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# Electrically Conducting Acetylene–Methylacetylene Copolymers. Synthesis and Properties

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ABSTRACT: Copolymers of acetylene and methylacetylene of four composition ranges were synthesized with a procedure which yielded free-standing films. Homopolymers were synthesized by the same method for direct comparison of properties, such as morphology, IR spectra, and thermal behavior. The EPR line width of the copolymers increases with increasing methylacetylene content, especially when the latter exceeds 50 mol %. Undoped poly(methylacetylene) is devoid of an EPR signal. Doping with either $I_2$ or $AsF_5$ imparts conductivity to the copolymers; the electrical conductivity decreases with increasing methylacetylene content. Poly(methylacetylene) can be doped with $I_2$ but exposure to $AsF_5$ does not cause a decrease in resistance. These results suggest that electron delocalization is sensitive to the coplanarity of the conjugated $\pi$ system. Both poly(methylacetylene) and the copolymers are very readily autoxidized and they are more readily thermally degraded than polyacetylene.

Polyacetylene is the simplest conjugated organic polymer. Recent demonstration[1,2] of the attainment of metallike properties upon chemical doping of polyacetylene has generated considerable interest in this material. The possible impact of this discovery on electronic technology can be very profound. However, this and other conducting polymer systems[3–6] suffer the disadvantages that they are not soluble, fusible, or even swellable, thus precluding rigorous characterization at the molecular level, elucidation of the conduction mechanisms, and processing by conventional methods.

The physical properties of a polymer can be markedly altered by the introduction of different pendant groups, as exemplified by polyethylene and homologous poly($\alpha$-olefins) and by poly(ethylene oxide) and various poly(alkylene oxides). In the case of substituted polyacetylenes, poly(methylacetylene) and poly(phenylacetylene)[7] have been shown to be soluble in organic solvents. However, upon doping, their electrical conductivities are several orders of magnitude smaller than those of doped polyacetylene. Two factors may contribute to the lower conductivity of these polymers. The first is a stereoelectronic effect, where the nonbonded steric interaction of the pendant groups causes a twisting of the polymer backbone and thus a decrease in $\pi$-orbital overlap and the effective conjugation length. The second effect is purely electronic in origin. The backbone carbon atoms in the substituted polyacetylenes are nonequivalent, giving rise to smaller $\pi$-orbital band widths and wider electronic band gaps than in the parent polyacetylene. Both of these effects are probably important in the homopolymers of substituted polyacetylenes, but their relative contributions cannot be readily assessed.

The rationale of this work is that experimental control of physical and electrical properties may be possible with copolymers of acetylene and other monomers through judicious choice of the comonomer and the copolymer composition. Studies of such materials may provide insight into the above-raised questions. The central purpose of this work is to develop a method for the preparation of poly(acetylene-*co*-methylacetylene) films suitable for conductivity measurements and to characterize some of their properties. The choice of methylacetylene as the most desirable comonomer for the purpose of this investigation is based on three considerations. First, the homopolymer of methylacetylene is soluble in common organic solvents. Second, the small methyl group would cause less steric interactions than most other substitutents, especially when separated by one or more acetylene units; it is also expected to minimally disrupt interchain interactions, thus allowing electronic transport to be determined primarily by structural intrachain properties. Finally, this monomer is a gas above ca. −25 °C and allows the adoption of the techniques developed to synthesize polyacetylene[8] films for the preparation of copolymer films.

## Experimental Section

**Materials.** Argon (Linde) was purified by passing the gas through a 50 cm × 4.5 cm heated column (ca. 110–120 °C) of "BTS"-supported copper catalyst (BASF Corp.) for removal of oxygen, followed by two 60 cm × 3 cm columns containing molecular sieves and KOH pellets, respectively, and small amounts of indicating Drierite for moisture removal. Prepurified nitrogen (Merriam Graves) for use with glovebags was usually passed through two columns of anhydrous $CaSO_4$. Toluene (Fisher) and pentane (Eastman Kodak White Label) were twice treated with concentrated $H_2SO_4$ overnight. They were washed twice with distilled water, washed three times with 10% NaOH, and further washed with distilled water until the aqueous layer was neutral to litmus paper. The solvent was dried with anhydrous $MgSO_4$ overnight, filtered, transferred to an oxygen-free still containing $CaH_2$ under a stream of argon, and kept under continuous reflux. Acetylene (Union Carbide purified grade) was further purified by passage through two bubblers of concentrated $H_2SO_4$ and a U-tube containing $P_2O_5$ and then admitted into a storage bulb on the vacuum line, frozen into an attached cold finger, and pumped at −196 °C to remove traces of $N_2$ or air. Methylacetylene from Air Products and Chemicals, Inc., was dried over $P_2O_5$ in a Schlenk tube at −78 °C for 20–30 min and received the same treatment in the vacuum line as described for acetylene.

Titanium tetrabutoxide, Ti(O-*n*-Bu)$_4$ (Alfa Inorganics), was purified by reduced-pressure distillation under a slow argon bleed, using standard techniques. The outlet of the distillation apparatus had a glass "Y-tube" fitted with ground glass joints for attachment of Schlenk tubes as receiving flasks. A low-boiling, colorless liquid (presumably *n*-butyl alcohol) was collected and discarded. The Ti(O-*n*-Bu)$_4$ was distilled as a light yellow, viscous liquid and was stored under argon in the Schlenk tube. The tube was usually wrapped with black electrical tape to protect the solution from light. Triethylaluminum (Ethyl Corp.) was used as received. It was shipped and stored in an Alkyltainer under argon, which is essentially a metal Schlenk tube. Arsenic pentafluoride (Ozark Mahoning Co.) was degassed at −196 °C immediately before use.

