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Study of Radical Polymerization of Arylacetylenes. Composition, Structure, and Some Properties of the Generated Products

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ABSTRACT

Radical polymerization of 2-methyl-5-ethynylpyridine (MEP) and the structure and some properties of phenylacetylene and pentafluorophenylacetylene polymers were investigated. As the first step in polymerization of MEP in the presence of azo-1-cyclohexylcarboxylic acid dinitrile at 94-115°C the monomer conversion is proportional to the quantity of decomposed initiator: 1 mole of initiator causes transformation of 5-7 mole of monomer. At a high degree of polymerization the yield of polymer is not proportional to the initial initiator concentration. The products generated in MEP polymerization initiated thermally or by azo compounds were investigated by means of gel-permeation chromatography, ozonation, ^{1}H-NMR, IR, and UV spectroscopy. Initiation with azo compounds afforded cyclic trimer (tripicolylbenzene) and a fraction with a number average molecular weight $\overline{M}_n$ of 1550. Thermal polymerization yielded the dimer (picolyl-substituted quinoline or isoquinoline), tripicolylbenzene, hexamer, and fractions with $\overline{M}_n$ = 1500 and 1800. Composition and properties of the polymerization products enable one to assume the presence of poly-MEP hexadiene rings in the main chain. Formation of cyclodiene structures by facile aromatization in the course of arylacetylenes polymerization was confirmed by investigations of the structure and some properties of polyphenylacetylenes and polypentafluorophenylacetylenes. A mechanism of radical polymerization of arylacetylenes is proposed.

INTRODUCTION

Critical analysis of experimental data on the polymerization of acetylenes and structure and properties of the generated products summarized and systematized in some reviews [1-4] and monographs [5-7] leads to the following conclusions.

The polyene chain structure is assigned with confidence to polyacetylenes (polyvinylenes) obtained under different initiation methods. Differences in the behavior of polyalkyl- and polyarylacetylenes are explained by hydrogen migration from a side alkyl group into the main chain, giving rise to the alkylidene side groups and distorting the main chain conjugation. However, experimental data that support the conclusions on structure of polyacetylene chains are rather contradictory and in some cases could be interpreted alternatively.

Sharply different properties of polyphenylacetylenes obtained by different methods are usually explained by variable chain conformation on the basis of less vigorous experiments.

At low degrees of polymerization, independent of the nature of the monomer and polymerization method, chain scission is associated first of all with "fading" of active centers, i.e., with intra- and intermolecular unpaired electron delocalization in the growing macroradical over the conjugate bond system generated. However, this is inconsistent with the impossibility of delocalization of active center radicals over the conjugation chain because of their spatial location and with the data of molecular weight distribution of the phenylacetylene polymerization products [8].

This paper is an attempt to explain the specificity of arylacetylenes polymerization and the structure of the generated products by using results of radical polymerization of 2-methyl-5-ethynylpyridine, the structure and some properties of polyphenylacetylene and polypentafluorophenylacetylene.

EXPERIMENTAL

Synthesis and Preparation of the Starting Materials

2-Methyl-5-vinylpyridine was obtained by fractional distillation of a commercial product. The mean fraction was dried over $MgSO_4$ and repeatedly fractionated, bp 74°C/15 Torr, n_D^{20} 1.5443 (lit. [9]: bp 75°C/15 Torr, n_D^{20} 1.5454).

2-Methyl-5-ethynylpyridine (MEP) was obtained from 2-methyl-5-vinylpyridine by the method of Kost et al. [10]. Crystallization from petroleum ether and drying over KOH gave mp 51°C (lit. [10] mp 51-52°C).

Pentafluorophenylacetylene was prepared by method proposed by Coe et al. [11] [Eq. (1)].

$$C_6F_5Cl \xrightarrow[C_2H_4Br_2]{\text{Mg, ether}} C_6F_5MgCl \xrightarrow[\text{(2) } H_2O]{\text{(1) } CCl_3C(O)H}$$

$$C_6F_5CH(OH)CCl_5 \xrightarrow{PCl_5} C_6F_5CHClCCL_3 \xrightarrow{AlBr_3}$$

$$C_6F_5CH{=}CCl_2 \xrightarrow[\text{THF}]{\text{Mg}} C_6F_5C{\equiv}CH \tag{1}$$

After drying over CaO and distillation (bp 130.5°C; lit. [11] bp 131°C), the generated product contained (gas chromatography) THF (less than 1-2%), pentafluorostyrene, and some unidentified impurities (less than 1%). After purification via copper acetylenide and decomposition with HCl [12], pentafluorophenylacetylene had no impurities (IR and NMR data, Fig. 10).

2,2'-Azobisisobutyronitrile (AIBN) was crystallized from methanol, mp 102-103°C (dec.).

Perdeutero-2,2'-azobisisobutyronitrile (AIBN-D_{12}) was prepared by the method described for AIBN [13] and crystallized from absolute ether; mp 103-104°C (dec.).

Azo-1-cyclohexylcarboxylic acid dinitrile (ACD) was obtained from cyclohexanone [13]. Crystallization from 95% ethanol gave product with mp 113-114°C. Volumetric analysis of the nitrogen evolved after ACD decomposition showed no less than 98% of the main component.

1,1,2,2-Perdeuterotetramethylsuccinyl dinitrile was prepared by thermal decomposition of AIBN-D_{12} in benzene solution. The solvent was evaporated and the residue employed for gel-permeation chromatography without further purification.

Benzoyl peroxide was purified by precipitation from chloroform with methanol; mp 105°C.

The solvents used in reactions were purified by the usual procedures. Ozonation was performed in CCl_4 and $CHCl_3$, UV-spectroscopy grade. $CHCl_3$ was used as eluent in gel-permeation chromatography without additional purification.

Argon was purified from oxygen impurities over chromium-nickel catalyst and dried over molecular sieves.

