	-

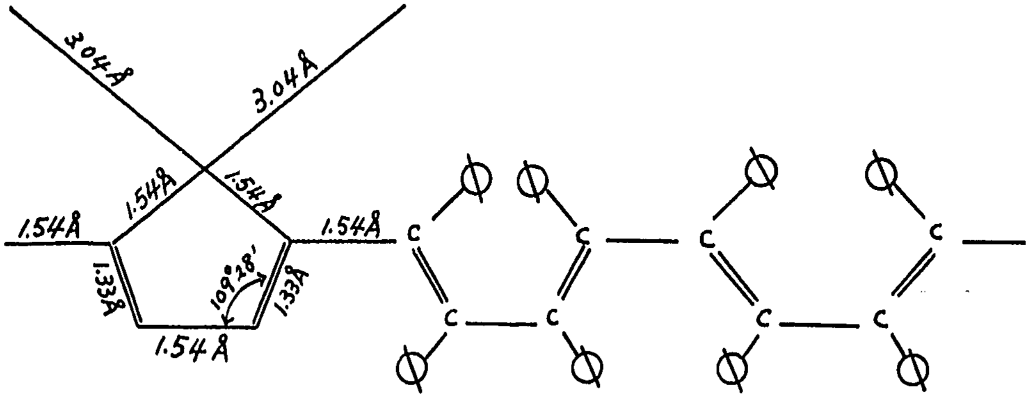
can be represented by a convention popularized by Natta.[112] The atoms of the chain backbone lie in a plane and form the zig-zag corresponding to the maximum chain extension compatible with the bond angles. Of course, the polymer chain can assume numerous conformations by rotation around the single bonds, none of which is of special importance except those extremes corresponding to energy maximum or minimum. Analysis of the structure of the diphenylacetylene polymer reveals that the polymerized product can have either the cis or the trans chain configurations.



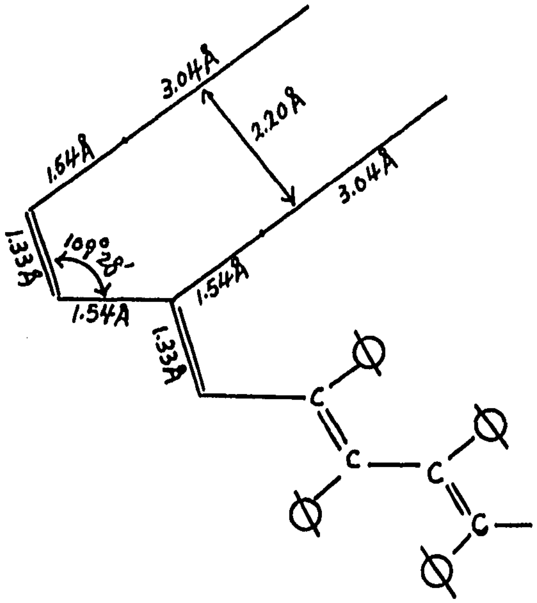
The chain conformation of the structure which has all its conjugated double bonds in the cis position has the trans (t)-gauche (g) sequence in the chain backbone. This conformation of tg sequence is the same expected from isotactic polypropylene, polystyrene, etc.[113] However, a simplified analysis indicates that the all cis structure may be prohibited since the two nearest phenyl groups may cross each other. We have assumed the benzene group is planar, and has a 3.04 Å distance between the 1,4 carbons. The bond lengths of C-C is 1.54 Å, of C=C is 1.33 Å and a valence angle of 109°28' between the



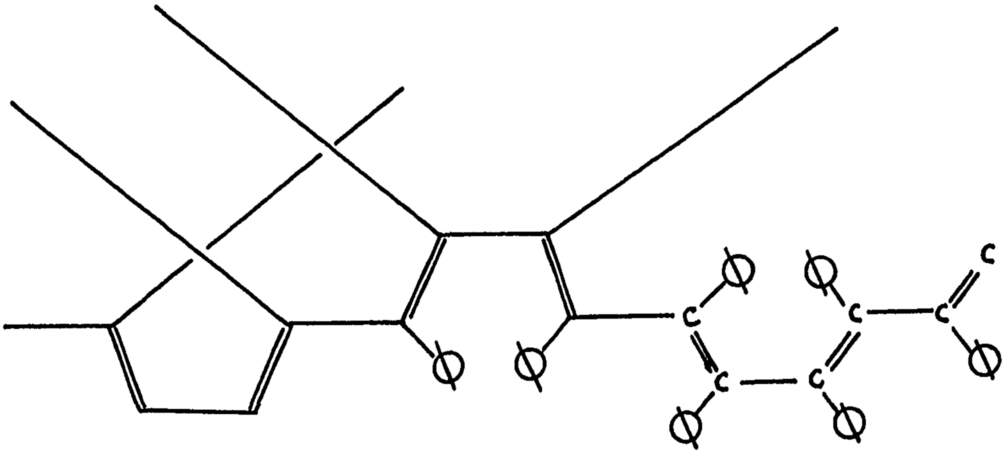
bonds.[114]



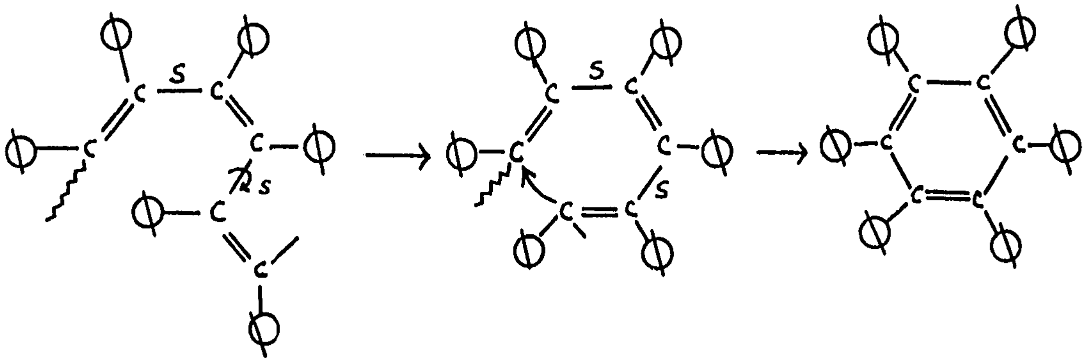
The chain conformation of the structure which has all its conjugated double bonds in the trans position has the trans-trans sequence in the chain backbone. This tt sequence is the same expected from syndiotactic polypropylene.[113] A simplified analysis indicates this may be allowed, since no nearest phenyl groups will cross each other. The perpendicular distance between two phenyl groups which have the planes parallel is about 2.2 Å that is just a bit larger than the Van der Waal radius or the half-thickness of the benzene ring, 1.85 Å.[114] Although not prohibitive, it represents a situation of extreme high steric strain. This crowding can be relieved by spiralling into a helix through internal rotation around the C-C bond slightly over or below 180° value. However, spiralling into a helix



necessarily destroys the coplanarity of the molecular chain so that conjugation will not be continuous. The other possibility is when the chain conformation having the double bonds in the cis-trans position will have the trans-trans, trans-gauche tttg sequence.

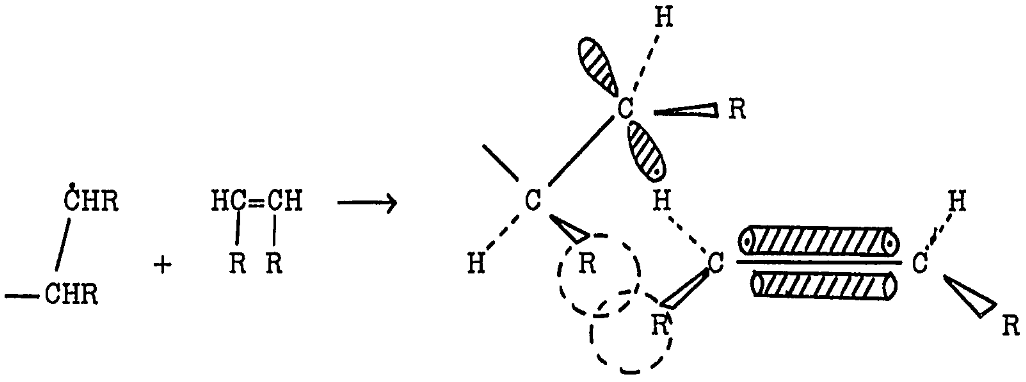


Again, when the double bonds are in the cis positions, the phenyl substituents will cross each other. Since the major product of polymerizing diphenylacetylene is hexaphenylbenzene, the following cis-trans structure must be very important.



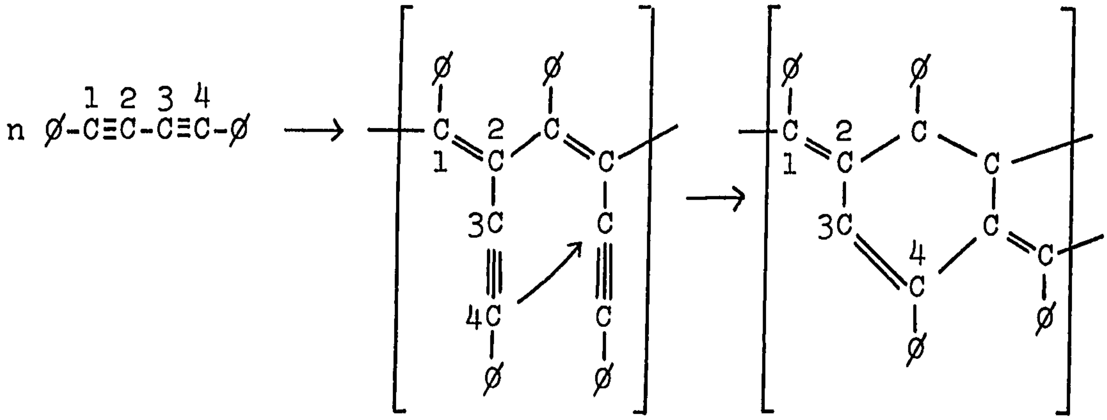
2-s-cis,4-s-trans 2,4-di-s-cis product

The inability of most 1,2-disubstituted vinyl monomers like stilbene, maleic anhydride, etc., to polymerize is also caused by steric inhibition, due to the steric interaction between one of the two substituents on the olefin and the β-substituent of the end group radical on the polymer chain.[115] This interaction hinders the

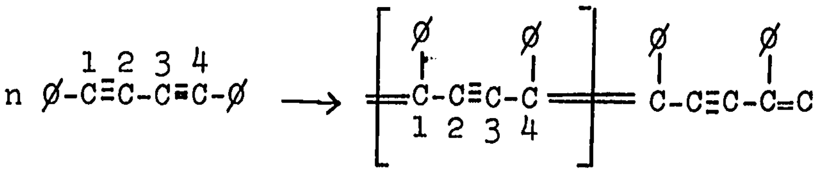


approach of one molecule to the other, and subsequently, also imposes a strain on the bonds being established in the transition state. The existence of such steric interaction is supported by the fact that all 1,2-disubstituted olefins which do not homopolymerize will easily copolymerize with 1,1-disubstituted olefins.

For diphenyldiacetylene, if addition involves the 1,2 position, the acetylenic side group can cyclize.



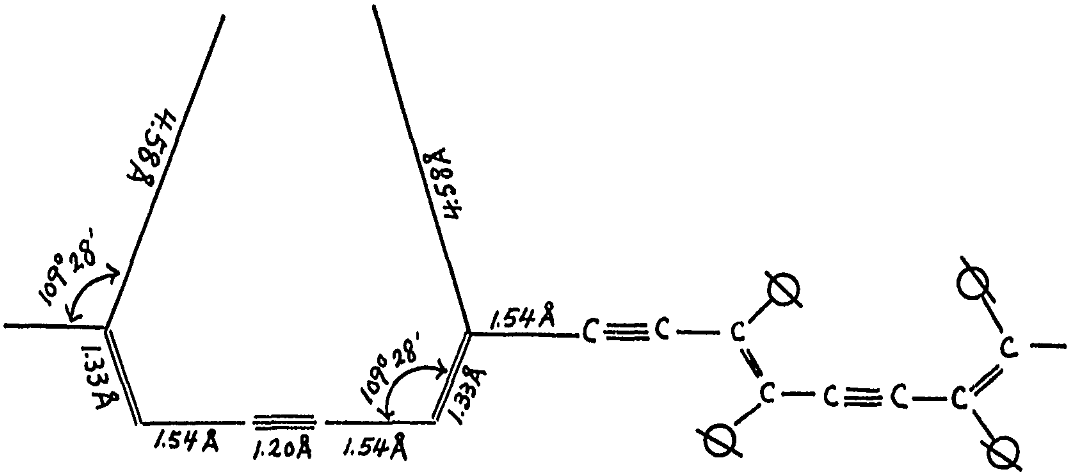
If, on the other hand, addition involves the 1,4 position, in analogy to the butadiene polymerization, a linear structure would be formed, with one acetylenic bond alternating between two double bonds.