**Comonomer Feed.** A 2-L storage bulb was used to contain the comonomer feed gases. The total pressure of the gas mixture in the bulb was ca. 720 torr for all copolymer preparations. The gases were assumed to be ideal and mole ratios were determined simply by the partial pressure of the gases in the bulb.

Typically, after the bulb and the submanifold of the vacuum line were evacuated, methylacetylene was allowed to fill the bulb

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to the desired pressure and then condensed into the cold finger of the bulb (-196 °C) followed by pumping before closing of the connecting stopcock to the main manifold. Next, the connection between the acetylene purification train and the submanifold was pumped while the train was purged. After the submanifold was isolated from the remainder of the vacuum line and the methylacetylene in the bulb was expanded into the submanifold, acetylene was allowed to enter the system to bring the total gas pressure to ca. 720 torr. The gas mixture was then condensed into the cold finger of the bulb (-196 °C) and the bulb was pumped to remove any trace of air. The stopcock to the bulb was then closed and the gases were allowed to warm to room temperature.

**Copolymer Film Synthesis.** Much effort was spent to develop a method for the preparation of free-standing copolymer film suitable for conductivity measurements. An essential condition is that the polymerization should be performed above the boiling point of methylacetylene, which is ca. -23 °C at 1 atm. At the usual temperature of -78 °C for the synthesis of polyacetylene film, the methylacetylene monomer would have condensed and greatly altered the comonomer feed composition. The procedure which evolved uses three times more concentrated catalyst solution with toluene as the solvent as compared to a more dilute catalyst solution commonly employed to make polyacetylene film.

The catalyst was prepared by adding 2.5 mL of $Ti(O\text{-}n\text{-}Bu)_4$ to 10 mL of toluene (previously distilled into the reactor from a solvent storage tube) at 0 °C. Next, 4.0 mL of $Et_3Al$ was added dropwise to this solution. All transfers employed Schlenk tube techniques. The dark orange-brown catalyst solution was then allowed to age at room temperature for 30 min. Meanwhile, the comonomer mixture in the bulb was degassed one final time.

The reactor was attached to the vacuum line via flexible stainless steel tubing and the catalyst solution was cooled to -78 °C. The solution, which was occasionally agitated, was degassed for 30–60 min in the reactor. The reactor was then warmed to room temperature and immersed in an ice–salt bath (ca. -10 °C). After the reactor was shaken in order to coat the walls with the catalyst solution, the feed gas mixture was immediately admitted. Typical reaction times were 20–40 min.

After the desired time period, the reactor was disconnected from the vacuum line and argon was introduced. The catalyst solution remaining at the bottom of the reactor was removed with a syringe and discarded. The reactor was closed under argon, cooled to -78 °C, and evacuated. Thirty milliliters of toluene was distilled into the reactor to wash the film. The liquid was tipped into the attached solvent reservoir bulb followed by distillation of toluene into the reactor. This procedure was repeated 10–20 times over a period of 2 days. It was observed that a large amount of deep red colored soluble material was removed during the toluene wash, the amount of which increased with increasing methylacetylene content in the feed. Even after this extensive treatment, the toluene was occasionally observed to have an orange color, indicating continued extraction of low molecular weight polymers.

The copolymers were handled primarily in a drybox although a glovebag was used on occasion. The films were found to peel off the reactor walls more readily when wetted with solvents such as pentane or toluene. The films were stored in Schlenk tubes in vacuo or under nitrogen at -78 °C.

For comparative purposes, a $(CH)_x$ film was also prepared by the method described above.

**Preparation of Poly(methylacetylene).** Since poly(methylacetylene) is soluble and can be solvent cast into films, the procedures employed above to obtain free-standing films of homo- and copolymers of acetylene are unnecessary. Instead, it was prepared by a simplified method. The catalyst solution was prepared in a Schlenk tube at room temperature by adding 1.7 mL of $Ti(O\text{-}n\text{-}Bu)_4$ and 2.7 mL of $Et_3Al$ to 20 mL of dry toluene, using syringe and Schlenk tube techniques. The orange-brown catalyst solution was allowed to age at room temperature for ca. 30 min. It was cooled to -78 °C and degassed for ca. 30–60 min. After the solution warmed to 0 °C (vigorous stirring), methylacetylene was admitted. The reaction mixture assumes a dark brownish-red color and becomes viscous as polymerization proceeds. A typical reaction time was 60–90 min and ca. 300–400 torr of methylacetylene was consumed. The polymer was precipitated with methanol–HCl, filtered, and redissolved in toluene. Another filtration separated the dissolved poly(methylacetylene) from black insoluble materials. The polymer was again precipitated with methanol–HCl and repeatedly washed with anhydrous and oxygen-free methanol. Vacuum drying yielded 300–600 mg of orange poly(methylacetylene) flakes, which were always stored in a Schlenk tube in vacuo at -78 °C.

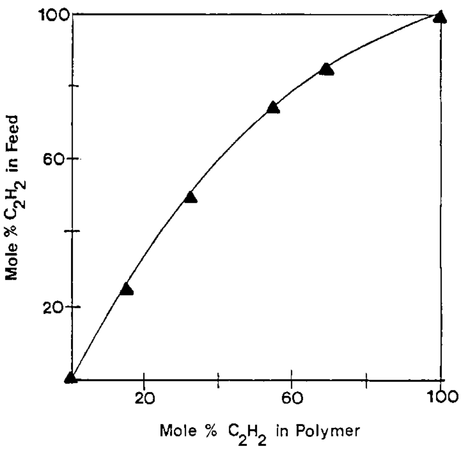


**Figure 1.** Variation of copolymer composition with comonomer feed.

**Spectroscopy.** IR spectra were recorded on a Perkin-Elmer 283 grating spectrophotometer. EPR spectra were obtained with a Varian E-9 X-band instrument with a variable-temperature insert and a dual cavity.

