or adsorbed byproducts and cyclization was complete. These conclusions are consistent with high molecular weight indicated by excellent viscosities for these polymers, especially for the polymer from 3-amino-4-hydroxyhydrocinnamic acid (**8**).

The most surprising observation for these two polymers was the catastrophic weight loss observed between 450 and 500 °C. Both the narrowness of the transition range (50 °C equals 5 min) and the amount of weight lost were remarkable, especially in comparison to the polymer containing a single backbone methylene group. We believe that these two species undergo a chain depolymerization that involves initial bond breaking followed by rapid radical unzipping. Thermolysis product identification and mechanistic studies of this process are currently under way.

Acknowledgment. Grateful recognition of Auburn University support of this research is made. Appreciation is expressed to Prof. B. F. Hajek, Auburn University, for assistance in obtaining TGA data.

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Acetylene–Carbon Monoxide Copolymers. Synthesis and Characterization

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ABSTRACT: Acetylene has been copolymerized with carbon monoxide to copolymers containing from 5 to 13 mol % of CO. Copolymer films were obtained at −78 °C with $\bar{M}_n \sim 4000$; only powdery products were formed at 25 °C with $\bar{M}_n \sim 1000$. The comonomer compositions in copolymers were determined by elemental analysis, radioassay of copolymers containing ^{14}CO monomer, and ^{13}C NMR. Carbonyl absorptions were observed by both IR and ^{13}C NMR. The copolymers have increasingly higher trans structure with the increase of CO content. TGA shows loss of CO at low temperatures. Pyrolysis GC-MS found CO, CO_2, H_2O, and CH_3CHO in addition to the previously observed products for polyacetylene. The copolymers are completely amorphous and are without the fibrillar morphology characteristics of polyacetylene. The CO units in the copolymers are easily protonated. The copolymers have undoped room-temperature conductivities, σ_{RT}, greater than the undoped *trans*-$[CH]_x$. Upon doping of the copolymers, their σ_{RT} increased greatly to within one-half to one-third of the values for similarly doped *trans*-$[CH]_x$.

Introduction

One of the structural requirements for a conducting polymer is an extended conjugated backbone. However, the question about the value of n for $-(CH{=}CH)_n-$ needed to exhibit electronic transport upon doping has not been seriously addressed. If carrier migration is mainly via the polymer backbone, then the value of n should be as large as possible. If the function of conjugation is to decrease the energy difference for the π–π^* transition, i.e., the energy gap, then according to the Hückel molecular orbital theory $\Delta E = 4\beta \sin [\pi/2(n + 1)]$,[2] where β is the exchange integral. The values of ΔE for polyenes are independent of values of n for $n \geq 10$. Finally, an unpaired spin or a charge in $[CH]_x$, polyacetylene, is delocalized; the former was estimated from EPR line width[3] to have n = 6–8 and the latter was said[4] to have a domain width of ca. n = 8–10. However, in order to sustain a moving domain excitation, soliton, the conjugated backbone should have very large values of n. To elucidate the relationship between conjugation length and electrical conductivity, it will be in-

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structive to study acetylene copolymer which has its backbone conjugation interrupted every 6–10 polyene sequences.

One obvious approach to interrupt the polyene chain is to insert two methylene units by the copolymerization of acetylene and ethylene. Few attempts at copolymerization were unsuccessful. In the presence of both monomers, the $Ti(O\text{-}n\text{-}Bu)_4/4AlEt_3$ catalyzed only the homopolymerization of acetylene according to magic angle spinning (MAS) solid ^{13}C NMR. Whereas $Ti(O\text{-}n\text{-}Bu)_4$/LiBu is a good catalyst for acetylene polymerization, the introduction of ethylene caused precipitation and inactivation of the catalyst.