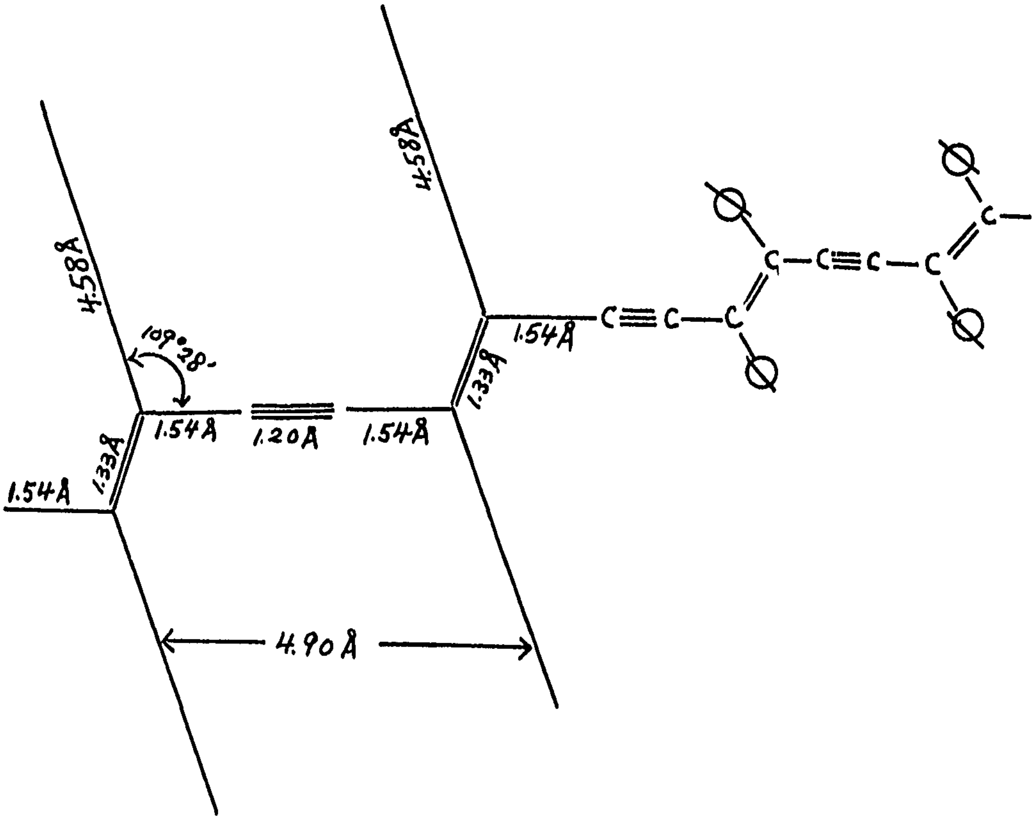
$$n\,\overset{1}{\phi\text{-}C}\equiv\overset{2}{C}\text{-}\overset{3}{C}\equiv\overset{4}{C}\text{-}\phi \longrightarrow \left[=\underset{1}{\overset{\phi}{C}}\text{-}\underset{2}{C}\equiv\underset{3}{C}\text{-}\underset{4}{\overset{\phi}{C}}=\right]=\overset{\phi}{C}\text{-}C\equiv C\text{-}\overset{\phi}{C}=C$$

The 1,4 addition polymer can have the double bonds all in the cis position or all in the trans position. The all cis configuration has the tg tg conformation sequence.

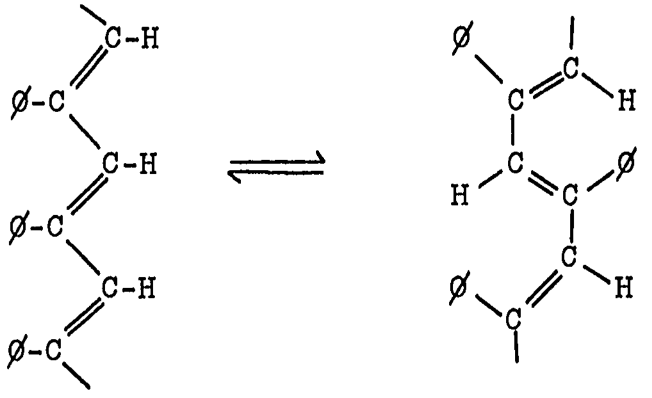
However, the two nearest phenyl groups are now about 2.1 Å apart which is too close to the half-thickness of benzene, 1.85 Å. In analogy to the all cis structure of polydiphenylacetylene, the structure below is highly crowded.



The all trans configuration of polydiphenyldiacetylene which has the tt conformation sequence is less sterically hindered than the all cis configuration, and would be the more favorable structure.

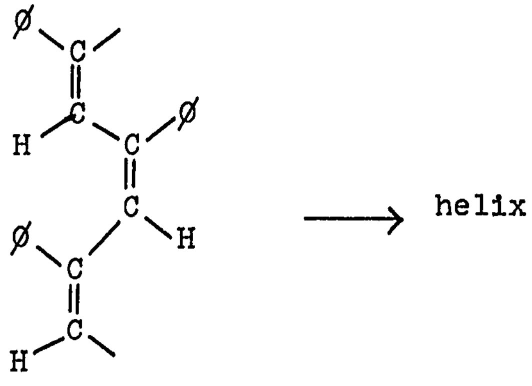


For phenylacetylene, it is analogous to diphenylacetylene except a hydrogen now replaces a phenyl group, and the steric conditions are more favorable than those of diphenylacetylene. An important difference between all-trans and all-cis conjugated chains becomes apparent from rotation about single bonds in the chain. A trans-transoid form converts to a trans-cisoid (and vice versa) by allowing 180° rotation about the C-C single bonds of the chain.



trans-transoid trans-cisoid

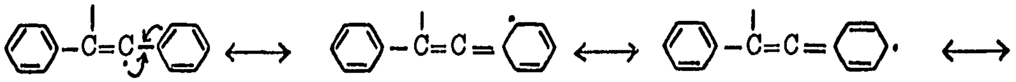
A different situation exists for the cis polymers. A sequence of three double bonds in cis-cisoid relation forms a six-membered ring. This may explain the formation of very small amount of trisubstituted benzene in the polymerization. In a chain of alternating cis double bonds, this limits the rotation about the C-C bond, and the consequence is helix formation.



cis-transoid

Similarly, 2-ethynylnaphthalene would be expected to have the same conformation like polyphenylacetylene.

Another reason why polymerization failed to give high molecular weight material may be due to the fact that during the polymerization step, the reactivity of the propagating radical (or ion) of the main chain decreases as the length of the conjugation double bond system increases. The decrease in reactivity of the macro-radical (or ion) which is the propagating species can be due to stabilization by resonance. It is well known that the styrene radical is much less reactive than the vinyl acetate radical because of resonance stabilization. Wallach has done some quantum mechanical calculations on the decrease of activity of a living anion to initiate polymerization as the length (or molecular weight) of the living anion increases.[103] The diphenylacetylene radical or ion can be stabilized by resonance as follows:



Finally, cyclization of the monomers will always yield a lower molecular weight than the linear polymers. Phenylacetylene can cyclize into a trimer of trisubstituted benzene, while diphenylacetylene can cyclize to hexaphenylbenzene. Cyclization after the linear polymer was formed will not affect the molecular weight like the 1,2 addition polymer of diphenyldiacetylene, but if cyclization predominates before the linear polymer was formed, low molecular weight is expected.

4.3.2.2 Spectral Properties of the Polymers

A. Diphenyldiacetylene. Since the polymers are a mixture of many stereoisomers and molecular weight, the ultraviolet and NMR spectra would be very diffuse. The infrared spectra, on the other hand, give valuable information. The infrared spectra of diphenyldiacetylene monomer, a polymer by Ziegler-type catalyst, and a polymer by thermal initiation were shown in Figure 17. The 2215 cm.$^{-1}$ band of the $C\equiv C$ bond of the monomer disappeared, and the 1600 cm.$^{-1}$ band of the $C\equiv C$ conjugated bond increases in intensity, suggesting that polymerization is taking place. Moreover, the higher the molecular weight, the more intense is the 1600 cm.$^{-1}$ band as seen in the ratio of band intensities of 1600 cm.$^{-1}$ to 1495 cm.$^{-1}$ in Table 21. The spectra of two polymers prepared by two different Ziegler catalysts are identical suggesting changing the organometallic does not change the polymer structure. The infrared spectra indicate no cyclic structure because the vibrations and substitution patterns of the following cyclic products are absent. The monomer spectrum in figure 17 was recorded with a Perkin Elmer IR521 , was a linear wave number scale. The scale is not linear with the other spectra.

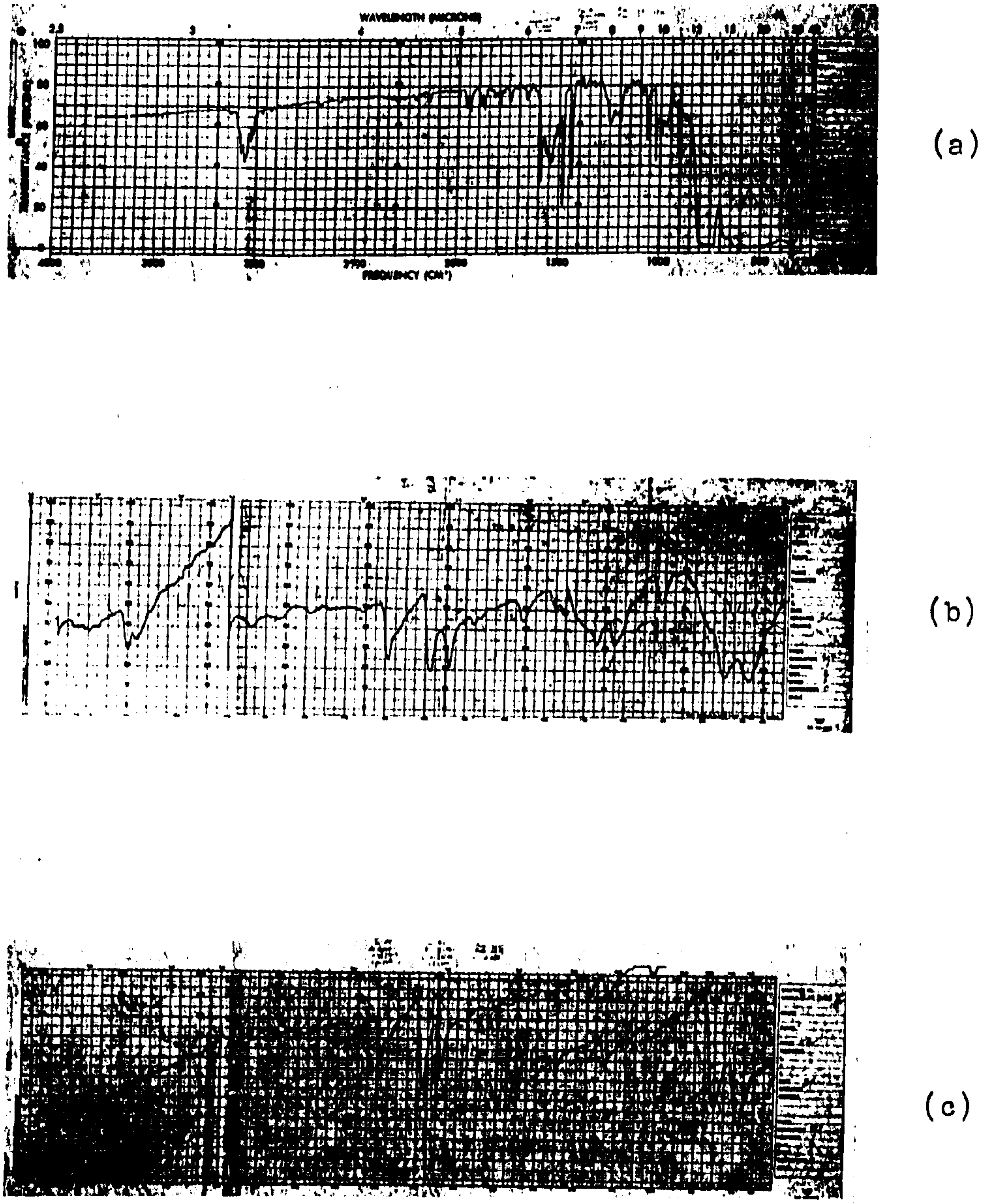
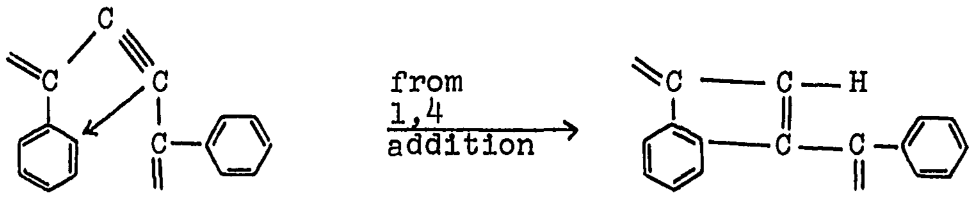
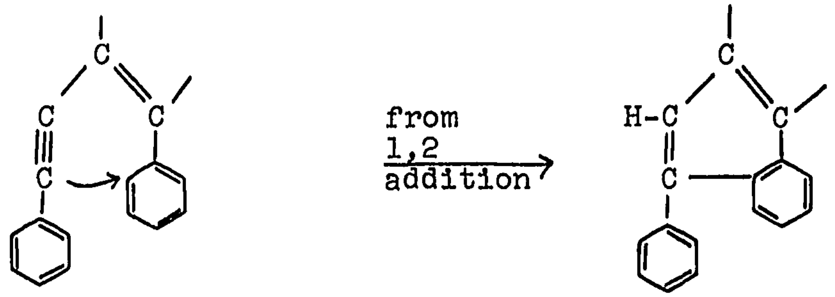