**Doping.** Doping was performed in a vacuum-tight apparatus fitted with four platinum wires. A polymer film sample was mounted on the platinum wires with the aid of Electrodag. The conductivity of the film was monitored during doping. In addition, several preweighed films were placed in the bottom of the doping apparatus for subsequent determinations of uptake of dopant and spectroscopic and electron microscopic studies.

Doping with iodine was achieved by passing argon over iodine crystals and subsequently over the polymer films. The doping rate was easily controlled by the argon flow rate. Uniform doping with $AsF_5$ is achieved only when it is carried out slowly. To accomplish this, $AsF_5$ in a storage bulb was maintained at -95 to -100 °C with a methanol slush bath, thus reducing its vapor pressure to ca. 20–30 torr to ensure slow doping. Incidentally, this method also helps to trap traces of HF which may result from the reaction of $AsF_5$ with traces of moisture in the reservoir and vacuum line. The doping was done by admitting very small doses of $AsF_5$ into the four-probe apparatus. The procedure was repeated until the desired doping level was reached. Doping with Na was achieved by immersing the polymer film in a THF solution of sodium naphthalide for a few minutes and subsequently washing thoroughly with pure THF.

**Conductivity Measurements.** Polymer films were measured for thickness by using a micrometer (accurate to $10^{-4}$ in) and its other dimensions were obtained by using a caliper (accurate to $10^{-3}$ in). A four-probe technique was used to eliminate contact resistance contributions. Current was applied across the two outer electrodes and the potential difference across the inner electrodes and a known reference resistor was measured with a Keithley 149 millivoltmeter.

## Results

Copolymer films of four composition ranges were synthesized. The comonomer feed ratios and elemental analysis results of the copolymers are summarized in Table I. The relationship between comonomer feed and copolymer composition as determined by the elemental analysis is shown in Figure 1. It should be noted that since the H/C ratios of the homopolymers are larger than the anticipated values, it is likely that the copolymers are somewhat more rich in acetylene content than the data indicate.

A polyacetylene film was prepared with the catalyst system employed for copolymer film syntheses simply for comparative purposes. The film so prepared was quite

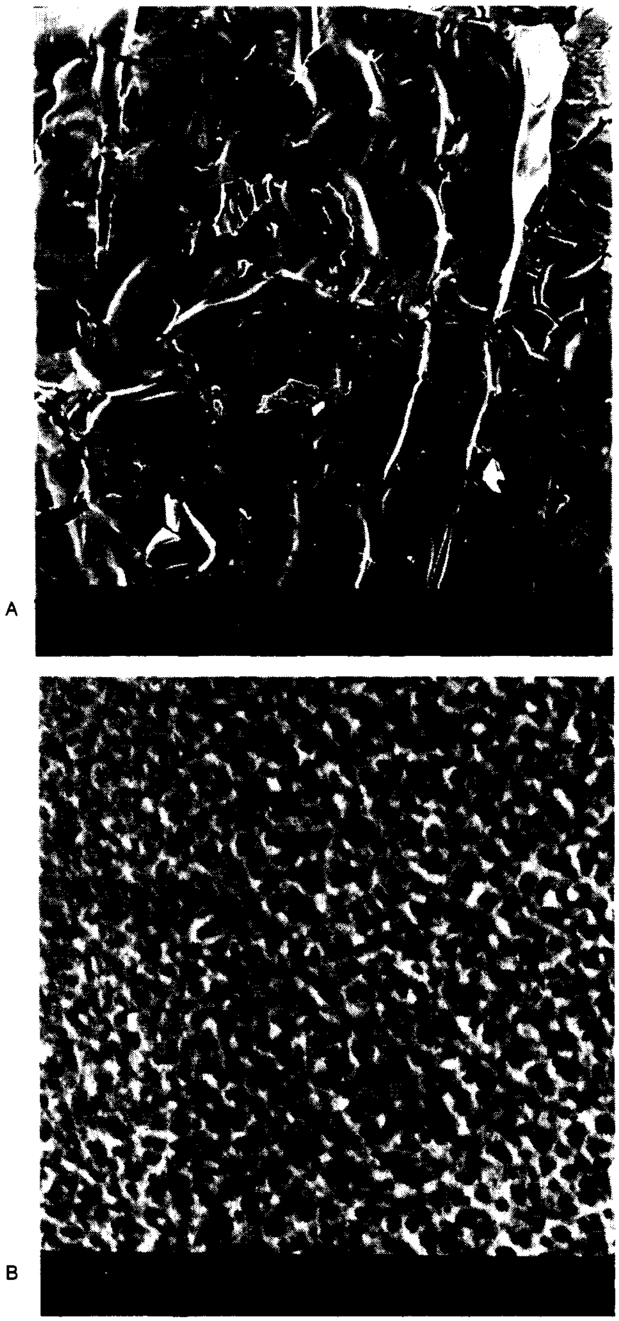


**Figure 2.** Electron micrographs of polyacetylene films prepared with high catalyst concentration: (A) film surface at X7.5 magnification; (B) crack in film surface at X3000 magnification.

different in appearance from those films prepared at lower catalyst concentration and temperature. First, the film possessed poor integrity and broke into several small pieces during washing. Second, the film was very thin (ca. 20 μm) and extremely brittle. In addition, although the side of the film which grew against the reactor wall (referred to as the "front side") possessed the coppery luster characteristic of poly(*cis*-acetylene), the backside displayed a shiny green coloration. Finally, the film surfaces were very irregular and displayed a macroscopic "rippled" appearance as indicated by the electron micrograph in Figure 2A. A region of the film between a surface crack is magnified in Figure 2B.