Polymerization and Product Separation

The kinetics of ACD decomposition was studied in an ampoule joined consecutively to a measuring buret and pressure balancing vessel. The buret and vessel were filled with p-xylene. An ampoule containing the ACD sample (0.05 g in 1 ml of p-xylene) was placed in an oil bath. The evolved nitrogen volume was recorded in the buret by balancing the pressure in the system. In a reference run (p-xylene without ACD) a correction for volume expansion was determined at all temperatures. The quantity of nitrogen evolved upon decomposition of ACD in the course of polymerization showed that the presence of MEP does not change the kinetics of ACD decomposition. Thus the polymerization does not involve an essential temperature change owing to the polymerization heat effect, and MEP does not affect ACD decomposition.

MEP and ACD in selected ratios were carefully ground in an agate mortar; the mixture (0.03-0.1 g) was placed in glass ampoules (ca. 7 mm diameter, 4 ml volume) and sealed. All operations were carried out under argon. After polymerization the mixture was diluted with p-xylene to a concentration of ca. 0.012 g/ml. The monomer conversion was determined spectrophotometrically from the $\nu_{\equiv C-H}$ band at 3320 cm^{-1}. Preliminarily it was shown that in the range of concentrations from 0.008 to 0.013 g/ml the band intensity change follows Beers' law.

MEP in the presence of AIBN was polymerized in glass ampoules flushed with argon (ca. 20 mm diameter, ca. 30 ml capacity) and sealed at 60-120°C (± 0.1°C). A 1-g sample contained 0.5-7 wt % AIBN. The polymerization products were dissolved in 6 ml of benzene and precipitated in 50 ml of n-hexane. The solid was washed with n-hexane on a filter and dried under vacuum over P_2O_5. MEP was polymerized analogously in the presence of AIBN in p-xylene.

The MEP polymerization products were analyzed by means of gel-permeation chromatography. Sephadex LH-20 was used as stationary phase and chloroform as mobile phase. Detection was performed with a UR-20 spectrophotometer (NaCl cuvette, 0.59 mm thickness) at 1592 cm^{-1} (pyridine ring absorption) and 2240 cm^{-1} (CD_3 group). After MEP polymerization in the presence of AIBN, the ampoule was opened and the contents diluted with chloroform to ca. 20% concentration. The 0.5-0.7 ml samples were placed on a column (320 × 22 mm); elution rate was 1.1-1.3 ml/min. The fractions obtained were evaporated and dried in vacuo over KOH. The MEP thermal polymerization products were analyzed analogously on a 720 × 22 mm column (ca. 0.8 ml samples, ca. 20% concentration, elution rate 1.3-1.5 ml/min).

Catalytic PPAC [14] and thermal polyphenylacetylene (PPAT) (150°C, 6 hr) were supplied by laboratory colleagues. There were additionally dried in vacuo over P_2O_5. PPAC unsaturation was determined by an ozonation method as 37-40%.

Anal. Calc for $(C_8H_6)_n$ (PPAC): C, 94.11%; H, 5.89%. Found: C, 92.90%; H, 5.78%; no inorganic residue.

PPAC Aromatization

PPAC (0.3 g), $CuCl_2$ (1 g), and benzene (10 ml) were heated to 40°C for 30 min and then 20 ml of 18% HCl was added after cooling. The mixture was shaken, the benzene layer was precipitated in 150 ml of methanol, the solid filtered off, washed with methanol on a filter, and dried in vacuo. Unsaturation detected by ozonation method was 32%.

PPAC (0.738 g), $CuCl_2$ (1.028 g), and o-xylene (2 ml) were heated to 70°C for 1 hr, 20 ml of water was added, and the mixture extracted three times with o-xylene (2 ml each). The combined xylene extracts were precipitated in 120 ml of methanol. The solid was filtered off, washed with methanol on a filter, and dried in vacuo. Unsaturation as detected by an ozonation method was 26%.

PPAC (0.3 g), tetrachloro-o-benzoquinone (0.37 g), and benzene (5 ml) were kept at room temperature and 70°C for 48 and 15 hr, respectively. The mixture was precipitated in methanol (100 ml). The solid was extracted in a Soxhlet apparatus with methanol and dried in vacuo. The obtained products had molecular weights of 2300 and 3340 and unsaturations of 11 and 10%, respectively.

Anal. Calcd for the product aromatized at 70°C under action of tetrachloro-o-benzoquinone, $[(C_8H_6)_{13}\cdot C_6Cl_4O_2]_2$: C, 83.97%; H, 4.96%; Cl, 9.03%. Found: C, 83.96%; H, 5.03%; Cl, 8.76%.

Instrumental Investigation Methods

Samples were ozonized in CCl_4 or $CHCl_3$ at -20 to -30°C by using methods analogous to those described by Berlin et al. [15]. A 1-ml sample was used, and trans-stilbene and decene-1 were used as standards. Concentrations of standard and ozonized polymer were 0.001-0.006 mole/liter and 0.005-0.01 mole/liter, respectively. For 2-methyl-5-ethylpyridine no oxidation of the picoline nucleus is observed under ozonation conditions.

After ozonation of PPAC of molecular weight 3650 (0.120 g) (completion of ozone absorption) the solvent ($CHCl_3$) was evaporated and the residue decomposed for 6 hr at 64°C/10^{-2} Torr. Repeated ozonation of the product with molecular weight 520 (0.116 g) revealed no double bonds.

The number-average molecular weights ($\overline{M}_n$) were determined by using thermoelectric [16] and ebullioscopic methods [17].

IR spectra were recorded on a UR-20 spectrophotometer (GDR) in solutions (NaCl cuvette, 0.59 mm thickness) or as KBr disks.

UV spectra were recorded on Specord UV-Vis (GDR) instrument in 1-cm cuvettes.

NMR spectra were measured on Tesla BS-487B spectrometer (Czechoslovakia) at 80 MHz. Concentrations in CCl_4 or deuteroacetone solutions were 10-15%. Hexamethyldisiloxane with 0.5 ppm chemical shift was used as internal standard (with δ of tetramethylsilane equal to 0). The temperature varied from 30 to 90°C.