FIG. 17 INFRARED SPECTRA OF POLYDIPHENYLDIACETYLENE
(a) Monomer (CCl_4)
(b) Polymer, Catalyst Initiated (KBr)
(c) Polymer, Thermally Initiated (KBr)

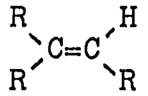
Table 21 Ratio of Absorption Band Intensities of the 1600 cm.$^{-1}$ to 1495 cm.$^{-1}$ of the Polymers

	Monomer	Ziegler Catalyst	$\overline{M}_n$	Thermal	$\overline{M}_n$
Diphenyldiacetylene	0.72 (CCl_4)	0.97 (CCl_4)	3067	0.77 (CCl_4)	747
		0.86 (KBr)	3067	0.70 (KBr)	747
Diphenylacetylene	0.91 (KBr)	0.95 (KBr)	Insoluble		
		1.00 (KBr)	596		
Phenylacetylene	0.46 (Neat)	0.72 (CCl_4)	1507	0.64 (CCl_4)	1080
		0.55 (KBr)	1507	0.65 (KBr)	1080
2-Ethynylnaphthalene	0.90 (Neat)	1.11 (KBr)	1050		





The first one resulting from intramolecular cyclization of the 1,4 addition polymer should have a 1,2 disubstituted pattern from 2000-1650 cm.$^{-1}$ and the out-of-plane deformation for four adjacent hydrogens at 750 cm.$^{-1}$ In addition, there should be a band due to a trisubstituted ethylene


$R_2C{=}CHR$

around 840-800 cm.$^{-1}$ which was not seen in NMR as well. The second one from 1,2 addition polymer should have one isolated hydrogen in the benzene ring besides the 1,2 disubstituted ring, and the band occurs at 860-900 cm.$^{-1}$ They are not observed. There is some difference between the Ziegler catalyst initiated and thermally initiated diphenyldiacetylene. In the former case, there is a band at 2920 cm.$^{-1}$ due to aliphatic C-H stretching, 1380 cm.$^{-1}$ and 1250 cm.$^{-1}$ possibly due to aliphatic C-H bending, otherwise they are identical. The presence of aliphatic groups in the Ziegler catalyst initiated polymer is consistent with the polymerization mechanism which requires that one end group of the polymer comes from the alkyl group of the organometallic catalyst. Such an aliphatic group in the polymer chain was also indicated by NMR spectra. Figure 18 gives the NMR spectra of the diphenyldiacetylene monomer, a polymer prepared by Ziegler catalyst and one prepared by heating only. As seen, the NMR spectra are quite diffuse, and rather featureless except for the phenyl proton region, centering around 2.9 τ . This is expected from the polymer structure because the monomer contains only phenyl protons. The polymer from Ziegler catalyst has a small singlet at 9.9 τ , which was a highly shielded aliphatic proton. Like the infrared spectra, the thermally prepared polymer has no aliphatic protons. According to the Ziegler-Natta mechanism, one end group in the polymer chain should be an alkyl group from the original organometallic compound which in the present case is an isobutyl group shown for a 1,2 addition. The other end group in the polymer chain depends on how it is terminated for which there are several competing processes like transfer with catalyst to get the same alkyl group, or transfer with active hydrogen compound like water, HCl to get an unsaturated end group. We do not see any unsaturated group in infrared and NMR, but we do see an aliphatic group in infrared. The τ value of the aliphatic group in NMR is too high as well as the

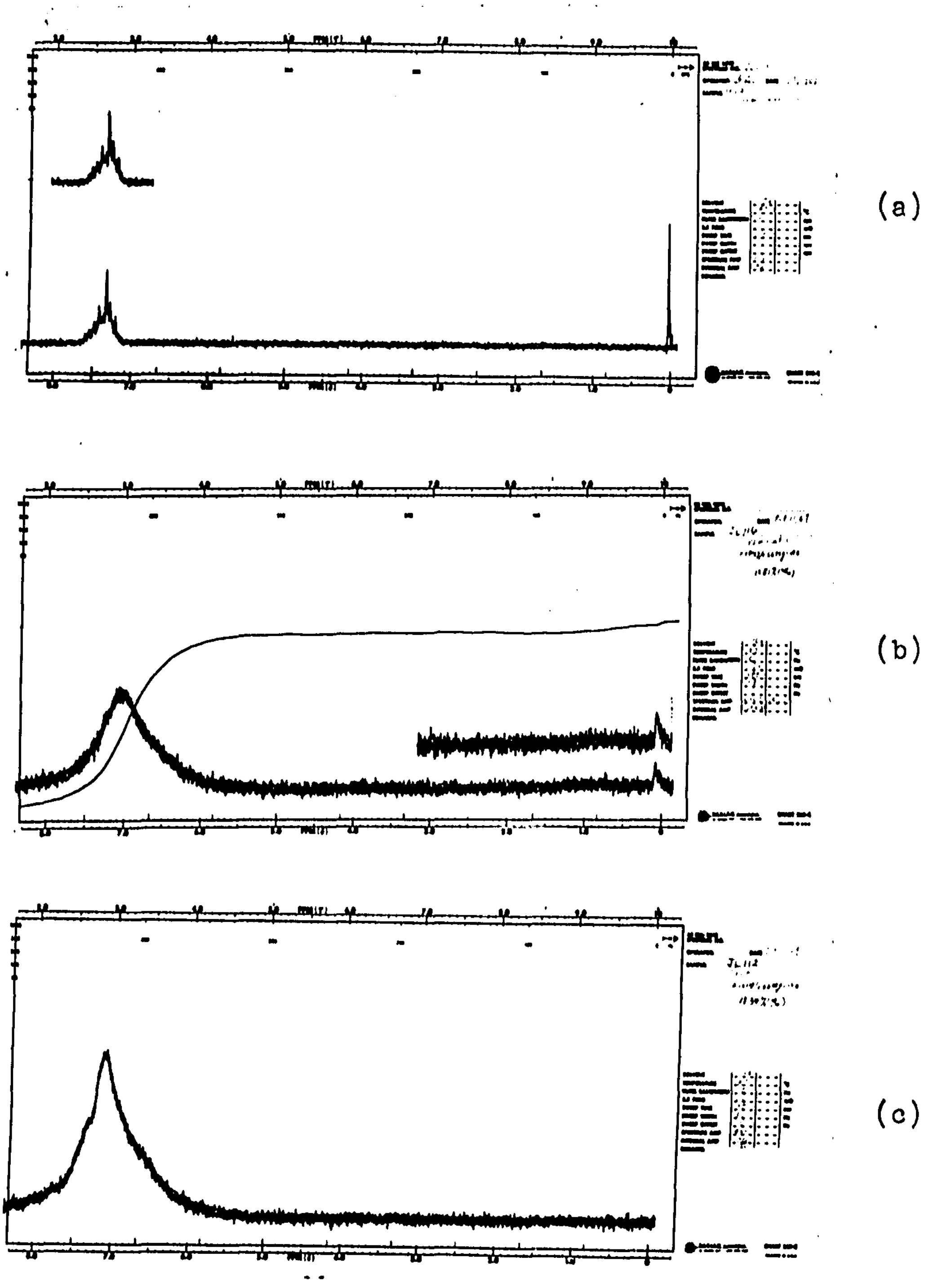
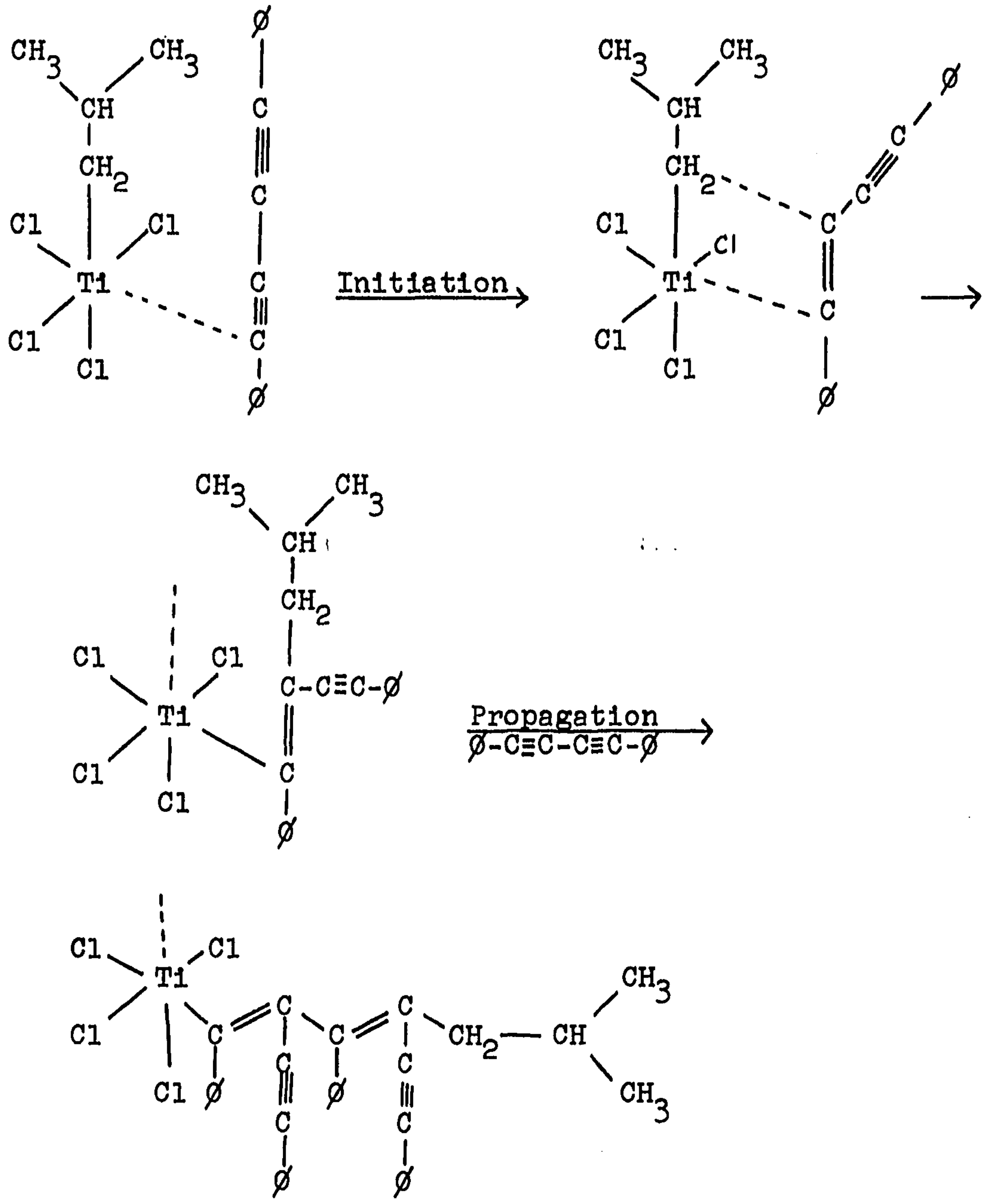


FIG. 18 NMR SPECTRA OF POLYDIPHENYLDIACETYLENE
(a) Monomer
(b) Polymer, Catalyst Initiated
(c) Polymer, Thermally Initiated


Initiation
Propagation
Ø-C≡C-C≡C-Ø

splitting pattern of the isobutyl group was not observed. The nature of this small singlet is not understood.