Copolymer sample AMA-61 exhibited lustrous and rippled surfaces similar to those of the $(CH)_x$ film described above. The material was also very brittle and disintegrated into several small pieces during washing.

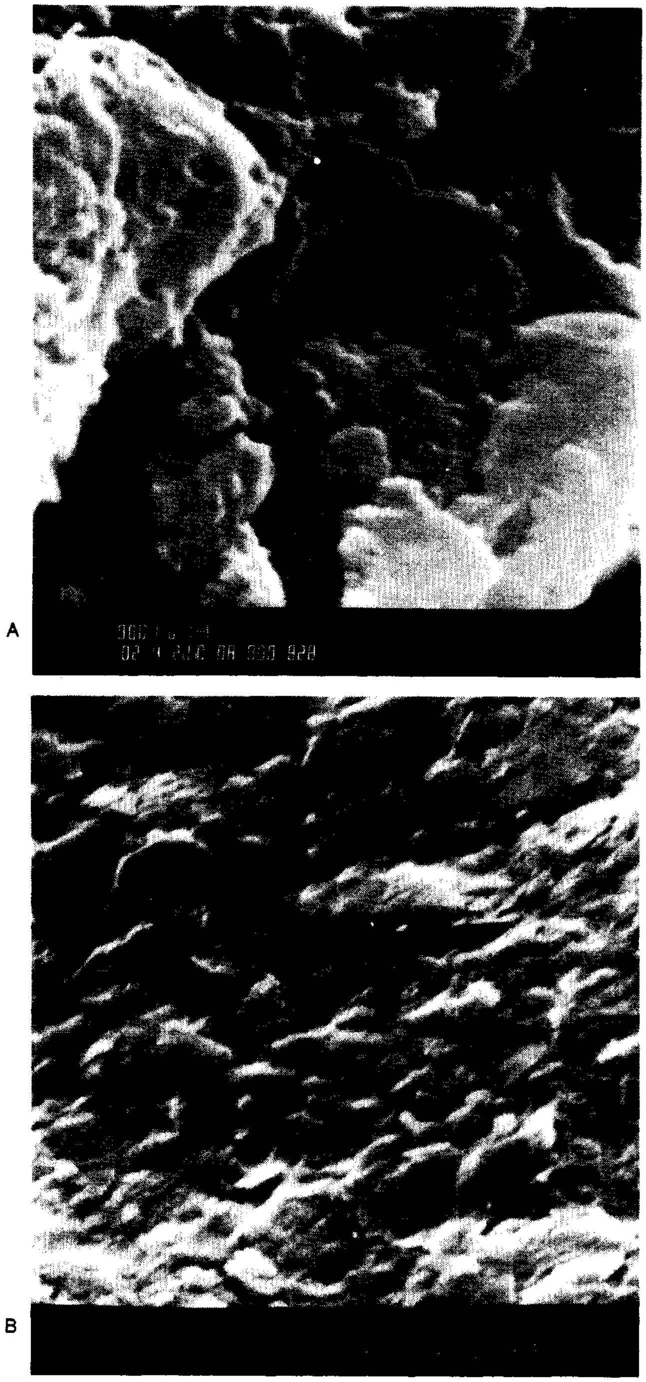


**Figure 3.** Electron micrographs of AMA-31 copolymer film: (A) shiny side at X37 500 magnification; (B) dull side at X15 000 magnification.

Sample AMA-31 more resembled typical polyacetylene films; the front side, although shiny green, possessed a relatively smooth macroscopic surface while the backside displayed a dull gray-black coloration. However, the electron micrographs in Figure 3 show no evidence of the fibrillar texture of typical $(CH)_x$ films. Rather, irregular and ill-defined "clumps" are observed.

Copolymer AMA-11 displayed a dull greenish-gold luster on both sides of the film. The morphology of this material (Figure 4A) is similar to that observed for AMA-31. It is important to point out that the luster was lost and the film became black upon wetting with a solvent (e.g., pentane, toluene), suggesting solvent swelling of the polymer occurred. The luster was recovered upon evaporation of the solvent.

Table I
Comonomer Feed and Copolymer Composition

| sample[b] | $C_2H_2/C_3H_4$ mole ratio in feed | mol % $C_2H_2$ in feed | chemical analysis of polymers[a] | | | | |
|---|---|---|---|---|---|---|---|
| | | | % C | % H | total % C,H | H/C | mol % $C_2H_2$ in polymer |
| $(CH)_x$ | ∞ | 100 | 84.16 | 7.61 | 91.77 | 1.08 (1.00 theor) | (100) |
| AMA-61 | 6 | 85 | 86.31 | 8.15 | 94.46 | 1.13 | 70 |
| AMA-31 | 3 | 75 | 87.31 | 8.61 | 95.92 | 1.18 | 55 |
| AMA-11 | 1 | 50 | 86.36 | 8.94 | 95.30 | 1.24 | 53 |
| AMA-13 | 0.33 | 25 | 84.53 | 9.30 | 93.83 | 1.31 | 15 |
| $(C_3H_4)_x$ | 0 | 0 | 88.81 | 10.95 | 99.76 | 1.48 (1.33 theor) | 0 |

[a] Galbraith Laboratories, Inc. [b] AMA, acetylene-methylacetylene; $C_2H_2/C_3H_4$ mole ratio in feed indicated by digits following AMA.

It was also observed that the AMA-11 film became very elastic upon wetting with a solvent. In fact, wetted films could be stretched to extension ratios as high as ~7 and, upon solvent evaporation, a fixed elongation could be achieved. Alternatively, wetting of a stretched, dried film resulted in considerable retraction. It is interesting to note that the wet films are somewhat tacky and stick together tenaciously upon drying. This was observed, for example, during the washing process when fairly large sections of film separated from the reactor walls and folded over on themselves. The film sections could usually be separated with a tweezers when contacted with a solvent.