RESULTS AND DISCUSSION

Kinetics of Radical-Initiated MEP Polymerization

At the same monomer/initiator ratios, the polymer yield is much higher in the presence of AIBN than with benzoyl peroxide. This may be due to a chain decay of benzoyl peroxide under the action of MEP or poly-MEP as in the benzoyl peroxide-phenylacetylene system [18]. Oxidation of the picoline nucleus and the polymer chain cannot be excluded as well.

At 60-80°C, the efficiency of initiation of MEP polymerization by AIBN is low. Depending on the concentration in benzene, 1 mole of decomposed initiator causes transformation of 2-5 mole of MEP. This is evidence for predominant intracell recombination of the primary radicals and agrees with the concept of the low acetylenes activity towards the free-radical addition reactions [19]. To obtain experimentally observable conversions, one has to employ a substantial quantity of initiator (5-10 mole %), which interferes with kinetical investigation.

High synthesis temperature (90-120°C) increase the apparent initiation efficiency. Polymer yield increases twofold at the same initial initiator concentration; however, $\overline{M}_n$ (800-1000) is practically the same. AIBN decomposition at 100-120°C is sufficiently fast, requiring no more than 1 hr, but the polymer yield increases upon further exposure of the mixture (Fig. 1). On the other hand, no MEP polymerization occurs without initiator or in the presence of poly-MEP obtained independently. Thus "quasiradical" polymerization [20] does not take place. Active postpolymerization centers could be gradual regeneration products of some stable radicals at the first step and the polymer chain degradation products. The absence of initiating activity with polymer shows that the polymer loses its activity in the course of synthesis and separation.

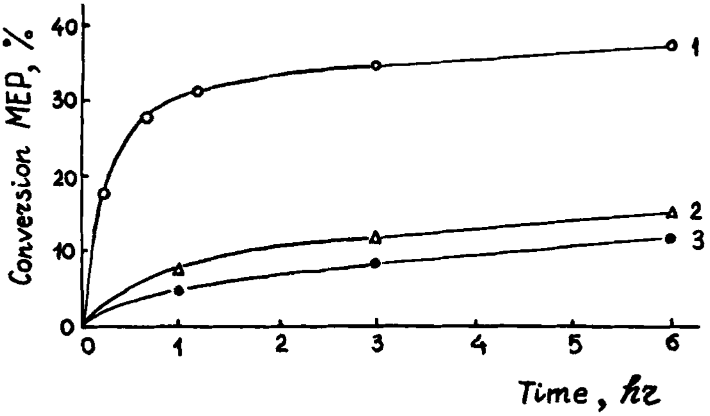


FIG. 1. Effect of reaction time and temperature on polymerization of MEP (1) in bulk and (2, 3) in p-xylene solution: (1) 120°C, 7 wt % AIBN; (2) 120°C, 1.4 wt % AIBN, 19 wt % MEP; (3) 100°C, 1.4 wt % AIBN, 19 wt % MEP.

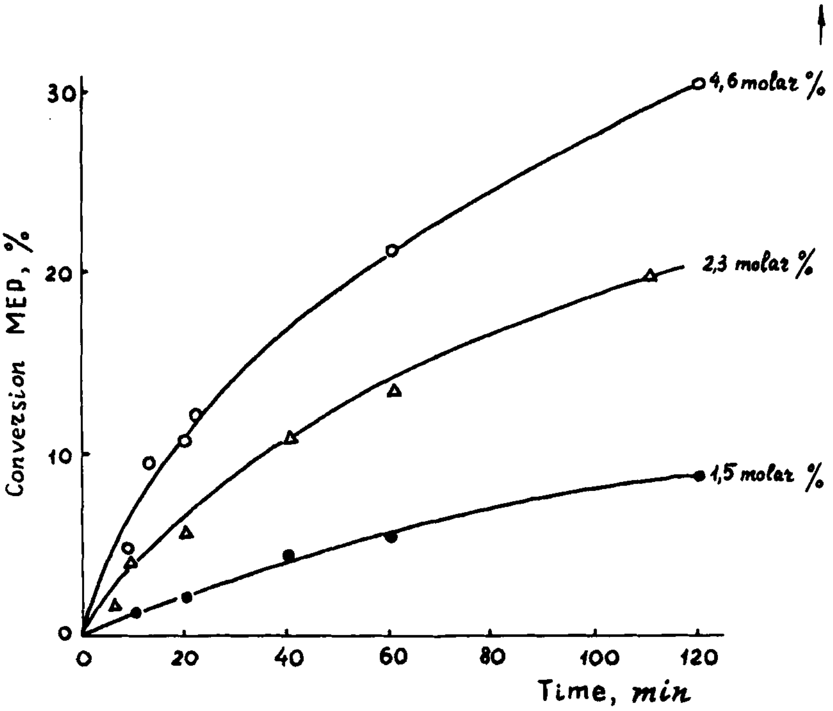


FIG. 2. Effect of initiator concentration on bulk polymerization of MEP (105 ± 0.1°C).

The kinetics of MEP polymerization at 80-120°C was studied with ACD. The rate constants of ACD decay via monomolecular mechanism measured in p-xylene at 94, 105, and 115°C are 0.44×10^{-4}, 1.64×10^{-4}, and 5.60×10^{-4} sec^{-1}, respectively. The obtained activation energy of ACD decay, 37 ± 1 kcal/mole, is in good agreement with the value obtained earlier [21]. MEP and its generated polymer do not alter the kinetics of ACD decay.