The ultraviolet and visible spectra of the diphenyldiacetylene monomer, a polymer from Ziegler catalyst and one from thermal initiation are given in Figure 19. There are three sharp peaks for the monomer at 290, 309 and 330 mu. The polymers have no discrete maxima in the curve. Instead, they have a broad absorption around 255 to 290 mu. There is a continuous absorption from UV into the visible region in the form of a gradual slope. Intensity is stronger at short wave lengths. Such a curve can be attributed to polymers in which there are a number of chromophores each having different absorption maxima. It can come about in a polymer that has conjugated unsaturation with increasing number of double bonds in the conjugated sequence. Such a curve would appear as a smooth integration of all absorption maxima, and no maximum should appear separately unless one particular chromophore dominated the structure of the polymer. As the conjugated system grows, the length of each single and double bond will converge to an intermediate value,[116] and greater delocalization of the π-electrons will occur. Kuhn showed that the energy separation between the ground state and the first excited state of a conjugated double bond system can be calculated quantum mechanically.

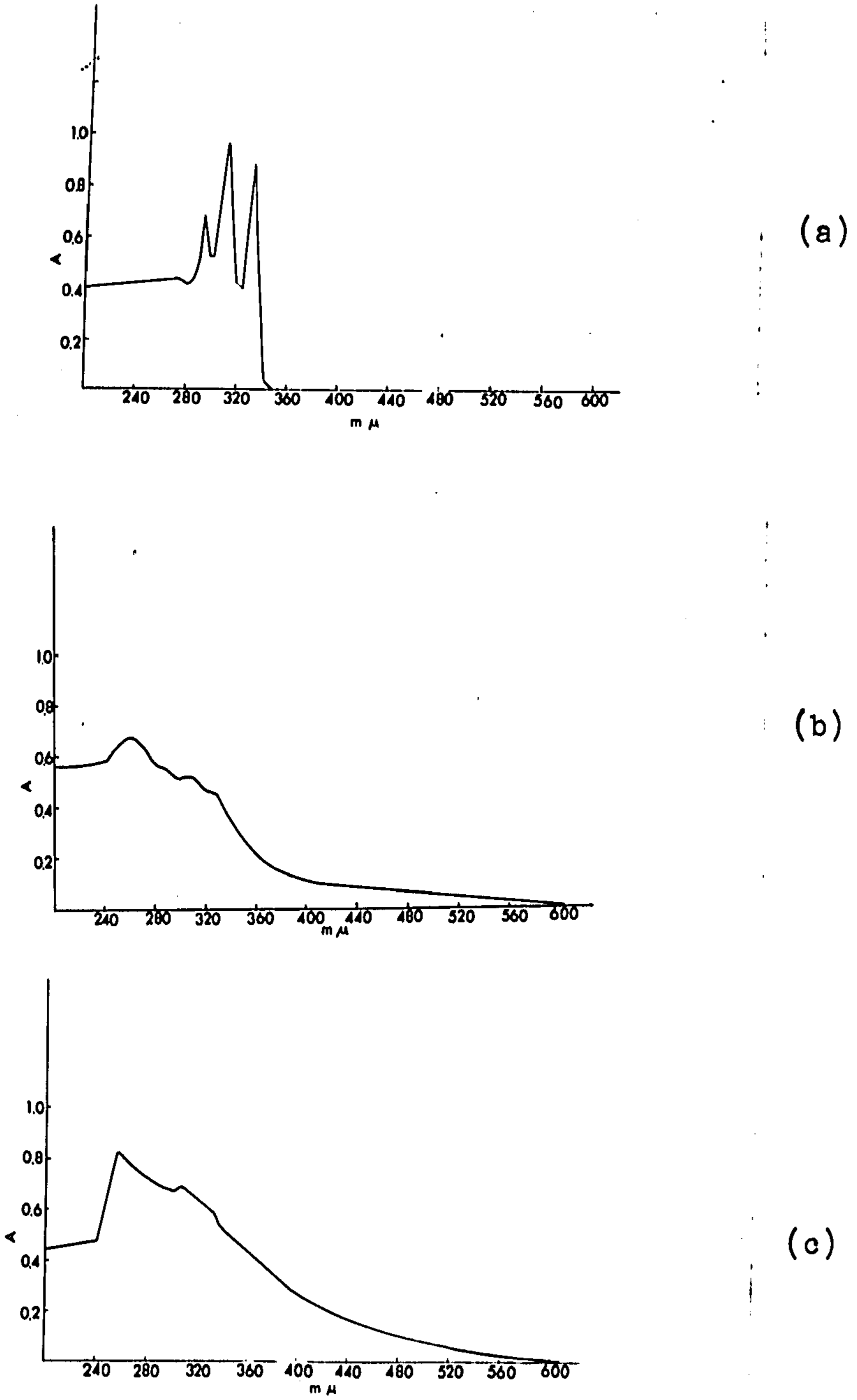


FIG. 19 ELECTRONIC SPECTRA OF POLYDIPHENYL DIACETYLENE
(a) Monomer
(b) Polymer, Catalyst Initiated
(c) Polymer, Thermally Initiated

$$\Delta E = \frac{h^2}{8md^2}\left(\frac{1}{2n+1}\right) + 0.83\left(1-\frac{1}{2n}\right)V_o$$

where h is the Planck's constant, m the mass of an electron, n the number of double bonds in a length d, and $V_o = 2.46$ eV is the amplitude of a sine function to approximate the variation of the potential energy along the chain. Good agreement between the theoretical and the experimental band positions was reported for polymethines, cyanines, polyenes, porphyrines, and oxanole dyes. Using the above equation, and correction for the effect of a phenyl group adjacent to each double bond (one phenyl group has the effect of $1\frac{1}{2}$ double bond),[117] the first excitation energy for phenylacetylene monomer was calculated. This gives a value of 4.92 eV which corresponds to the longest wave length absorption at 252 mu. (cf. styrene λ max. 248 mu.) Our experimental value of phenylacetylene has an absorption range of 220-250 mu. The calculated values for the monomers and their n^{th}-mers are given in Table 22. It is seen that as n the number of double bonds increases, the absorption band converges to around 620 mu. The calculated value for n=1 and the found value agree pretty well for phenylacetylene and diphenylacetylene, but not for diphenyldiacetylene, probably because diphenyldiacetylene has two triple bonds in the monomer instead of one. The experimental values of the absorption band of the monomers

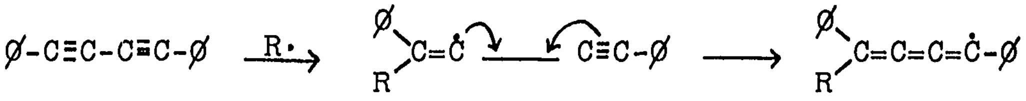
Table 22 Calculated Electronic Absorption Bands for the Longest Wavelength Maxima of the Monomers and n^{th}-mers

	Observed λmax.	n=1 (mu)	n=2 (mu)	n=4 (mu)	n=5 (mu)	n=10 (mu)
Phenylacetylene (styrene)	220-250 mu $\varepsilon = 2.7 \times 10^6$ 248 mu	252	614	636	635	622
Diphenylacetylene (trans-stilbene)	270-305 mu $\varepsilon = 5.1 \times 10^5$ 296 mu	311	611	626	624	617
Diphenyldiacetylene* (diphenylbutadiene)	280-340 mu $\varepsilon = 1.5 \times 10^5$ 328 mu	(380)	612	627	625	618

*Shown for 1,2 addition from n=2 to n=10.

n=1 was calculated by $\Delta E = \frac{h^2}{8md^2}(2n+1)$

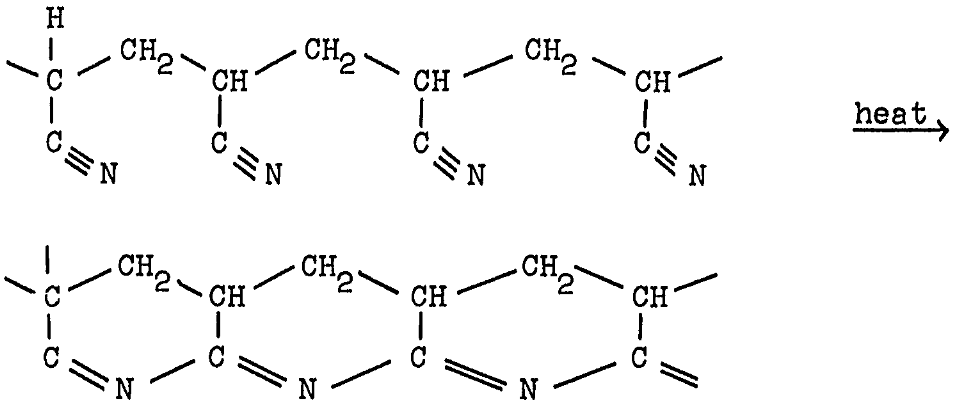
come very close to that of the vinyl analogue. As shown in Figure 19, for the molecular weights we are dealing with, the predicted absorption maxima for the polymers occurred at much longer wave length than those observed experimentally. If the calculation has even semiquantitative significance, the data implies that the effective conjugation length is less than the actual chain length. This could come about by partial rotation at one of the formal single bonds, breaking the π-electron delocalization at that point. The polymer chain then functions as a connected group of smaller conjugated sequence. For this reason, we favor the structure resulting from 1,2 addition of diphenyldiacetylene. For the 1,4 addition gives a triple bond alternating between two double bonds that makes the structure planar and this yields the best condition for π-electron delocalization, and it should absorb around 620 mu. Moreover, the 1,4 addition mechanistically will involve the allene-acetylene isomerization, and infrared spectra did not show a 1950 cm.$^{-1}$ band, characteristic of the allene stretching.



$$\phi\text{-C}\equiv\text{C-C}\equiv\text{C-}\phi \xrightarrow{\text{R}\cdot} {}^{\phi}_{\text{R}}\!>\!\text{C}=\dot{\text{C}}\ \text{C}\equiv\text{C-}\phi \longrightarrow {}^{\phi}_{\text{R}}\!>\!\text{C}=\text{C}=\text{C}=\dot{\text{C}}\text{-}\phi$$

Although sterically crowded, the 1,2 addition structure could rotate or spiral to relieve the steric strain, breaking the extended conjugation, and causing the absorption band to appear at much shorter wave length.