The same general observations concerning sample AMA-11 apply to the characteristics of the AMA-13 film, although the latter was less lustrous and even more elastic when wetted with solvent. The irregular, "clumplike" morphology of the film is exemplified in Figure 4B. It should be noted that an attempted preparation of an AMA-14 copolymer failed to produce a tractable film. The material was extremely rubbery and tacky when wetted with solvent and, as the result of poor mechanical integrity, was washed away from the reactor walls as black, tacky masses. Thus, it appeared that the methylacetylene content of AMA-13 (Table I) was nearly the upper limit for the production of free-standing films.

The morphology of poly(methylacetylene) was not investigated. An infrared spectrum of it (evaporated from toluene on an NaCl plate) is shown in Figure 5. The two IR bands at 1020 and 960 cm$^{-1}$ are probably related to the =CH out-of-plane deformation of trans units in the polymer. No bands characteristic of the cis unit in the range 700–750 cm$^{-1}$ are observed. This result is not surprising in view of the unfavorable steric interactions anticipated between the methyl and hydrogen substituents in a cis structure. The bands at 2960, 2920, 2875, 1440, and 1370 cm$^{-1}$ are consistent with the presence of methyl groups in the polymer.

It is important to point out that poly(methylacetylene) is much more sensitive to oxidation than polyacetylene. The orange powder became white-yellow upon overnight exposure to oxygen, suggesting that the conjugated backbone was considerably disrupted. In contrast, polyacetylene lost its luster and became discolored after several weeks of air exposure. Copolymers rich in methylacetylene content (e.g., AMA-11, AMA-13) became yellow-white and extremely brittle merely upon overnight air exposure, resembling poly(methylacetylene).

All copolymer samples and polyacetylene displayed Lorentzian EPR resonances with $g$ values in the range 2.0023–2.0026. The line widths ranged from ca. 7 to ca.

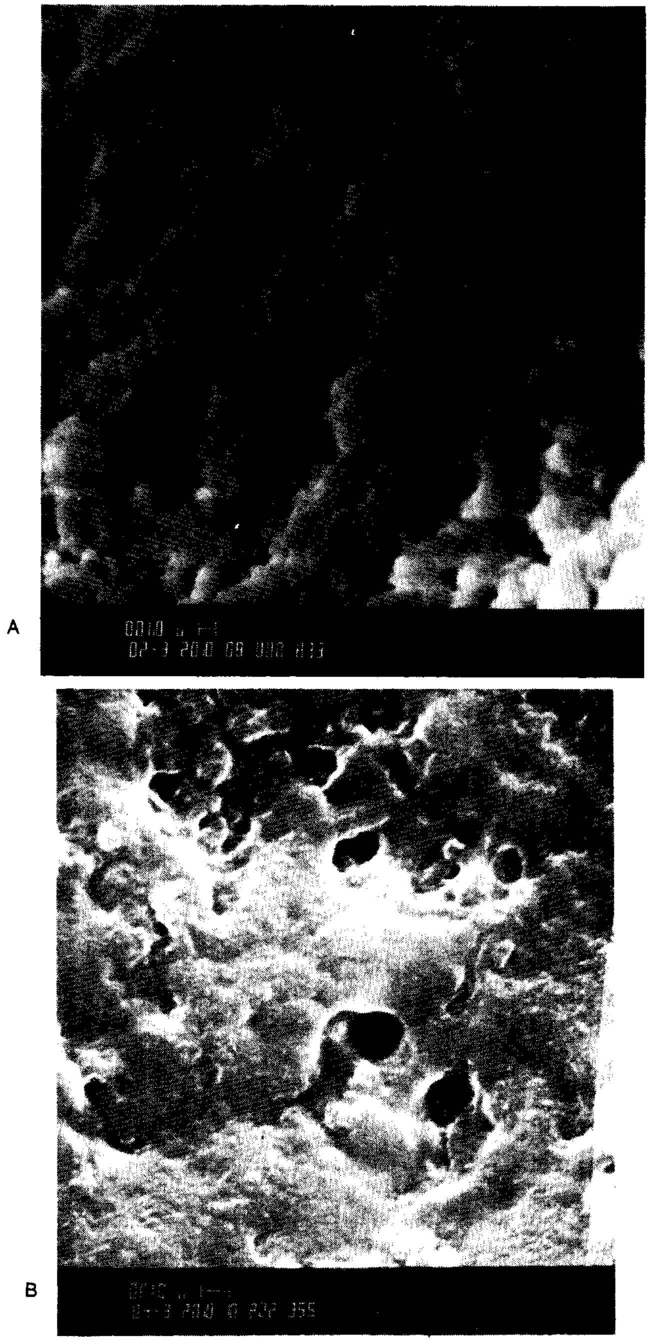


**Figure 4.** Electron micrographs of copolymer films: (A) AMA-11 at X1500 magnification; (B) AMA-13 at X3000 magnification.