Analysis of MEP transformation curves under action of ACD (Figs. 2 and 3) shows that at the primary steps conversion of MEP is proportional to the quantity of initiator decomposed:

$$w = k_1[\mathrm{ACD}]$$

and

$$w = k_2 w_{\mathrm{ACD}}$$

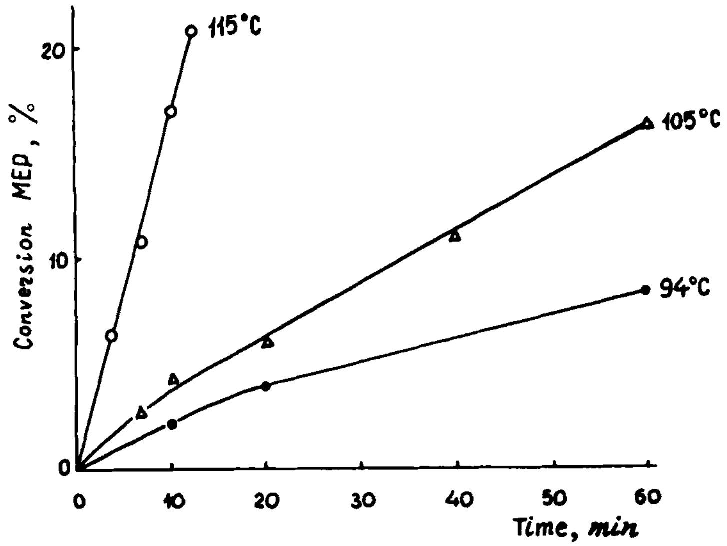


FIG. 3. Effect of temperature on bulk polymerization of MEP (2.3 mole % ACD).

where w is polymerization rate and w_{ACD} is the rate of ACD decay. The numerical value of k_2 varies from 5 to 7 with polymerization temperature; thus it is not possible to specify the scheme of MEP transformation under action of ACD (ACD + 5 - 7 [MEP] products).

This is valid only at the primary steps. Above 10% conversion the polymer has a basic effect on the polymerization process, probably due to reaction of primary radicals with the polymeric chain. In such a case, the limiting polymer yield is not proportional to the starting initiator concentration (Fig. 3).

Thus, by investigating MEP polymerization kinetics in the presence of radical initiators one cannot ascertain the processes occurring or explain the formation of low molecular weight products. Therefore it is important to establish the composition and structure of polymerization products.

Products of Initiated MEP Radical Polymerization

MEP polymerization products were separated by means of gel-permeation chromatography. Preliminary experiments show that this method provides satisfactory separation of an artificial mixture of the

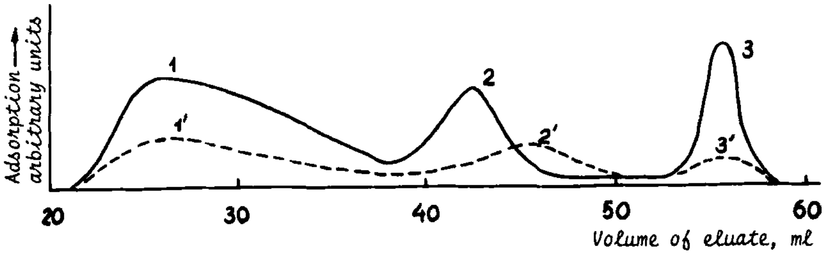


FIG. 4. GPC of products of bulk polymerization of MEP (4 wt % AIBN-D_{12}, 75°C, 20 hr) with detecting at (—) 1594 cm^{-1} and (--) 2240 cm^{-1}: (1) $\overline{M}_n$ = 1550; (2) $\overline{M}_n$ = 310 (see text).

lowest phenylacetylene analogs (phenylacetylene, 1,4-diphenylbutadiene-1,3, 1,3,5-triphenylbenzene). Figure 4 shows a gel chromatogram of MEP polymerization products obtained with AIBN-D_{12} after complete decomposition of initiator.

The apparent initiation efficiency of ca. 0.5 estimated by comparison of 1' and 2' + 3' band intensities is close to that of polymerization of vinyl monomers in the presence of AIBN [22].

Fraction 2 with $\overline{M}_n$ = 310 corresponds to the cyclotrimer. Its IR spectrum (Fig. 5) contains no absorption specific for the olefinic and acetylenic compounds [23]. Its UV spectrum (Fig. 6) shows no double bonds conjugated with the pyridine ring [24]. IR and UV spectra of fraction 2 coincide with the spectra of cyclotrimer isolated from the products of thermal MEP polymerization whose structure has been confirmed earlier [25, 26]. Moreover, formation of cyclotrimers in the initiated radical polymerization of arylacetylenes was confirmed by investigating polymerization of pentafluoroacetylene by an NMR method which is discussed later. Thus fraction 2 is tripicolylbenzene.

A considerable quantity of cyclotrimer (fraction 2 constitutes ca. 25% of fractions 1 + 2) and the absence of linear low molecular weight polyenes in the initiated radical polymerization of arylacetylenes are hardly explained in terms of the modern concepts on their polymerization mechanism [1]. In our opinion, intramolecular cyclization of the growing polyenic chain (I) generates hexadiene radicals (III, IV) whose elimination leads to tripicolylbenzene (VIII). The cyclization takes place in the propagation step but not in the course of polymer degradation (II → I → VIII, II → V → VIII); i.e., with exposure of

FIG. 5. IR spectra of products (CCl_4 solution) of MEP polymerization (AIBN-D_{12}). Spectrum numbers correspond to fraction numbers given on Fig. 4.