In the course of our kinetic study of acetylene polymerization,[5,6] we used isotopic carbon monoxide to tag the number of propagating chains. It was observed that if C*O is injected into a polymerization mixture, the ^{14}C specific activity increases monotonically with the time of reactions. On the other hand, if unconsumed monomer is removed by evacuation prior to the introduction of C*O, the specific activity of the polyacetylene attains a constant and maximum value after about 5 h of contact time. This observation showed that CO, instead of being an inhibitor as it is generally thought to be, is acting merely as a retarder in acetylene polymerization. In other words, the titanium acyl bond formed upon the insertion of a CO molecule causes only a pause before the addition of another acetylene monomer followed by the resumption of chain propagation. If this were true, then copolymers of acetylene and carbon monoxide could be synthesized. In such copolymers the backbone conjugation is frequently interrupted by the CO units; the material will be unlikely to be crystalline. Therefore, this system offers a study of the effect of disruption of the backbone π-system on the electrical conductivity of polyacetylene.

The central purpose of this paper is to describe the synthesis of acetylene–carbon monoxide copolymer (AC copolymer) films and to present detailed characterization results which establish that copolymers were indeed obtained. The electronic and transport properties of these copolymers will be published elsewhere.[7] A brief note has already been submitted to report that the conductivities of doped copolymers are comparable to those of doped polyacetylene.[9]

Experimental Section

Materials. Acetylene was purified by passage through concentrated H_2SO_4 and molecular sieves were kept at −78 °C. Argon was purified by passage through BTS-supported copper catalyst (BASF), molecular sieve, and KOH pellet columns. Toluene was purified by treatment with concentrated H_2SO_4, neutralized, washed, dried, distilled, and kept refluxing under an argon atmosphere in the presence of CaH_2. $Ti(OBu)_4$ was distilled under reduced pressure; $AlEt_3$ (Ethyl Corp.) was used as received. Normal CO from Matheson (99.9% purity) was used in most copolymerization. ^{14}CO was purchased from New England Nuclear.

A stock solution of tritiated methanol (CH_3OH^*) was prepared by adding a minute quantity of $H_2{}^*O$ of very high tritium specific activity to anhydrous methanol and stored under dry argon.[9,10]

Copolymerization. The comonomer gases were mixed at feed composition and stored in a 2-L reservoir by procedures assuming the ideal gas law behaviors. For instance, for a 1:1 feed ratio, each of two 1-L round-bottom flasks on a submanifold of a vacuum line was filled to 1 atm. They were then opened to the reservoir and its cold finger was subjected to repeated freeze–thaw cycles between −196 and 25 °C to promote mixing. This mixing was done immediately before a polymerization.

The catalyst $Ti(OBu)_4/4AlEt_3$ is prepared and aged as previously described.[6] Copolymerizations were carried out at both −78 and 25 °C for feed ratios of acetylene:CO of 4:1, 2:1, and 1:1; the products are referred to as AC-41, AC-21, and AC-11, respectively, even though it will be shown that the comonomer contents in the copolymers differ considerably from the feed compositions.

Copolymer films were formed immediately upon contact of the monomers with a layer of catalyst deposited on the reactor wall. The copolymer film was washed more than 20 times with pentane; the washed film was allowed to be immersed in pure pentane overnight and then vacuum dried. The Ti and Al in the copolymers are 0.2–0.3%, which is comparable to these residues in polyacetylene films.

The AC-41 and AC-21 copolymer films can be readily dislodged from the reactor wall. However, the AC-11 films were difficult to obtain in good size pieces because it oftentimes broke into small fragments. The copolymer specimens were stored in Schlenk tubes under nitrogen at −78 °C.

The copolymers containing isotopic CO were prepared in a different manner in order to conserve the expensive ^{14}CO. The polymerizations were carried out in a 200-mL crown capped glass pressure reactor equipped with side arms to function like the Schlenk-type apparatus.[6] At the end of the reaction, the polymers were washed with 10% methanolic HCl and then with cold methanol, dried under vacuum, and radioassayed by New England Nuclear laboratories. Under these conditions the copolymerizations carried out at 25 °C yielded powdery products. At −78 °C the copolymers were produced in three distinct reaction zones with different microscopic morphologies: films on the reactor wall, gel on the surface of the catalyst solution, and powder beneath the gel. The copolymers isolated from these reaction zones differ in their compositions.