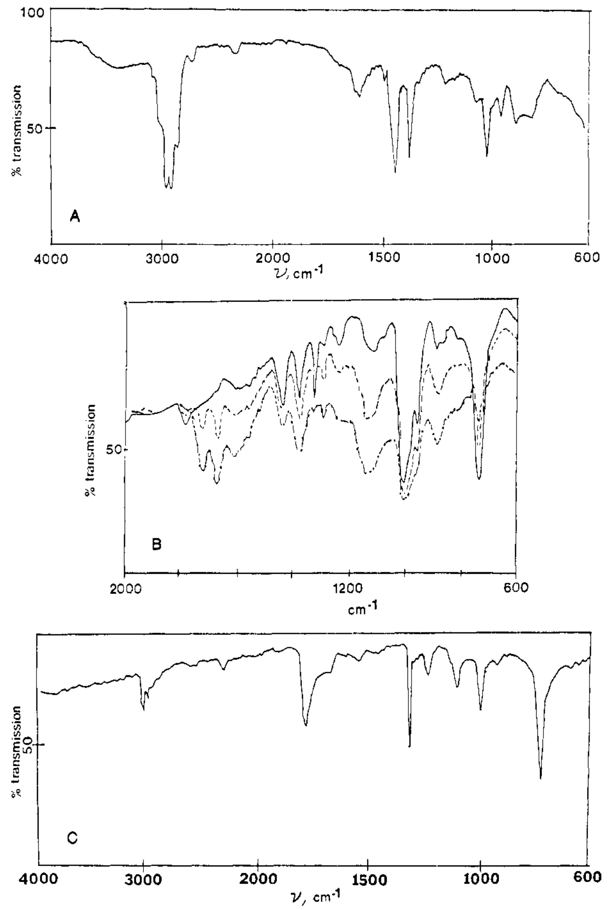


**Figure 5.** Infrared spectra of (A) poly(methylacetylene), (B) AMA-11 [(—) initial scan; (- - -) after 10 min of exposure to air in IR beam; (···) after 20 min of exposure to air in IR beam], and (C) poly(*cis*-acetylene).

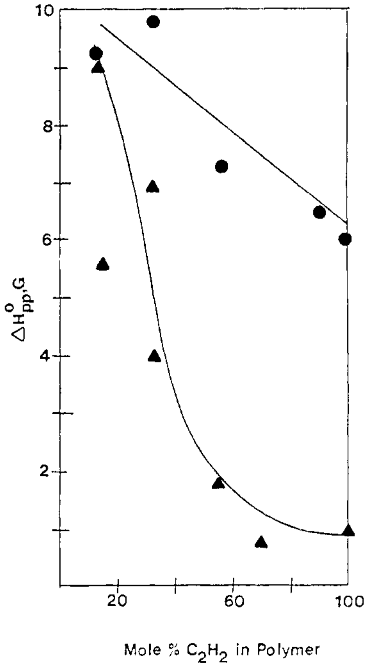


**Figure 6.** Variation of EPR line width with acetylene content in copolymer films: (●) room temperature; (▲) after heating to 150 °C for 30 min and then cooling to room temperature.

10 G and, in general, increased with increasing methylacetylene content in the copolymers (Figure 6). Heating each to room temperature resulted in much greater variation of EPR line width with copolymer composition. It is important to note that poly(methylacetylene) is devoid of any EPR signal even when heated to 150 °C.

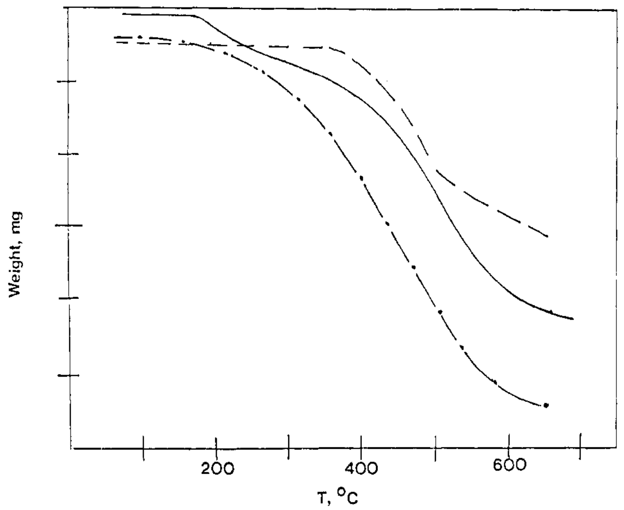


**Figure 7.** TGA curves: (- - -) polyacetylene; (-··) poly(methylacetylene); (—) AMA-11.

AMA-11 was the copolymer investigated in the greatest detail since it could be prepared fairly easily and reproducibly. Figure 5B shows an infrared spectrum of an AMA-11 film. Comparison of this spectrum with that of poly(methylacetylene) (Figure 5A) and polyacetylene (Figure 5C) indicates that bands characteristic of both polymers are present in the copolymer. The intense bands observed at ca. 730 and 1010 cm$^{-1}$ are characteristic of the =CH out-of-plane deformations of *cis*- and *trans*-CH=CH groups, respectively.[9] A shoulder at ca. 960 cm$^{-1}$ may be due to a similar vibration in the *trans*-CH=CMe group. Figure 5B also shows three IR scans of AMA-11 recorded in air at approximately 10-min intervals. In this short period of time, intense carbonyl absorptions in the region 1650–1750 cm$^{-1}$ appeared, demonstrating the sensitivity of the copolymer toward oxidation. Of particular interest, however, is the observation that the 1010-cm$^{-1}$ band increases in intensity while that at 730 cm$^{-1}$ decreases, suggesting that cis–trans isomerization occurred. Such an effect has never been observed with polyacetylene under similar conditions.

Thermogravimetric analyses in nitrogen of the two homopolymers and AMA-11 are shown in Figure 7. The onset of decomposition of polyacetylene is near 350 °C and is in good agreement with literature values;[10] as much as 50% of the polymer was converted to char. Poly(methylacetylene) has a greatly reduced thermal stability, with decomposition being observed near 180–200 °C, and the pyrolysis consumed more than 90% of the polymer. The TGA curve for the copolymer AMA-11 is quite interesting. The onset of degradation is at the same temperature as for poly(methylacetylene), indicating that it is the methylacetylene unit which is the weak linkage. On the other hand, the weight loss is only one-sixth of the total copolymer before the temperature for polyacetylene pyrolysis. This suggests that consecutive methylacetylene sequences are more prone to pyrolysis than the isolated ones. Finally, the amount of char residue is only dependent upon the acetylene monomer content; i.e., AMA-11 leaves a residue halfway between those of polyacetylene and poly(methylacetylene).