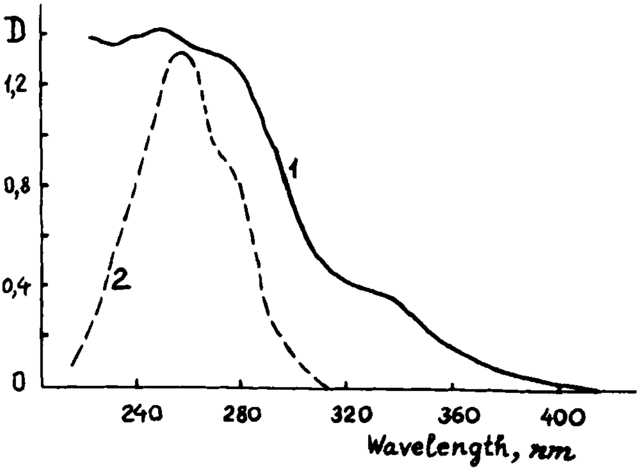
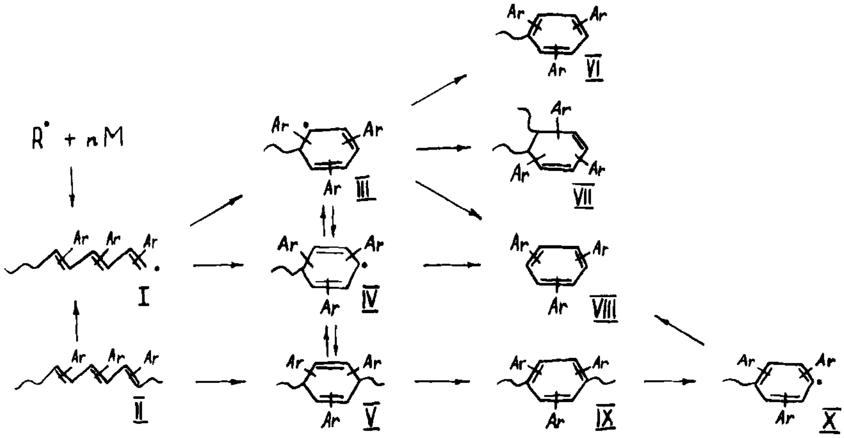


FIG. 6. UV spectra of products (methanol solution, 0.01 g/l) of MEP polymerization (AIBN-D_{12}). Spectrum numbers correspond to fraction numbers given on Fig. 4.



poly-MEP in the presence of AIBN at 80° C, no cyclotrimer formation was detected. Cyclohexadiene structures could also be generated via Diels-Alder intermolecular reaction (I + monomer → IV).

The presence of cyclic structures in the main chain agrees with the degree of poly-MEP unsaturation (double bond content per monomer unit). According to ozonation data and corrected on the basis of initiator fragments, this value is 70 ± 5% (for the polyenic chain it should be equal to 100%).

The poly-MEP absorption in the region of 320-340 nm (Fig. 6) may be due to 1,3-cyclohexadiene structures. Analysis of the spectrum shows that polyene segments separating the cyclohexadiene units in the polymer do not exceed two monomer units in length. The absorption above 400 nm may be due to impurities. This is evident from the very low band intensity and from the intense blue zone upon separation of MEP polymerization products (in the presence of ACD and AIBN above 90° C) which practically does not elute on chromatographic column.

Products of Thermal Polymerization of MEP

Figure 7 shows a gel chromatogram of the products of thermal bulk polymerization of MEP at 160° C. Fraction 6 corresponds to unreacted MEP. Fraction 5 with $\overline{M}_n = 243$ is a dimer, which according to the IR spectra [23] (Fig. 8) (CD_3 group: 2960, 2860, 1470, 1380 and 1040 cm^{-1}; picoline ring: 3025, 2930, 1605, 1560, 1489 and

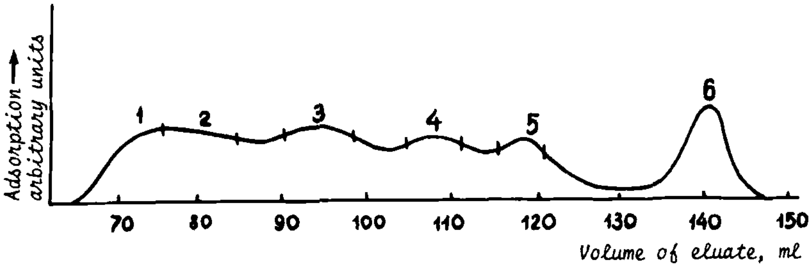


FIG. 7. GPC of products of thermal polymerization of MEP. The ranges of collection of analytical samples are shown (see text).

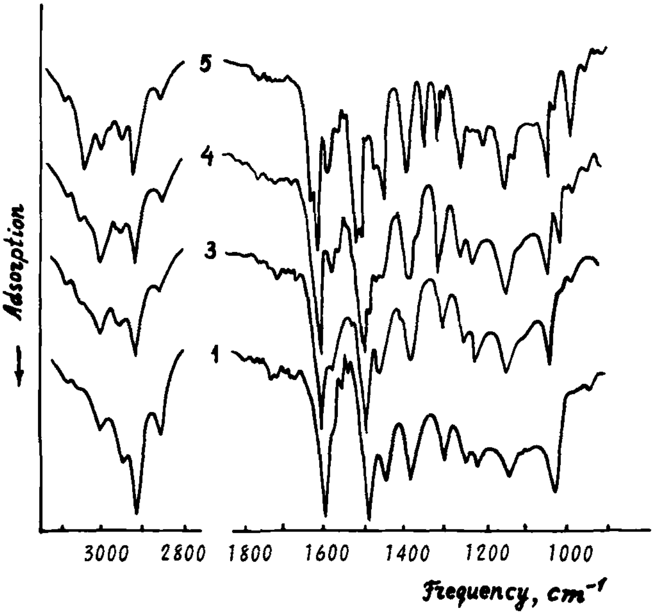


FIG. 8. IR spectra of products (CCl_4 solution) of thermal polymerization of MEP. Spectrum numbers correspond to fraction numbers given on Fig. 7.