Characterization. As all the copolymers are insoluble in any common solvents, the methods of characterization are restricted to those applicable to solid polymers. All measurements were made on samples within 1 week of preparation and kept at −78 °C under argon before use.

The comonomer content in copolymer was determined by three methods: (1) elemental C, H analysis (O by difference); (2) radioassay of copolymer synthesized with ^{14}CO; (3) magic angle spinning ^{13}C NMR.[11] In the last method the integrated peak areas of the $>C{=}O$ and the cis and trans $-CH{=}CH-$ resonances gave directly the percentages of the two monomers in a copolymer.

The $\bar{M}_n$ of the copolymer was determined by the radioquenching method described earlier for the determination of $\bar{M}_n$ of polyacetylene.[9,10] Infrared spectra were obtained with a Perkin-Elmer 283 spectrophotometer.

Ultrathin films of copolymers (~100 nm thick) were polymerized directly onto electron microscopy (EM) gold grids for transmission EM and electron diffraction with a Jeol 100 CX STEM instrument as described previously.[12–14]

The conductivity of the copolymer was measured by the usual four-probe technique.[15] About 100 μg of copolymer was pyrolyzed with a pyroprobe at 650 °C for 20 s in He. The products were separated either with a Chromosorb 102 column (6 ft × $^1/_8$ in.) for the low-boiling fraction or with a SE-30 fused silica capillary column (13 m × 0.324 mm) for the high-boiling fraction and the products identified by mass spectrometry.[16,17]

Results and Discussion

Copolymer Composition and Molecular Weight. The copolymers were analyzed for C, H, Ti, and Al. The metal residues were less than 0.3%. If the excess of C over H is taken to be the C of the CO comonomer, then the total C + H + O ~ 98–100%. The results of copolymer composition obtained by this method are given in column 5 of Table I.

The CO content in a copolymer was obtained by tracer technique also. ^{14}CO was copolymerized with acetylene. The copolymer compositions determined by radioassay are found in column 6 of Table I.

The magic angle spinning solid ^{13}C NMR spectra[11] contain three resolved resonances. The resonances at 127 and 136 ppm are attributable to the carbon atoms in the cis and trans $-CH{=}CH-$ units, respectively.[18] The new peak at 178 ppm can be assigned to the carbonyl resonance.

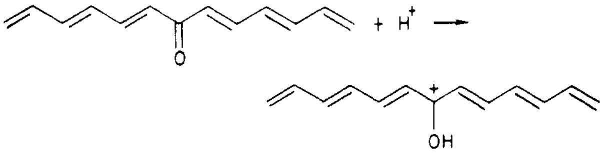
Table I
Comonomer Feed and Copolymer Composition

sample	C_2H_2/CO mol ratio in feed	elemental anal.[a]			C_2H_2, mol %		av C_2H_2, mol %
		C, wt %	H, wt %	C_2H_2, mol %	by radioassay[b]	by ^{13}C NMR	
AC-11	1	84.40	8.34	85	89	*c*	87
AC-21	2	86.34	7.82	88	91	90	90
AC-41	4	89.43	7.85	95	96	95	95

[a] Microanalysis Lab, University of Massachusetts. [b] Radioassay by New England Nuclear. [c] Not determined.

The copolymer compositions calculated from the integrated intensities of these resonances are given in Table I column 7. The results of the three determinations of copolymer compositions are in excellent agreement; the average values are listed in column 8.

It is worthy of note that the carbonyl resonances were converted to carbinal resonances at high field by washing the copolymers with acidic methanol alone. This shows very facile protonation of the conjugated carbonyl group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With the present polymerization method, the maximum CO content in a copolymer is about 13%. The copolymerizations have progressively slower rates and lower yields with increasing amount of CO in the comonomer feed. For CO greater than 1:1 in the feed, no copolymer film was obtainable because of rapid drainage of the catalyst solution down from the reactor wall.