Finally, the differential thermograms of polydiphenyldiacetylene prepared by Ziegler catalyst and thermal initiation are given in Figure 20. The former shows a continuous baseline shift to the exothermic direction, indicating a continuous increase in thermal conductivity or a decrease in the heat capacity of the sample, while the latter shows a broad exotherm at about 270°. The data may mean the onset of decomposition with partial loss of the sample or some exothermic reaction is taking place like cyclization. Since decomposition usually is accompanied by an increase in noise level, it may indicate that cyclication is taking place in support of the 1,2 addition structure that can cyclize easily. Polyacrylonitrile is known to cyclize on heating.



Qualitatively, cyclization should be exothermic to the extent of about 22 Kcal/mole since we are breaking a triple bond (210 Kcal/mole) to form a double bond and a single bond (148 + 84 = 232 Kcal/mole).

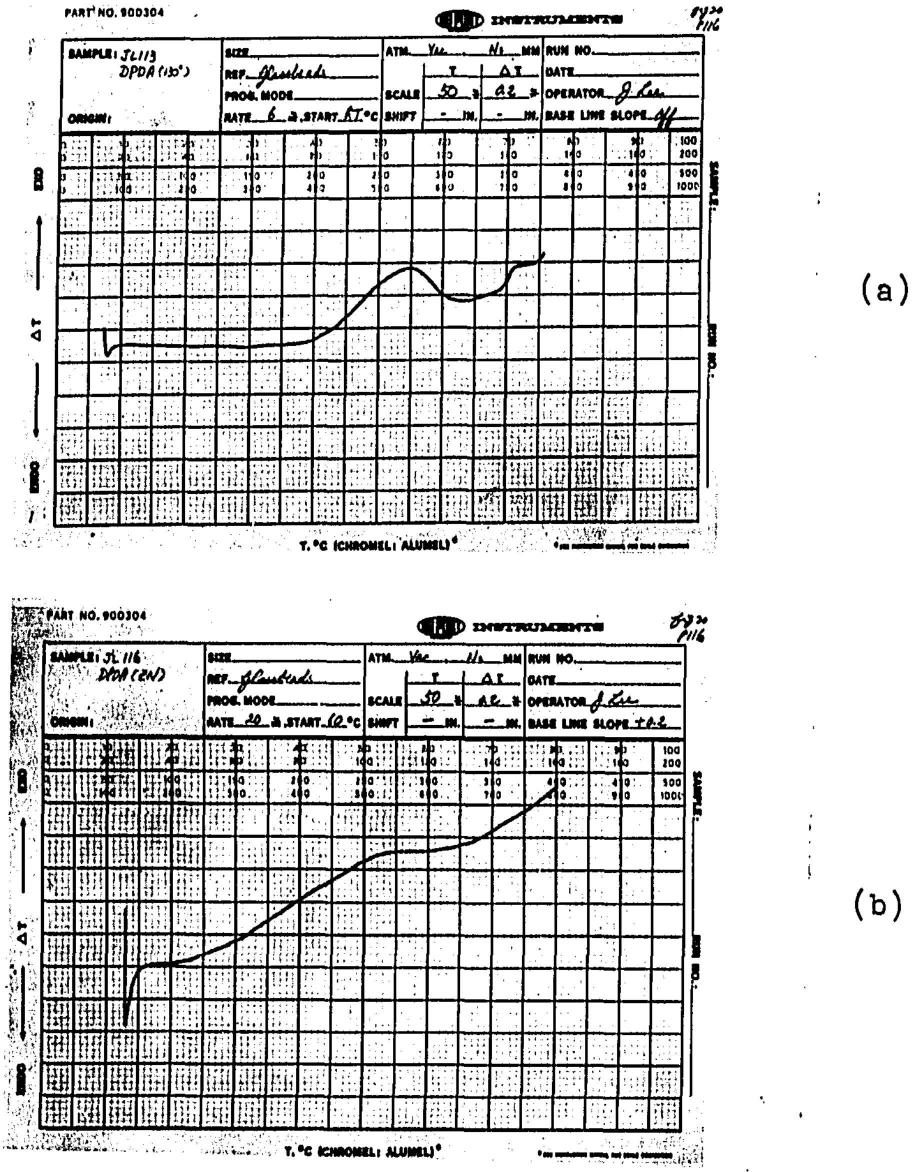


FIG. 20 DIFFERENTIAL THERMOGRAMS OF POLYDIPHENYLDIACETYLENE
(a) Thermal Initiation
(b) Catalyst Initiation

B. Diphenylacetylene. For one thing, polydiphenylacetylene prepared by Ziegler-type catalyst is colorless, does not give a positive color test with antimony trichloride, and shows no EPR signal.

The infrared spectra of the polymer and the monomer are shown in Figure 21. A group of new bands, not seen in the monomer, appear in the polymer at 1400, 820, 780 and 725 cm.$^{-1}$ while the band at 750 cm.$^{-1}$ in the monomer disappeared. Shown also in Figure 21 is the spectrum of hexaphenylbenzene, which has the same bands of the polymer. This is highly deducive that the structure of the polymer and hexaphenylbenzene must be very similar. If the electronic spectrum of the polymer is compared with the spectrum of hexaphenylbenzene, which is shown in Figure 22, they are quite similar and it is concluded here that their structures must be very similar.

However, the differential thermogram of the polymer reveals some interesting information, that the major portion of the polymer is hexaphenylbenzene, melting around 460° with a major endotherm. There is a fraction melting at 325° and also very small endotherms at 445°, as shown in Figure 23. It is known that ultraviolet irradiation of diphenylacetylene gave trace amounts of 1,2,3-triphenylnaphthalene, m.p. 152°; 1,2,3-triphenylazulene, m.p. 217°; octaphenylcuban, m.p. 429°.[102] The other traces in the thermogram would represent products not yet identified for diphenylacetylene.

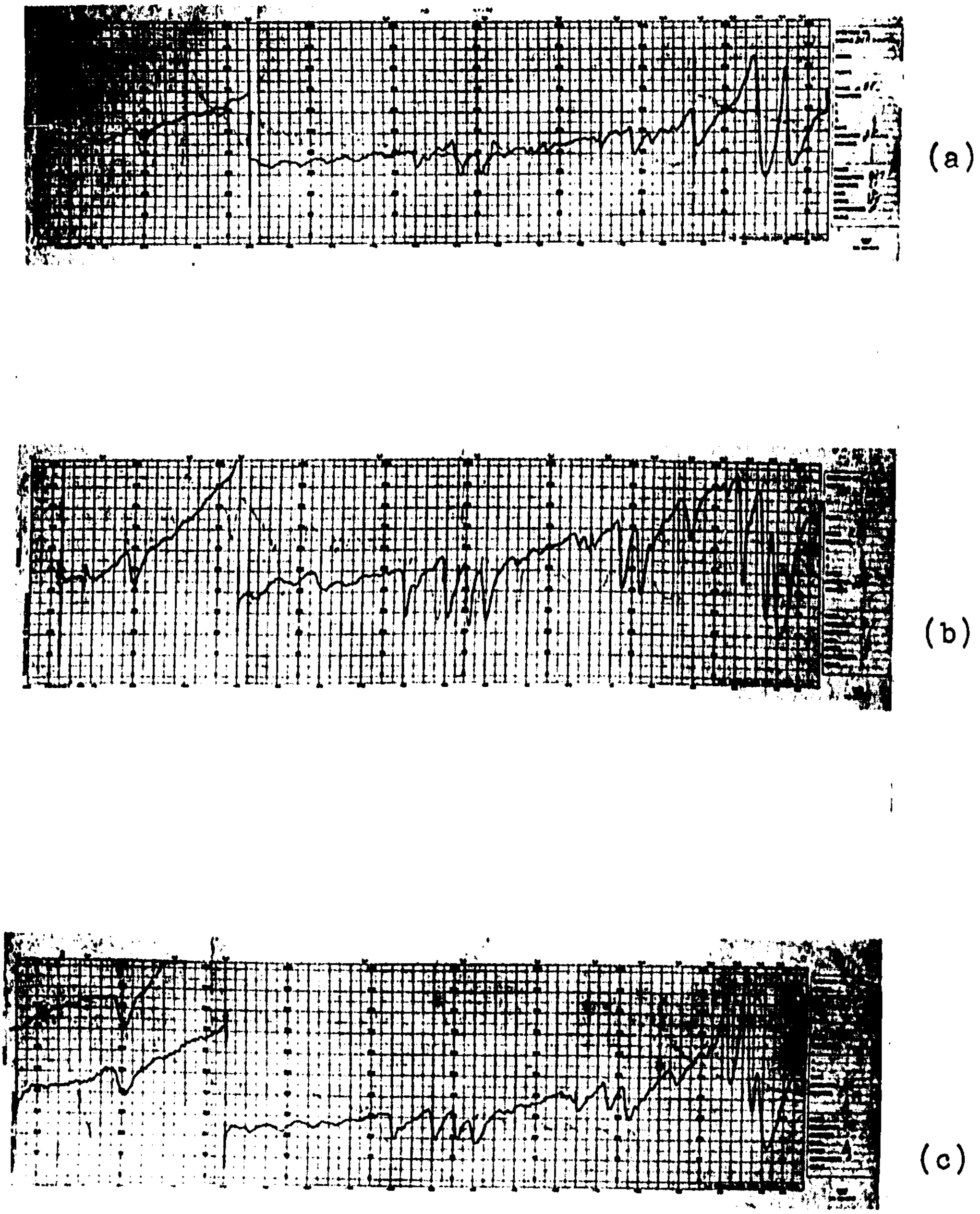


FIG. 21 INFRARED SPECTRA OF POLYDIPHENYLACETYLENE
(a) Monomer
(b) Catalyst Initiation
(c) Hexaphenylbenzene

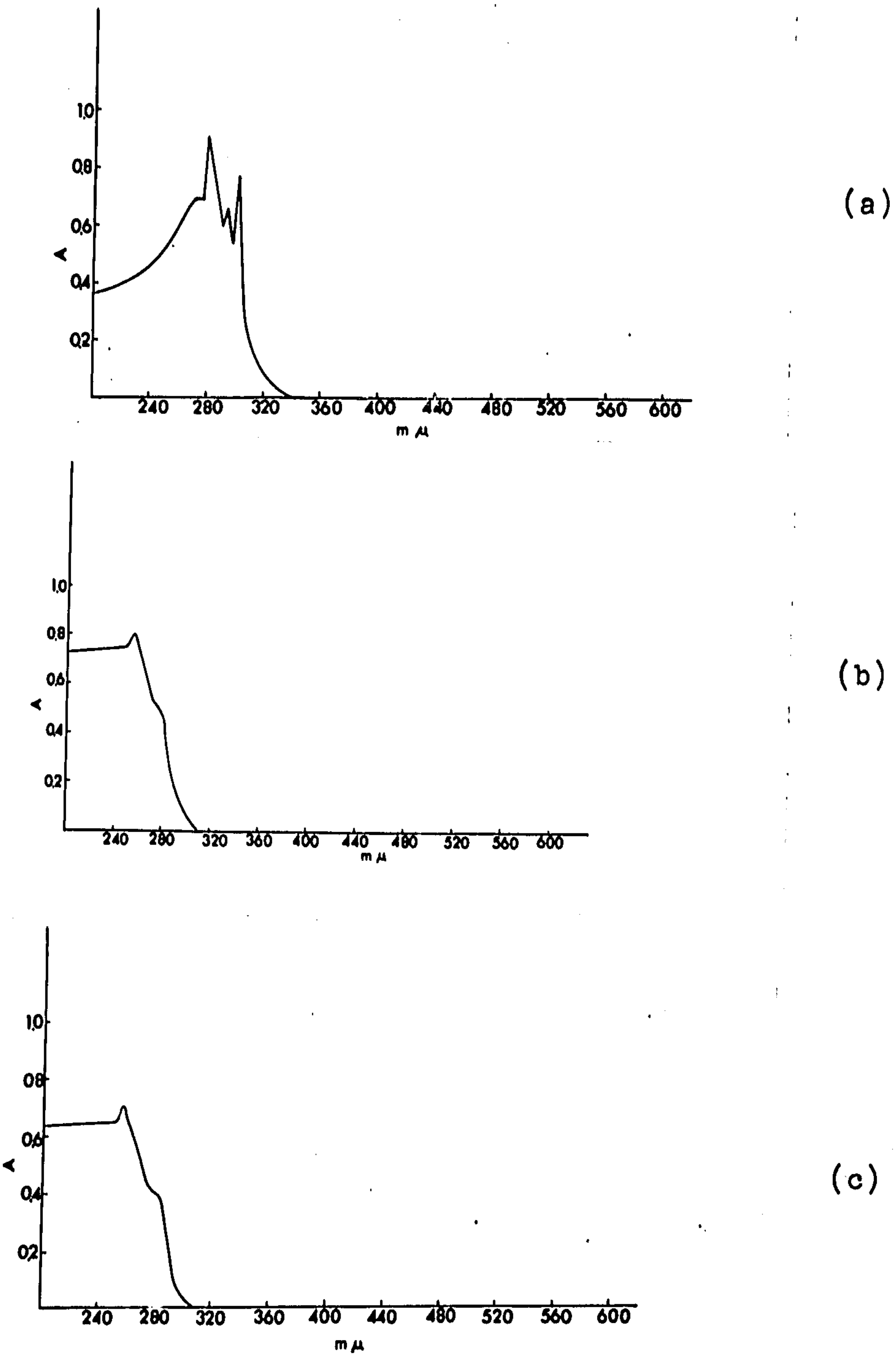


FIG. 22 ELECTRONIC SPECTRA OF POLYDIPHENYLACETYLENE
(a) Monomer
(b) Catalyst Initiation
(c) Hexaphenylbenzene