Conductivities and dopant concentrations for various samples are given in Table II. The conductivities are observed to decrease with decreasing acetylene content. This relationship is shown graphically in Figure 8 for

Table II
Conductivities and Compositions of Doped Homo- and Copolymers

| sample[a] | mol % $C_2H_2$ in polymer | composition of doped polymer | $\sigma$, $cm^{-1}$ $\Omega^{-1}$ |
|---|---|---|---|
| $(CH)_x$ | 100 | $[CH(AsF_5)_{0.12}]_x$ | 400 |
| AMA-31 | ~55 | $[CH_{1.18}I_{0.24}]_x$ | 36 |
| | | $[CH_{1.18}I_{0.16}]_x$ (after pumping above sample overnight) | 18 |
| | | $[CH_{1.18}(AsF_5)_{0.08}]_x$ | 45 |
| | | $[CH_{1.18}Br_{0.17}]_x$ | $4 \times 10^{-2}$ |
| | | Na doped; composition not determined | $2.5 \times 10^{-1}$ |
| AMA-11 | ~33 | $[CH_{1.24}I_{0.16}]_x$ | 1.5 |
| | | $[CH_{1.24}(AsF_5)_{0.1}]_x$ | 1.0 |
| AMA-13 | ~15 | $[CH_{1.31}I_{0.11}]_x$ | $2 \times 10^{-2}$ |
| | | $[CH_{1.31}(AsF_5)_{0.05}]_x$ | $2 \times 10^{-3}$ |
| $(C_3H_4)_x$ | | $[CH_{1.33}I_{0.17}]_x$ | $10^{-3}$ |

[a] Designation same as in Table I.

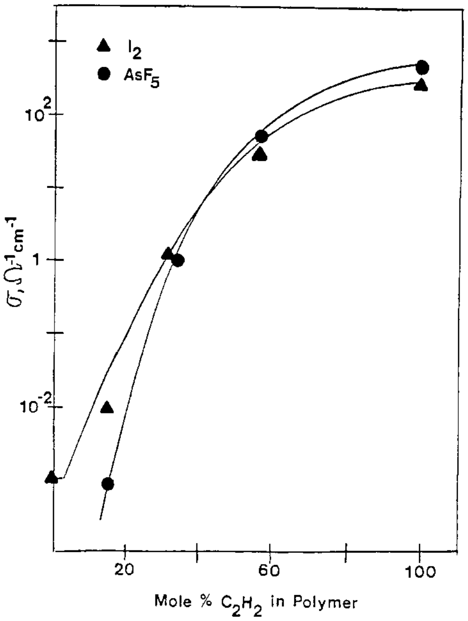


**Figure 8.** Variation of conductivity with copolymer composition for films doped with iodine and $AsF_5$.

polymers doped with iodine and $AsF_5$. Iodine becomes a progressively better dopant than $AsF_5$ as the methylacetylene content of the polymers increases. The electrical conductivity of poly(methylacetylene) is not influenced by exposure to $AsF_5$.

## Discussion of Results

Polyacetylene films prepared at low catalyst concentration and low temperature routinely in our laboratories are notably free of impurities; their total carbon and hydrogen analyses are better than 99%. This is not the case for the polyacetylene and copolymers prepared at higher catalyst concentration and temperature (Table I). This is undoubtedly the result of considerable catalyst "entrapment" in the materials. The effect was most pronounced in the case of polyacetylene since it is not swellable with solvents. However, the impurities do not seem to affect the important properties. For instance, this polyacetylene sample has an $AsF_5$-doped conductivity comparable to that obtained with highly pure materials. The sample also displayed identical EPR behavior compared to typical highly pure polyacetylene,[11] i.e., the narrowing of the line width from 6 to 1 G upon isomerization. Thus the purity of the polyacetylene appears to affect neither its "dopability" or its soliton domain width,[13] and this suggests that the results regarding the copolymers are also not particularly dependent upon sample purity.

The qualitative results concerning morphology, solubility, and swellability as described above suggest that true copolymers were synthesized rather than a mixture of homopolymers. The IR spectra also support this conclusion. Definitive evidence is, however, available. First, pyrolysis–GC–mass spectrometry[14] showed that the most abundant pyrolysis product of polyacetylene is benzene followed by toluene and xylenes but no mesitylene. The reverse order was obtained upon pyrolyzing poly(methylacetylene). For the copolymers, depending upon their composition, it is toluene or xylenes which are the dominant pyrolysates.

Second, undoped poly(methylacetylene) is devoid of any EPR signal, whereas polyacetylene shows soliton spectra of reproducible line width. The EPR spectra of the copolymers have intermediate line widths, depending upon composition. A mixture of homopolymers would be expected to have reduced EPR intensity but the same line width as polyacetylene.

Third, polyacetylene of variable density has been prepared.[15] Upon doping, the conductivity was shown to bear a semilog relationship to the density.[16] In other words, conductivity depends on the volume-filling factor. Since poly(methylacetylene) is not doped by $AsF_5$, then if the copolymers were merely a blend of homopolymers, a semilog plot of conductivity with mole percent of $C_2H_2$ should be linear. Figure 8 shows this not to be the case. Furthermore, above 30 mol % acetylene the conductivity of the copolymers doped with $AsF_5$ and $I_2$ is the same.