The number-average molecular weight, $\bar{M}_n$, of the copolymer was determined by radioquenching with tritiated methanol. In the case of homopolymerization of acetylene, the reactions involved are

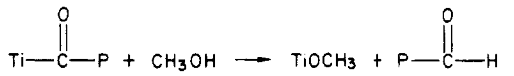
$$\text{Ti-P} + CH_3OH \rightarrow TiOCH_3 + PH \qquad (2)$$

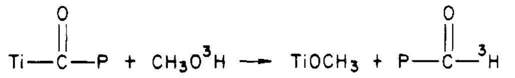
$$\text{Ti-P} + CH_3O^3H \rightarrow TiOCH_3 + P^3H \qquad (3)$$

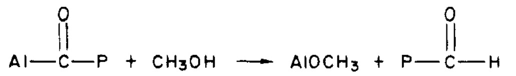
$$\text{Al-P} + CH_3OH \rightarrow AlOCH_3 + PH \qquad (4)$$

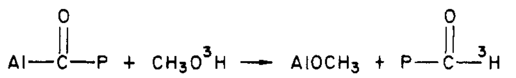
$$\text{Al-P} + CH_3O^3H \rightarrow AlOCH_3 + P^3H \qquad (5)$$

where P is the polyene. The average value of the kinetic isotope effect (KEF) for the acetylene polymerization was found to be 2.8.[9,10] In the present copolymerization, there are additional reactions


$$\text{Ti—}\overset{O}{\overset{\|}{C}}\text{—P} + CH_3OH \longrightarrow TiOCH_3 + \text{P—}\overset{O}{\overset{\|}{C}}\text{—H} \qquad (6)$$


$$\text{Ti—}\overset{O}{\overset{\|}{C}}\text{—P} + CH_3O^3H \longrightarrow TiOCH_3 + \text{P—}\overset{O}{\overset{\|}{C}}\text{—}^3H \qquad (7)$$


$$\text{Al—}\overset{O}{\overset{\|}{C}}\text{—P} + CH_3OH \longrightarrow AlOCH_3 + \text{P—}\overset{O}{\overset{\|}{C}}\text{—H} \qquad (8)$$


$$\text{Al—}\overset{O}{\overset{\|}{C}}\text{—P} + CH_3O^3H \longrightarrow AlOCH_3 + \text{P—}\overset{O}{\overset{\|}{C}}\text{—}^3H \qquad (9)$$

which are probably more important than reactions 2–5 since CO is a retarder. We did not determine the KEF for the copolymerization but use the value of 2.8 to calculate $\bar{M}_n$ of the copolymers. The resulting error would be comparable to that of the polyacetylene molecular weight.[10] The value of $\bar{M}_n$ is obtained from

$$\bar{M}_n = A_{MeOH}(2.22 \times 10^6)/A_{(CH)_x(CO)_y}(k_H/k_T) \qquad (10)$$

where A_{MeOH} and $A_{(CH)_x(CO)_y}$ are the tritium specific activities of the isotopic methanol and copolymers, respectively.

Table II
Number-Average Molecular Weights of Acetylene–Carbon Monoxide Copolymers

copolymer	$\bar{M}_n$	
	film[a]	powder[b]
AC-11	3560	*c*
AC-21	3560	940
AC-41	4200	1000

[a] Copolymer film obtained at −78 °C polymerization. [b] Copolymer powder obtained att 25 °C polymerization. [c] Amount of product too small for $\bar{M}_n$ determination.

The values of $\bar{M}_n$ are summarized in Table II.