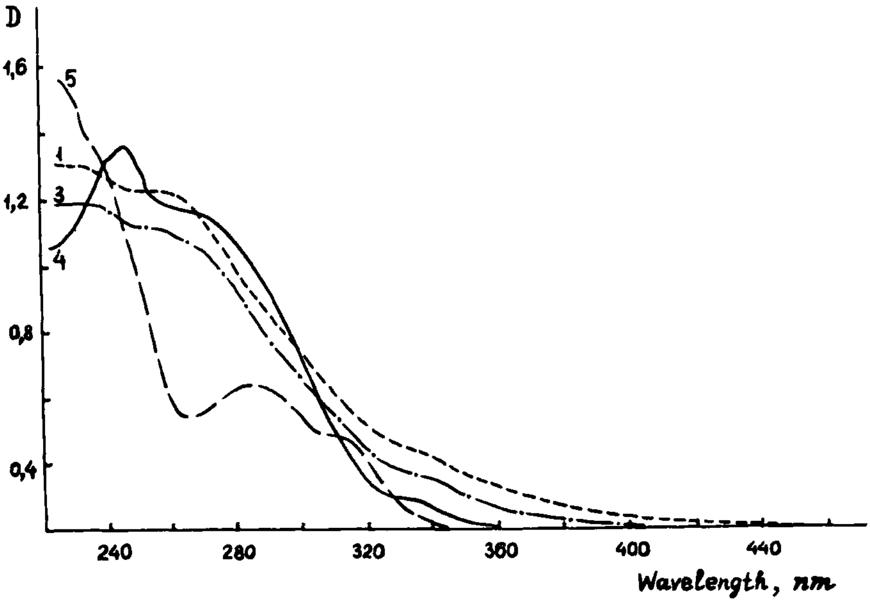


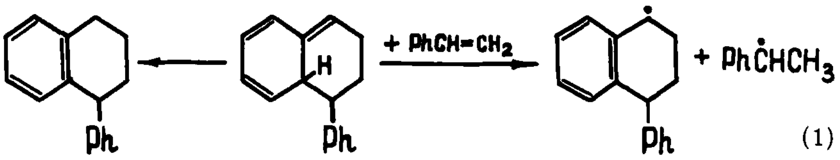
FIG. 9. UV spectra of products (methanol solution, 0.01 g/liter) of thermal polymerization of MEP. Spectrum numbers correspond to fraction numbers given on Fig. 7.

1300 cm^{-1}; quinolinic or isoquinolinic structure: 3052, 1609, 1580 and 1435 cm^{-1}) and UV spectra (Fig. 9) has the structure of picolyl-substituted quinoline or isoquinoline.

Fraction 4 with $\overline{M}_n$ = 310 is MEP cyclotrimer, tripicolylbenzene (Figs. 8 and 9); its formation has been observed in thermal polymerization of MEP [25, 26].

Fraction 3 with $\overline{M}_n$ = 720 is probably hexamer. Its spectra are similar to those of fractions 1 and 2 with $\overline{M}_n$ = 1800 and 1500, respectively (Figs. 8 and 9).

Formation of picolyl-substituted quinoline (isoquinoline) allows one to compare thermal polymerization of MEP and of styrene. Mayo has assumed [27] that Diels-Alder styrene dimerization (styrene vinyl group and a conjugate benzene double bond produce a "dimer" which joins with vinyl group of another styrene molecule-dienophile) occurs via compound (XI) as an intermediate, which isomerizes to 1-phenyltetraline (XII) or reacts with monomer with generation of free radicals.



XII XI

(1)

Also in the course of thermal MEP polymerization, the ethynyl group and its conjugate ring double bond may produce a dimer to which an ethynyl group of another MEP molecule, a "dienophile" adds. However, the absence of kinetic data does not allow one to assume the formation of intermediate products responsible for MEP polymerization.

The detection of cyclotrimers in the course of thermal polymerization of arylacetylenes served as the main argument of the biradical initiation mechanism [1]. In thermal polymerization of MEP (as well as polymerization in the presence of radical initiators) the cyclotrimer may form in the chain-propagation step via intramolecular cyclization followed by scission. Primary initiation may proceed in the presence of impurities with subsequent "self-initiation" by the radicals generated from the polymer chains: V → IV, III → VII, IX → X. This should result in an increase of polymerization rate with increasing conversion, which has been actually observed for thermal polymerization of MEP [26]. These reactions may be responsible also for "quasiradical" polymerization and copolymerization on polyarylacetylenes [1, 20].

Cyclohexadiene structure may be generated in the course of thermal polymerization of MEP via an intermolecular Diels-Alder reaction (II → V). This is confirmed by formation of 2-phenylbutadiene-1,3 adduct (140° C) with 2-phenylacetylene partially aromatized to terphenyl [28].

Fraction 3 may include bicyclohexadiene hexamer generated, for example, by recombination of two cyclohexadiene radicals.

Analogously to the initiated polymerization, the UV absorption in the region of 320-340 nm of the thermal MEP polymerization products (Fig. 9) may be explained by the presence of 1,3-cyclohexadiene structures. The change in intensity of the spectrum with respect to the polymer obtained with AIBN may be due to aromatization and possible generation of 1,4-cyclohexadiene structures.

Polypentafluorophenylacetylenes

Principally the cyclohexadiene ring methyne protons generated by MEP polymerization should appear in the ^{1}H-NMR spectra of the polymers. However, analogously to other polyarylacetylenes [1], in this case a large region of the spectrum is overlapped by the aromatic ring proton absorption. Thus it was of interest to investigate polymerization of arylacetylenes which had a single acetylenic proton. Deuteroexchange in phenylacetylene with DCl by use of the method proposed for benzene [29] with subsequent replacement of deuterium at the triple bond by proton via acetylenide, yielded a product with ca. 20% of unsubstituted protons. To obtain additional information on polymerization and for more reliable spectral interpretation, polypentafluorophenylacetylene was prepared.

Pentafluorophenylacetylene was polymerized in the presence of AIBN-D_{12} directly in a cell of the NMR spectrometer. Even at the low conversion of monomer the conditions of recording of the spectrum deteriorate sharply, probably as a result of increasing viscosity of the system. The doublet at δ = 7.80 and 7.74 ppm (Fig. 10b) may be assigned to the central ring protons in cyclotrimer, 1,3,5-tris(pentafluorophenyl)benzene. A corresponding signal of 1,3,5-triphenylbenzene (in CCl_4) is observed at δ = 7.63 ppm [30]. The doublet disappears upon precipitation of the polymer in n-hexane, which dissolves cyclotrimer (Fig. 10d). Thus polymerization of pentafluorophenylacetylene in the presence of AIBN-D_{12} affords symmetrical cyclotrimer. Its signal appears simultaneously with the signal attributed to polymer protons, which is further evidence for cyclization in the course of polymerization of arylacetylenes under action of radical initiators in the propagation step instead of on degradation of the polymer chains.