The effective conjugation length of the $\pi$ bonds in poly(methylacetylene) is expected to be smaller than in polyacetylene, as pointed out above. In fact, a UV–vis spectrum of poly(methylacetylene) in heptane shows two $\lambda_{max}$ absorptions at ca. 220 and 290 nm, as compared to $\lambda_{max}$ of ca. 600–700 nm for polyacetylene. In other words, the band gap in the former is considerably larger than that in the latter. As a result of steric factors, the poly(methylacetylene) backbone is rendered less rigid and, in conjunction with the disruption of intermolecular interactions, the polymer is soluble. Apparently, the methylacetylene content of copolymers AMA-11 and AMA-13 is insufficient to induce a great deal of solubility, although interchain interactions are disrupted to the extent that solvents can plasticize the materials.

A linear relationship between soliton mobility, as manifested by the EPR line width and the methylacetylene content of the copolymer, is anticipated if the introduction of strongly alternating $\sigma$ and $\pi$ bonds play a dominant role in limiting soliton mobility. On the other hand, if nonbonded interactions between the methyl groups and protons causing a backbone twist are the most important consideration, then the coplanarity of the backbone would be more distorted by the presence of two or more adjacent methylacetylene units than the isolated units. Figure 6 showed that after complete isomerization, the EPR line width is only slightly increased by the introduction of up to 50 mol % methylacetylene in the copolymer. However, further increase of the methylacetylene content greatly increased line width, implying restriction of the solitons to small domain widths[12,13] by the presence of adjacent methylacetylene units.

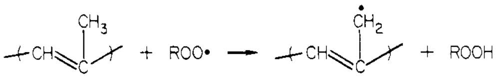
The electrical conductivity data of Table II and Figure 8 are consistent with the expected dependence of conductivity on copolymer composition. An increase in the methylacetylene content of the polymer is anticipated to increase both its band gap ($\pi \rightarrow \pi^*$ transition) and its ionization potential, making free-carrier generation more difficult. Furthermore, the reduction of the effective conjugation length with increasing methylacetylene content is expected to reduce carrier mobility. Thus, the methylacetylene units would act as barriers to conductivity. Carrier migration through (or around) these barriers should become progressively more difficult as the number of these barriers increases.

Figure 8 also shows that the copolymer conductivity is more sensitive to methylacetylene content when the copolymer is rich in this monomer; the dependence parallels that described above for the EPR line widths.

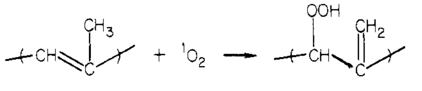
Other factors which may contribute to the magnitude of the electrical conductivity in a particular sample include morphology and the degree of crystallinity.[7] As described previously, all of the copolymer films display a similar "clumplike" morphology and thus the morphology should not play an important role in affecting the conductivity of the copolymer samples. In addition, it is interesting to note that the polyacetylene sample studied in this work possessed a morphology quite different from the fibrillar character[17] of typical polyacetylene films, although doping with $AsF_5$ afforded a comparable conductivity[1] (Table II). The degree of crystallinity of the samples, on the other hand, may play a very important role in determining electrical transport properties. An X-ray diffraction study of the copolymers is under way.

It is worthwhile to note that as the acetylene content of the copolymers decreases, $AsF_5$ becomes a progressively poorer dopant than $I_2$. Even the interaction of iodine with poly(methylacetylene) appears to be quite weak since essentially all the iodine in a doped sample can be removed by pumping, resulting in a six order of magnitude decrease in conductivity. In fact, $AsF_5$ produces no change in conductivity of poly(methylacetylene). This phenomenon might be due to a complicated combination of steric and electronic factors with regard to polymer–dopant interactions.

Poly(methylacetylene) and the copolymers are far more susceptible to autoxidation than polyacetylene. Since vinyl hydrogens are not easily abstracted by free radicals, radical attack will be limited to those hydrogens bound to $sp^3$-carbon atoms (eq 1). Alternatively, oxygen can add to the


$$-(CH{=}C(CH_3))- + ROO\cdot \rightarrow -(CH{=}C(\dot{C}H_2))- + ROOH \qquad (1)$$

double bonds. Isomerization of polyacetylene by oxygen has been described previously.[18] The presence of methylacetylene units facilitates autoxidation. Futhermore, the free spin in the polymer may even catalyze the production of singlet oxygen, which can then react directly via the "ene" reaction[17] (eq 2). Reaction 2 leads directly to the


$$-(CH{=}C(CH_3))- + {}^1O_2 \rightarrow -(CH(OOH)-C({=}CH_2))- \qquad (2)$$

disruption of the backbone conjugation and the formation of an unstable hydroperoxide. The "ene" mechanism is not available to polyacetylene if it is free of $sp^3$-carbon defects. An additional physical factor probably contributes toward the ease of autoxidation of the copolymers. This is the greater solubility and permeability of oxygen in them than in polyacetylene, as evidenced by the ability of solvents to swell the copolymers. On the other hand, this latter property may also permit the incorporation of oxidation inhibitors to stabilize the copolymers.

Finally, there are proposals that electron conduction takes place mainly across polyacetylene chains via the charge transfer centers in contrast to the flow of carriers mainly along the conjugated backbone. The results in Table II show that the copolymers are capable of being doped to the same level of dopant as polyacetylene, which may be construed as the formation of similar numbers of charge transfer complexes. Yet the conductivity of the saturation-doped copolymers is much smaller than that of polyacetylene and is methylacetylene-content dependent. This dependence is consistent with, though in itself not conclusive evidence for, transport of carriers primarily via the conjugated $\pi$ system. We have other overwhelming evidence supporting this conduction mechanism which will appear in print in the very near future. Of course, if the carrier encounters a large barrier, such as chain ends or other large defects, i.e., backbone twists induced by autoxidation it may hop to the next polymer chain and the presence of charge transfer complexation may assist this process.

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