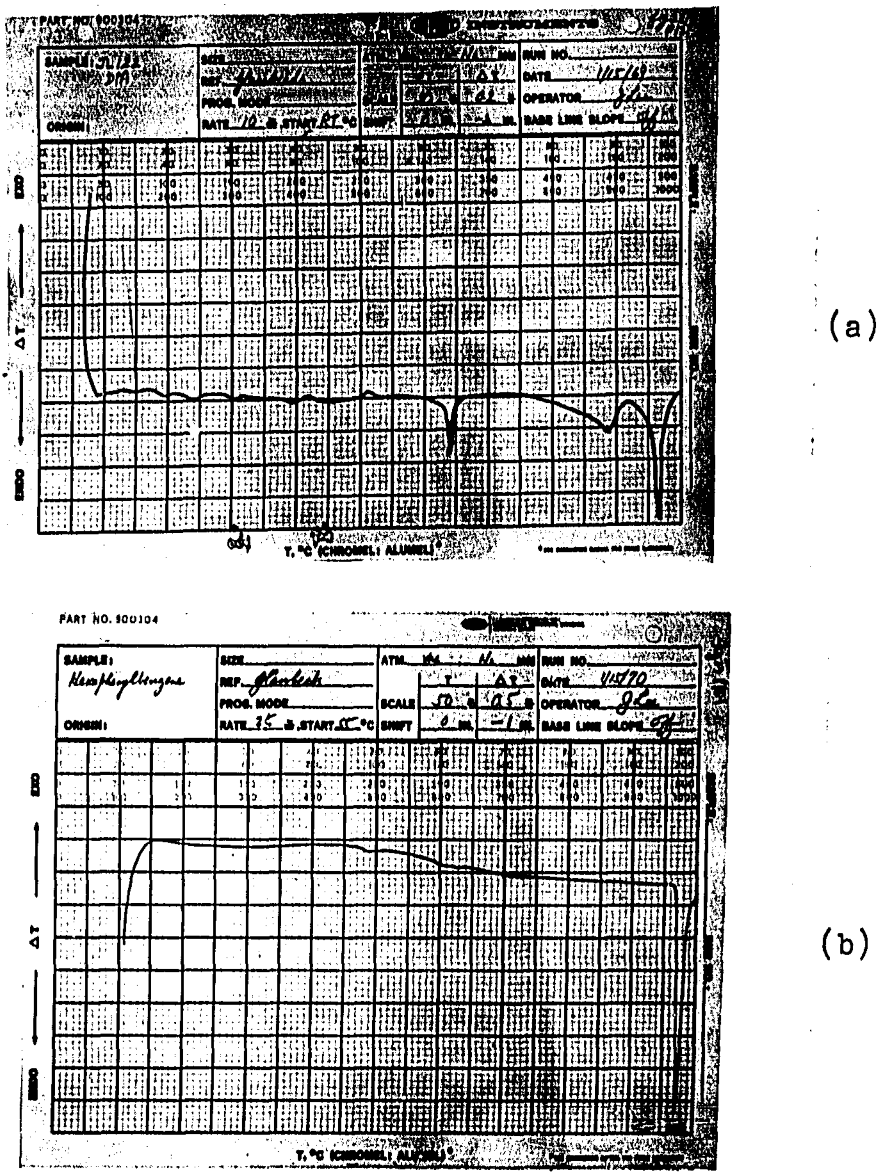


FIG. 23 DIFFERENTIAL THERMOGRAMS OF POLYDIPHENYLACETYLENE
(a) Catalyst Initiation
(b) Hexaphenylbenzene

C. Phenylacetylene. Polyphenylacetylene shows a positive color test with antimony trichloride, a big intensity increase in the infrared band at 1595 cm.$^{-1}$, a continuous absorption from ultraviolet into the visible region and an EPR signal.

The infrared spectra of the monomer and the thermally and catalyst polymerized polymer are shown in Figure 24. The bands at 3240 and 2100 cm.$^{-1}$ of the monomer are absent in the polymer, showing polymerization has taken place. The polymer by the Ziegler catalyst has new bands at 2940, aliphatic C-H stretching, increase in intensity at 1595, more conjugation and a small absorption at 890 cm.$^{-1}$, indicating a 1,3,5-trisubstituted benzene ring.[107] The thermal polymer also shows some absorption at 2900, increase in intensity at 1595, 1380 and a small absorption at 840 cm.$^{-1}$; the latter band is indicative of a 1,2,4-trisubstituted benzene ring. Although the aliphatic group in the polymer by Ziegler catalyst can be explained as coming from the organometallic in the form of a chain end, the aliphatic group in the thermal polymer may come from the chain transfer with the monomer to give a $>C=CH_2$ terminal group or it can polymerize once more into a saturated $-CH_2-$ group. There is no evidence from the ultraviolet data for the existence of a long sequence of planar conjugation as explained in Table 22.

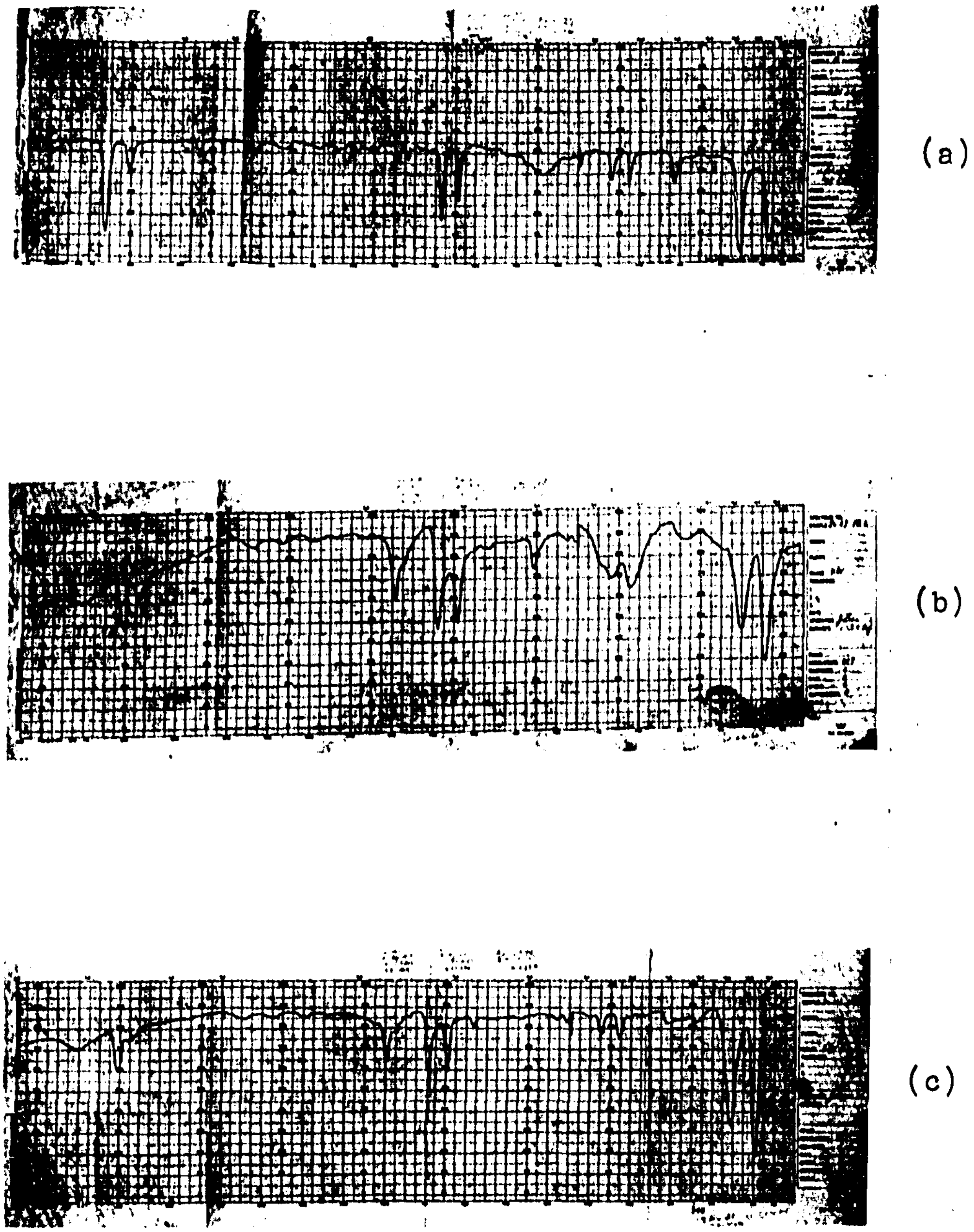
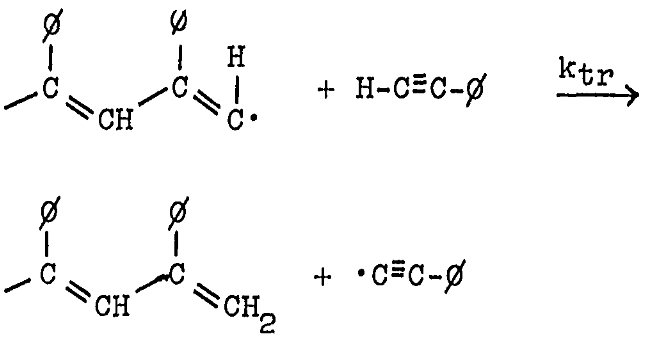


FIG. 24 INFRARED SPECTRA OF POLYPHENYLACETYLENE
(a) Monomer
(b) Catalyst Initiation
(c) Thermal Initiation



D. 2-Ethynylnaphthalene. Poly(2-ethynylnaphthalene) is a new member in the polyacetylene family. The polymer prepared under the above experimental conditions gives a positive color test with antimony trichloride, has an enhanced intensity at the 1600 cm.$^{-1}$ band in infrared, has no distinct absorption maximum in the electronic spectrum but a continuous absorption from ultraviolet into the visible, and shows an electron paramagnetic resonance signal.