The ^{1}H-NMR spectra of polypentafluorophenylacetylenes prepared thermally (Fig. 10c) and synthesized with AIBN-D_{12} (Fig. 10d) are different. A broad signal at 3-5 ppm in the thermal polymer, having an area about 20% of the area of all signals at 3-8 ppm, may be assigned to methyne protons in 1,4-cyclohexadiene structures. In the radical polymer this signal is less intense, which could be due to predominance of 1,3-cyclohexadiene structures or to considerable aromatization under action of radicals. Unfortunately the methyne proton signals which should be observed below 3 ppm [31] could not be recorded because of nondeuterated solvent impurities and hexadeuteroacetone which absorb in this region.

In the region of 6-8 ppm, the radical polymer signal has two maxima. An intense signal at 7.3 ppm could be assigned to aromatic protons and an upfield signal is due to olefinic protons of cyclohexadiene structures. These data confirm that cyclohexadiene fragments are essentially aromatized in the course of polymerization.

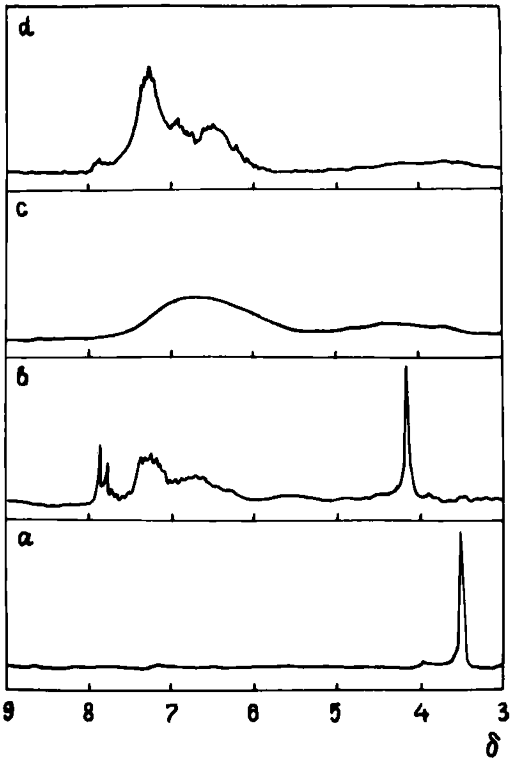


FIG. 10. ^{1}H-NMR spectra of (a) pentafluorophenylacetylene; (b) products of thermal bulk polymerization of pentafluorophenylacetylene, with AIBN-D_{12}, 80°C; (c) polyphenylacetylene obtained by thermal bulk polymerization, 150°C; (d) polypentafluorophenylacetylene obtained by bulk polymerization, AIBN, 80°C.

Polyphenylacetylenes

Physicochemical properties of polyphenylacetylenes reported in the literature are contradictory, and at the present time it is commonly accepted that polyarylacetylenes prepared by different methods have identical structures [1]. Thus it was of interest to ascertain the presence of cyclohexadiene structures in PPAC and PPAT chains.

The amount of ozone reacted with PPAC was equal to 0.37 ± 0.3 mole O_3/unit. This value is in good agreement with the data of PPAC halogenation [26, 32]. In spite of the fact that PPAC loses its solubility in the course of ozonation the polymer double bonds react completely. This conclusion follows from modern concepts on ozonation process [33] and is confirmed experimentally. The product of thermal decomposition of PPAC ozonide soluble in chloroform no longer reacts with ozone.

PPAC unsaturation based on ozonation data (37%) is essentially below that expected, even for a completely cyclohexadiene chain structure (67%). However, on taking into account the good agreement of the ozonation and halogenation results, these data could be explained by aromatization of cyclohexadiene rings as a result of the action of ozone-oxygen mixture or halogens. Our assumed aromatization of cyclohexadiene structures in the chain-scission step should also contribute essentially to a decrease in degree of unsaturation.

The UV spectrum of PPAC (Fig. 11) shows an absorption band at 320-340 nm, as observed earlier [34, 35]. Its origin has not been

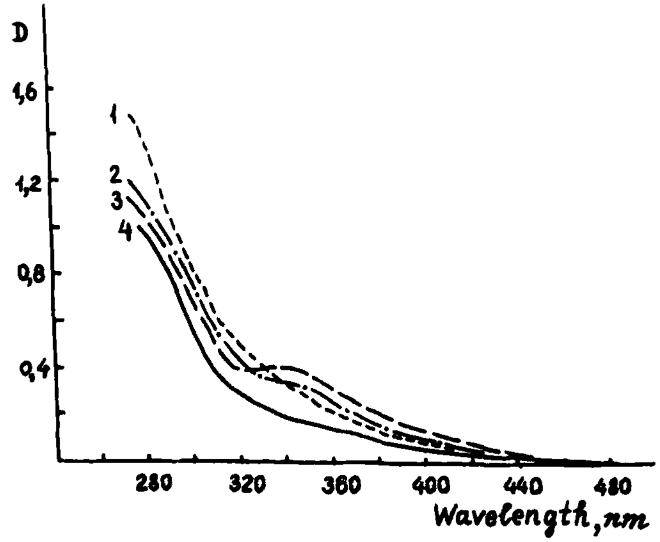
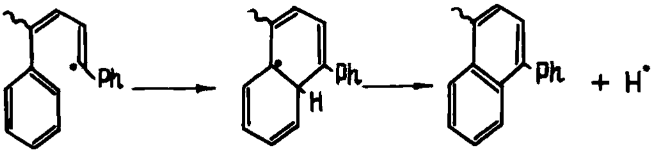


FIG. 11. UV spectra (chloroform solution, 0.027 g/liter) of (1) PPAT; (2) PPAC after the treatment with $CuCl_2$, 70°C, 1 hr; (3) PPAC; (4) PPAC after thermal treatment, 200°C, 15 hr.

elucidated. A priori, that this band is due to absorption of aromatic compounds generated in the phenylacetylene polymerization, for example in the course of intramolecular radical substitution [Eq. (2)] cannot be excluded.