The infrared spectra of the monomer and the polymer are given in Figure 25. The 3300 and 2100 cm.$^{-1}$ absorption of the monomer are absent in the polymer. The aliphatic group 2930 cm.$^{-1}$ is present. The band at 1600 cm.$^{-1}$ can be assigned to the stretching of conjugated double bonds in $-(CH=CR)_n-$, while the bands at 885 (1 isolated hydrogen), 850, 810 (2 adjacent hydrogens), and 745 cm.$^{-1}$ (4 adjacent hydrogens) are due to the out-of-plane vibrations of hydrogens in the naphthyl group. However, we are unable to determine any cyclic structures like the 1,3,5-triphenylbenzene (890 cm.$^{-1}$) and the 1,2,4-triphenylbenzene (840 cm.$^{-1}$) in polyphenylacetylene

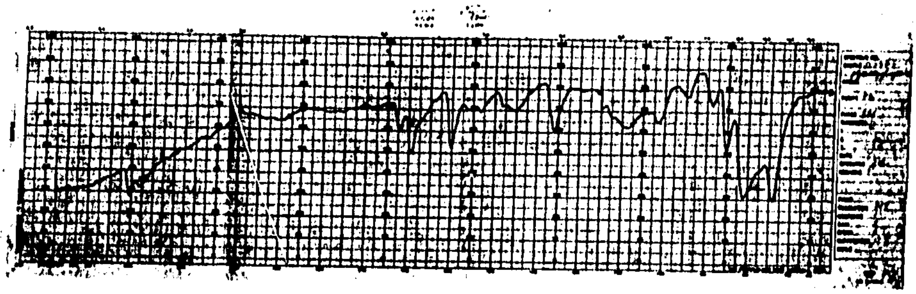


FIG. 25 INFRARED SPECTRA OF POLY(2-ETHYNYLNAPHTHALENE)

since in the present case, the naphthyl group also absorbs in this region. Nevertheless, it is reasonable to expect poly(2-ethynylnaphthalene) will closely resemble the properties of poly(ethynylbenzene).

The electronic spectrum of the monomer and the polymer is shown in Figure 26. There are three major peaks in the monomer, 277, 286 and 298 mu with three very weak peaks at 315, 325 and 336 mu. The polymer has no discrete maxima like the monomer. Instead, it shows a continuous absorption from ultraviolet into the visible region, in the form of a gradual slope. Intensity is stronger at short wave length than at long wave length. This is indicative of double bond conjugation although not necessarily planar conjugated.

The melting range of the polymers is between 190 to 230°.

E. Summary. To sum up, polydiphenyldiacetylene may have the 1,2 addition structure based on ultraviolet and infrared consideration although the 1,4 addition structure seems to be less sterically hindered on model. Polydiphenylacetylene has a cyclic structure similar to hexaphenylbenzene as the major product with perhaps trace amounts of many other products not yet identified. Polyphenylacetylene contains some 1,3,5-triphenylbenzene when polymerized with the Ziegler-type catalyst and some 1,2,4-triphenylbenzene with thermal initiation, besides the polymer. Poly(2-ethynylnaphthalene) is expected to behave

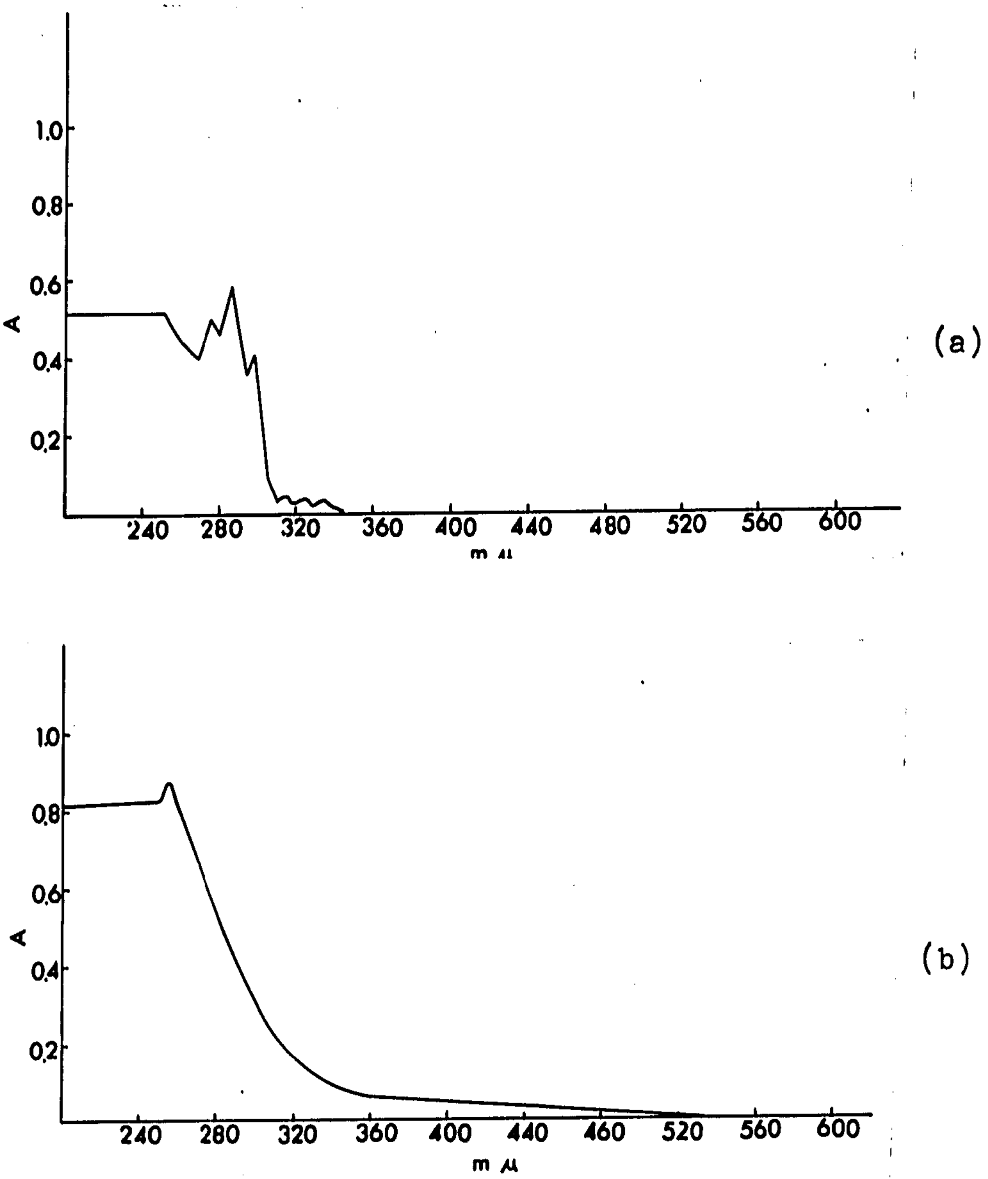


FIG. 26 ELECTRONIC SPECTRA OF POLY(2-ETHYNYLNAPHTHALENE)
(a) Monomer
(b) Catalyst Initiation

like polyphenylacetylene.

4.3.2.3 Charge-Transfer Complex Formation

It has been shown that a number of charge-transfer complexes can be prepared from the polymer which were made and characterized above. A weak charge-transfer band was observed in the electronic spectra for the color complexes of polydiphenyldiacetylene, polyphenylacetylene and β-carotene, a naturally occurring polyene with eleven conjugated double bonds. The spectra are shown in Figure 27. Antimony trichloride has an absorption around 240 mu, the polymers have a broad absorption around 300 mu, β-carotene around 462-490 mu and none of them has an absorption band at 600 mu. The new band was called a "charge-transfer band", and has been thoroughly discussed by Mulliken,[118] as characteristic of the charge-transfer complex.

Charge-transfer complexes are known to possess enhanced electrical conductivity over the parent compounds from which they are formed.[119,120] From a quantum theoretical point of view, strong concerted intermolecular mixing of the electronic molecular orbitals between the donor and the acceptor molecules will be required for the occurrence of enhanced electronic properties.[119] Molecules possessing a structure that permit a maximum orbital interlap between neighboring molecules favor high carrier mobilities and high carrier concentrations to give a high conductivity. There are two factors that tend to increase

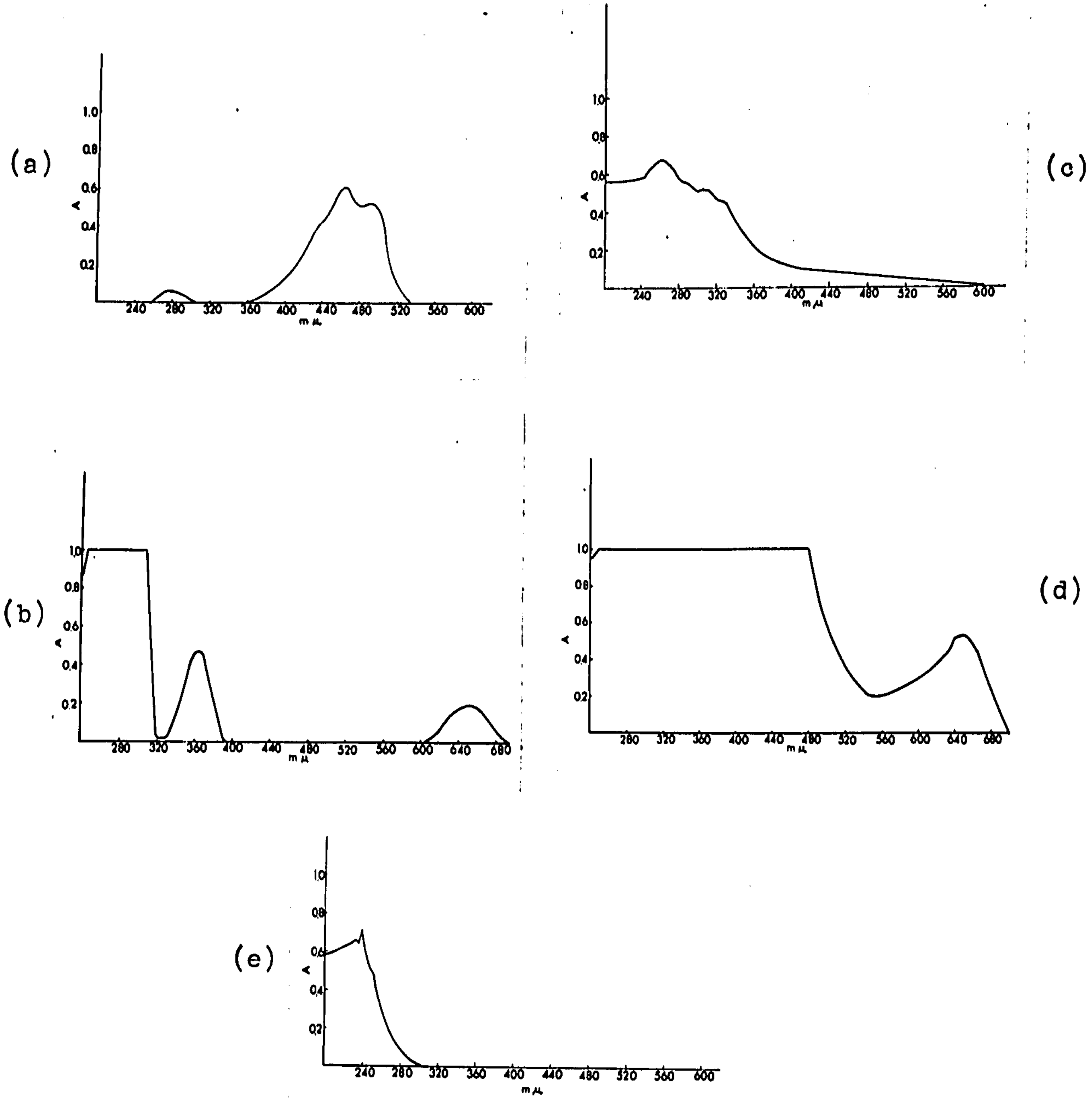


FIG. 27 ELECTRONIC SPECTRA OF POLYMER CHARGE-TRANSFER COMPLEXES

(a) β -Carotene
(b) β -Carotene/$SbCl_3$ Complex
(c) Polydiphenyldiacetylene (Catalyst)
(d) Polydiphenyldiacetylene/$SbCl_3$ Complex
(e) $SbCl_3/CHCl_3$

orbital interlap, coulombic and exchange effects. The coulombic effect may be thought of in terms of donor-acceptor action, like a charge-transfer complex. The exchange effect can be thought of in terms of mixing of states and energy band broadening, like the hypochromicity of the DNA molecular spectrum where strong π-electron interaction occurs among the planes of the base pairs. The former is intermolecular and depends on the donor-acceptor sites, while the latter is intramolecular and depends strongly on distance.