(2)

Such a reaction could well explain the scission at low degrees of polymerization and the substituted naphthalene generated could be responsible for the absorption of 320-340 nm. To check this hypothesis, PPAC was heated in a sealed ampoule under argon (200° C, 15 hr). The intensity of absorption of the generated product in the region of 320-340 nm is reduced (Fig. 11). Since under these conditions the naphthalene transformation is less probable, a decrease in intensity may be explained by the lower content of 1,3-cyclohexadiene structures.

Signal positions and intensities in PPAC ^{1}H-NMR spectra are also explained satisfactorily in terms of its cyclohexadiene chain structure. The signal at 4.5-6 ppm (Fig. 12) which could be due to the olefinic protons in 1,3- and 1,4-cyclohexadiene structures [31] is about 10.5% of the sum of all protons in PPAC (olefinic protons in cyclohexadiene ring constitute 11.1%). However, the most interesting are the upfield signals which have not been observed or interpreted earlier. The signal at 3-4.5 ppm is slightly enhanced, but it is practically lost in the noise due to an essential "polymeric" broadening. This signal could not be caused by traces of methanol in which the polymeric mixture was precipitated after polymerization. The signal did not change after long evacuation of PPAC (10^{-2} Torr, 64° C, 20 hr). When methanol was added to PPAC solution in CCl_4 its "monomeric" signals appeared at 3.62 and 3.25 ppm. Finally the 3-5 ppm signal was observed in polypentafluorophenylacetylene prepared without methanol. Thus the signal at 3-4.5 ppm may be assigned to methyne protons in 1,4-cyclohexadiene rings of the polymer chain [31]. Its area is 3.25% of the total proton content (this value should be equal to 5.55% for completely 1,4-cyclohexadiene structure with symmetric location of phenyl substituents). However, on taking into account the 1,3-cyclohexadiene signal at 2-3 ppm (at about 4.1% of methyne protons in PPAC) and cycloaromatic

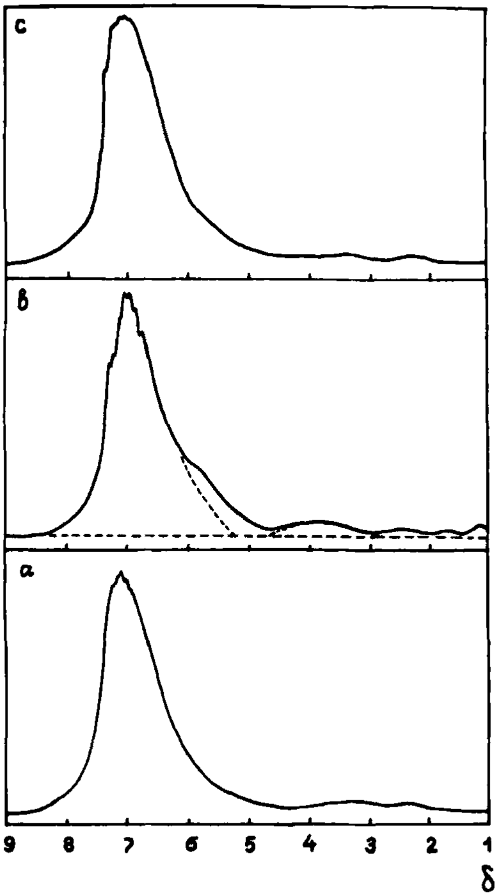


FIG. 12. ^{1}H-NMR spectra (CCl_4 solution) of (a) PPAT; (b) PPAC; (c) PPAC after the treatment with $CuCl_2$, 70°C, 1 hr.

structures generated after chain scission (III → VI) the NMR data show that the PPAC chain is composed almost entirely of cyclohexadiene rings.

The signals at 1-2 ppm should be assigned to ethyl protons of the catalyst.

In PPAT, the signal intensity is higher at 4.5-6 ppm and lower at 2-4.5 ppm than in PPAC (Fig. 12). This could be due to some side processes at high temperatures, e.g., Diels-Alder reaction between 1,3-cyclohexadiene rings and phenylacetylene molecules. The enhanced absorption at 7-7.2 ppm shows considerable aromatization of cyclohexadiene rings.

The ease with which the cyclohexadiene structures undergo aromatization may be explained by changes in PPAC upon its heating and action of radical agents. We used $CuCl_2$ and tetrachloro-o-benzoquinone to aromatize PPAC under mild conditions. That aromatization occurs is confirmed by ozonation. Under the action of $CuCl_2$, PPAC unsaturation was reduced from 40% to 32 and 26% at 40 and 70°C, respectively; in the case of tetrachloro-o-benzoquinone (room temperature and 70°C) these values were 11 and 10%, respectively. The aromatization was further substantiated by a decrease in the intensity of the absorption band at 320-340 nm in the UV spectrum (Fig. 11) and by a decrease of signal intensity at 2-6 ppm and enhancement of absorption of aromatic protons at 7-7.2 ppm in the ^{1}H-NMR (Fig. 12). Aromatization is followed by degradation of the polymer chain and its reaction with tetrachloro-o-benzoquinone, one of the final products.

CONCLUSION

A hypothesis was advanced that easily aromatized cyclohexadiene structures are present in polyarylacetylene (polyarylvinylene) chains. This enables one to explain satisfactorily some existing information (including contradictory and yet unexplained data) on acetylene polymerization. In some cases, polyacetylene chains may be suggested to include various fragments. The structural specificity of polymerization of acetylenes is probably defined by the conditions of synthesis and product isolation of monomer and catalyst. In the same way, all these factors influence the secondary processes of rather active structures generated at the syntheses.

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