The polymers, being π-electron donors should be able to form a series of complexes with transition metals that can function as an acceptor, intermolecularly. Antimony has the following electronic configuration:

$Sb(Z=51)$; $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^3$

Sb^{3+} ; $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^0$

Stannous chloride is isoelectronic with antimony trichloride and should form a color complex in the same way:

$Sn(Z=50)$; $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^2$

Sn^{2+} ; $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^0$

Niobium pentachloride has a completely empty d orbital and it does form a color complex with the polymer and β-carotene. Table 23 summarizes the results of the preparation of charge-transfer complexes of the polymers and various acceptors. The line width, line shape and the number of paramagnetic particles in the complexes as measured by electron paramagnetic resonance spectra are

Table 23 Results of EPR Measurement on Polymers and Their Charge-Transfer Complexes

Complex		Line Width ΔH, gauss	Line Shape	g Value	Spins Concentration spins/g.
DPDA (Ziegler)	-	4.8	Lorentzian	2.034	1.30×10^{18}
" "	+ $NbCl_5$	3.8	"	2.034	6.21×10^{17}
" "	+ I_2	4.8	"	2.033	8.50×10^{17}
" "	+ $SbCl_3$	4.9	"	2.033	2.35×10^{18}
" "	+ $SnCl_2$	6.3	"	2.033	4.10×10^{17}
DPDA (thermal)	-	13.6	Lorentzian	2.034	3.10×10^{17}
" "	+ $NbCl_5$	4.8	"	2.035	8.41×10^{17}
" "	+ I_2	6.0	"	2.034	7.98×10^{18}
" "	+ $SbCl_3$	5.6	"	2.034	1.08×10^{18}
" "	+ $SnCl_2$	7.5	"	2.034	3.60×10^{16}
DPA (Ziegler)		No signal			
PA (Ziegler)	-	9.5	Gaussian	2.034	2.55×10^{17}
" "	+ $NbCl_5$	6.9	"	2.033	1.54×10^{17}
" "	+ I_2	7.9	"	2.033	1.88×10^{17}
" "	+ $SbCl_3$	9.5	"	2.033	1.20×10^{17}
" "	+ $SnCl_2$	12.5	"	2.033	1.45×10^{17}
PA (thermal)	-	13.4	Gaussian	2.034	1.40×10^{17}
" "	+ $NbCl_5$	9.7	"	2.033	4.20×10^{16}
" "	+ I_2	9.3	"	2.034	1.07×10^{18}
" "	+ $SbCl_3$	10.1	"	2.033	1.70×10^{18}
" "	+ $SnCl_2$	-	-	-	-

Table 23 (Continued)

Complex		Line Width ΔH, gauss	Line Shape	g Value	Spins Concentration spins/g.
β-Carotene	-	22.0	Gaussian	2.033	6.80×10^{16}
"	+ $NbCl_5$	13.0	"	2.033	7.60×10^{16}
"	+ I_2	11.7	"	2.033	3.10×10^{17}
"	+ $SbCl_3$	12.7	"	2.033	9.90×10^{16}
"	+ $SnCl_2$	21.8	"	2.033	0.83×10^{16}
2-Ethynylnaphthalene (Ziegler)		12 - 21	Gaussian	2.033	$1.1\text{-}8.1 \times 10^{16}$

also included. The EPR spectra showed no resolved hyperfine structure, but a singlet and a g value of 2.033, very similar to that of a free electron. From Table 23 we see that the monomers are not paramagnetic, but polydiphenyldiacetylene and polyphenylacetylene are. The line width of the EPR signal is always narrower for the Ziegler catalyst prepared polymer than the thermal polymer. The line shape of the EPR curve is Lorentzian for polydiphenyldiacetylene and Gaussian for polyphenylacetylene and β-carotene. The line shape of the charge-transfer complex is governed by the line shape of the polymer. If the polymer has a Gaussian line, then the complexes also have a Gaussian line. At least for the polymer, the narrower the line width, the larger is the number of paramagnetic particles per gram in the sample. The line width of the complexes increases gradually in the order of $Sn > Sb > I_2 > Nb$. With iodine crystal and antimony trichloride, complex formation leads to an increase in the number of unpaired electrons per gram in the sample. This increase in paramagnetic properties and, hence, electrical conductivity properties is probably the result of the increased ease of the mixing of the ionic states that is caused by decrease of the excitation energy from the ground state to the excited states due to orbital delocalization.

It has been shown that if the EPR line is Lorentzian, the spin-spin relaxation time T_2, a measure of the mean life-time of a particular configuration is related to the line width ΔH by[91]

$$T_2 = \frac{1}{1.52 \times 10^7 \Delta H}$$

Since the range of ΔH values for polydiphenyldiacetylene is about 4 to 15 gauss, the range of the spin-spin relaxation time is from 1.6 to 0.5×10^{-8} sec., and the specific duration of the radical state cannot be shorter than this. T_2 for polyphenylacetylene calculated this way is 0.8 to 0.5×10^{-8} sec., and that for poly(2-ethynylnaphthalene) is 0.6 to 0.3×10^{-8} sec.

5. CONCLUSIONS

The polymerization of diphenyldiacetylene, diphenylacetylene, phenylacetylene, and 2-ethynylnaphthalene was studied under very carefully controlled conditions to exclude oxygen, moisture and light to which the resulting polyenes may be sensitive. The polymers thus prepared showed properties different from those prepared by other means. They have a higher molecular weight and form charge-transfer complexes with suitable π-electron acceptors. Poly(2-ethynylnaphthalene) is a new polymer. Their structures and stereochemistry are discussed.

Polymerization of diphenyldiacetylene by the stereospecific Ziegler-type catalyst with carefully controlled inert atmosphere gives consistently a higher molecular weight than reported in the literature. The structure is probably of the 1,2 addition type, with spiralling to relieve steric crowding. A structure of the 1,4 addition type that has a long sequence of planar conjugated double bonds is less likely, based on electronic spectral considerations. Thermal polymerization in the absence of catalyst is a second order reaction. The rate of polymerization is proportional to the square of the monomer concentration and the molecular weight of the polymer appears to be independent of the monomer concentration. It is concluded that thermal polymerization involves a bimolecular initiation and termination step.

Polydiphenyldiacetylene obtained this way is always soluble in aromatic solvents so that a three-dimensional crosslinked structure can be precluded. The softening temperature is 270-300° although no sharp endotherm is observed in differential thermal analysis. They are dark-brown in color, have an electron paramagnetic resonance signal without hyperfine structures and the spin concentration increases upon formation of charge-transfer complexes. Gamma irradiation with cobalt-60 yields a dimer.

Polymerization of diphenylacetylene by the stereospecific Ziegler-type catalyst gives mostly colorless trimer and some polymer. A benzene soluble polymer ($\overline{M}_n$ 466-859) can be separated from the benzene insoluble trimer which is hexaphenylbenzene. Based on infrared and ultraviolet measurements, the structure of the polymer must be also very similar to that of hexaphenylbenzene. However, differential thermal analysis reveals that trace amounts of many other products are present. Polydiphenylacetylene obtained this way has two fractions, about 10% benzene soluble fraction and about 90% benzene insoluble fraction. Both fractions do not react with antimony trichloride to give a positive color test for a conjugated double bond system and do not give an EPR signal. Their melting points are greater than 450°. There was no thermal polymerization up to 140° under our experimental conditions. Gamma irradiation gave a dimer in very low yield.

Phenylacetylene could be polymerized thermally or catalytically. Thermally prepared polyphenylacetylene contains a small amount of 1,2,4-triphenylbenzene and Ziegler-type catalyst initiated polymer contains some 1,3,5-triphenylbenzene, besides the expected polymer as detected by infrared spectra. Thermally prepared polymers are soluble in aromatic solvents. The catalyst prepared polymer becomes insoluble as the Al:Ti ratio increases. The presence of a long planar conjugated sequence is unlikely on the basis of ultraviolet data. Polyphenylacetylene obtained this way is orange colored, with a softening temperature of 160-200°, an EPR signal without hyperfine structures and forms charge-transfer complexes with suitable π-electron acceptors.

Poly(2-ethynylnaphthalene) was prepared by the Ziegler-type catalyst. It is the first polymerization of this monomer which was prepared in a pure form by a modified Robin's procedure. The highest number average molecular weight of the polymer is 2091, corresponding to a degree of polymerization of 14 monomer units. The polymer is reddish colored, soluble in aromatic solvents and has a softening temperature slightly higher than polyphenylacetylene, at 190-230°. Poly(2-ethynylnaphthalene), like polyphenylacetylene, is paramagnetic, has an EPR signal without resolved hyperfine structures. Infrared spectra and color test indicated a conjugated double bond system. However, long planar conjugated sequence is unlikely.

6. APPENDIX

In the thermal polymerization of diphenyldiacetylene, the following reaction scheme can be visualized.

1. $M_1 + M_1 \xrightarrow{k_i} 2M^*$ $\qquad V_i = 2k_i[M]^2$
2. $M_n^* + M \xrightarrow{k_p} M_n{+}1^*$ $\qquad V_p = k_p[M^*][M]$
3. $M_n^* + M \xrightarrow{k_{tr}} M_n{+}M^*$ $\qquad V_{tr} = k_{tr}[M^*][M]$
4. $M_n^* + M_m^* \xrightarrow{k_{t_2}} M_n{+}M_m$ or M_{n+m} $\qquad V_{t_2} = 2k_{t_2}[M^*]^2$
5. $M_n^* + \xrightarrow{k_{t_1}} P$ $\qquad V_{t_1} = k_{t_1}[M^*]$

where M is the monomer, M^* the chain radical, k and V are the rate constant and the rate of reaction. Reactions 2) the propagation and 4) bimolecular termination must be second order processes. Reaction 1) chain initiation cannot be first order (in the absence of catalyst) because Flory[100] has shown that the energy requirement for such a process is too great. It can be either second or third order. Reaction 5), a unimolecular termination indicates that the chain radical somehow loses its activity to polymerize and goes to product itself. Reaction 3) is a chain transfer reaction, and is also second order. We want to show the rate dependence on monomer concentration.

a. Bimolecular initiation and Bimolecular termination. Applying the steady-state condition, the rate of initiation equals the rate of termination.

$$V_i = V_{t_2}$$

$$[M^*] = \left(\frac{k_i}{k_{t_2}}\right)^{\frac{1}{2}} [M]$$

$$\text{Rate} \doteq V_p = k_p[M^*][M] = k_p \left(\frac{k_i}{k_t}\right)^{\frac{1}{2}} [M]^2$$

$$\text{Kinetic chain length} = \nu = \frac{V_p}{V_{t_2}} = k_p \left(k_t k_i\right)^{\frac{1}{2}}$$

In this case, the rate depends on second power of $[M]$ and the molecular weight independent of $[M]$.

b. Bimolecular initiation and Unimolecular termination.

$$V_i = V_{t_1}$$

$$[M^*] = \frac{2k_i}{k_{t_1}} [M]^2$$

$$\text{Rate} \doteq V_p = k_p[M^*][M] = \frac{2k_p k_i}{k_t} [M]^3$$

$$\text{Chain length} = \nu = \frac{V_p}{V_{t_1}} = \frac{k_p}{k_t} [M]$$

In this case, the rate depends on the third power of $[M]$, and molecular weight depends on the first power of $[M]$.

c. Termolecular initiation and Bimolecular termination.

$$V_i = V_{t_2}$$

$$[M^*] = \left(\frac{3k_i}{k_t} \right)^{\frac{1}{2}} [M]^{3/2}$$

$$\text{Rate} \doteqdot V_p = k_p[M^*][M] = k_p \left(\frac{3k_i}{k_t} \right)^{\frac{1}{2}} [M]^{5/2}$$

$$\text{Chain length} = \nu = \frac{V_p}{V_{t_2}} = \frac{k_p}{2} \left(\frac{k_t}{3k_i} \right)^{\frac{1}{2}} [M]^{-\frac{1}{2}}$$

In this case the rate depends on the five-half power of $[M]$ and the molecular weight depends inversely on the square root of $[M]$.

d. Termolecular initiation and unimolecular termination.

$$V_i = V_{t_1}$$

$$[M^*] = \frac{3k_i}{k_t} [M]^3$$

$$\text{Rate} \doteqdot V_p = k_p[M^*][M] = \frac{k_p 3k_i}{k_t} [M]^4$$

$$\text{Chain length} = \nu = \frac{V_p}{V_{t_1}} = \frac{k_p}{k_t} [M]$$

In this case, the rate depends on the fourth power of $[M]$, and the molecular weight depends on the first power of $[M]$.

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