The copolymer films obtained at −78 °C reaction have $\bar{M}_n$ between 3560 and 4200. Homopolymerization of acetylene at the same conditions produced films with $\bar{M}_n$ ~ 11000.[10] Therefore, the AC copolymer films have about one-third of the molecular weight of polyacetylene film obtained by the widely used procedure of Ito et al.[19]

The $\bar{M}_n$ of powdery polyacetylene obtained at los catalyst concentration has values very sensitive to the polymerization conditions.[10] Values as low as 480 were obtained. Therefore, the $\bar{M}_n$ of powdery copolymers of about 1000 is quite in line with those of powdery polyacetylenes.

Structure and Morphology of Copolymers. The copolymers are visibly and physically different from polyacetylene. The copolymer films are much thinner by comparison obviously because of the retardation effect of CO on the chain propagation. For the high acetylene containing copolymer, AC-41, the side of the film which grew against the reactor wall (front side) has a coppery luster like that of *cis*-$[CH]_x$. However the backside displayed a shiny green color. The film surfaces seem to be very irregular but the film is mechanically strong.

Copolymer AC-21 displayed a shiny green color on the front side while the backside has a dull gray coloration. The continuous film broke during washings. Copolymer AC-11 displayed a dull green luster on the front side and the backside was bluish green. The films were so thin that it was really difficult to remove the film from the reactor walls without fragmenting it.

Polymerization was carried out directly on the EM grids[12-14] for several comonomer feed, catalyst concentrations, and polymerization time. In all cases only thin, smooth copolymer films were produced; no fibrillar morphology characteristic of polyacetylene was observed.[20] Electron diffraction measurements on these in situ thin films revealed only amorphous halo without any Debye rings. Apparently, the AC copolymers are completely amorphous.

Infrared spectra of all AC copolymers showed bands for a polyacetylene[21] with both cis and trans double bonds. Figure 1 is that of pristine AC-11 copolymer. Those which are basically the same in frequencies and intensities are as follows: 3013 (B_{3u} C–H stretching in trans), 1800 (combination 1329 + 446 cm^{-1}), 1329 (B_{2u} C–H in-plane deformation in cis), 1290 (B_{1u} C–H in-plane deformation in trans), 1240 (B_{3u} C–H in-plane deformation in cis), 1010 (B_{2u} C–H out-of-plane deformation in trans), 740 (B_{1u}

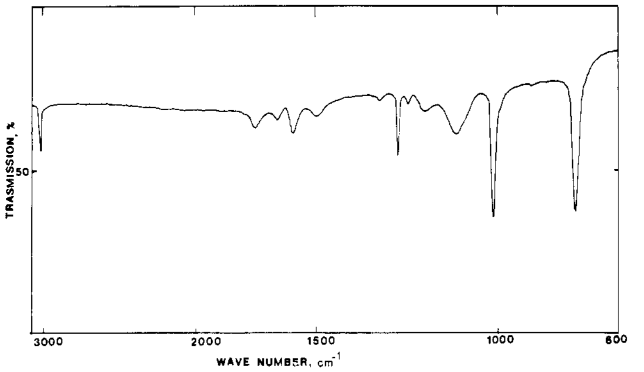


Figure 1. Infrared spectrum of pristine AC-11 copolymer film.

Table III
Cis-Trans Contents in Acetylene–Carbon Monoxide Copolymer

copolymer	cis, %	trans, %
AC-11	37	63
AC-21	58	42
AC-41	83	17

C–C–C deformation in cis) cm^{-1}. The B_{3u} C–C stretching in cis is found to be intense and broad at 1132 cm^{-1} in the copolymer, whereas it is very weak in $[CH]_x$. Three new bands appeared in the copolymer. The C═C stretching vibration at 1590 cm^{-1} in the copolymers is too weak to be resolved in $[CH]_x$. Also, there are two carbonyl bands at 1660 and 1710 cm^{-1} with the former being the more intense of the two. The former is attributable to the stretching vibration of the ketonic group between conjugated olefinic groups.[22] The latter is consistent with α,β-unsaturated aldehyde carbonyl modes, which are the end groups of the copolymers formed in eq 6–9.

A reviewer pointed out that a polystyrene chain containing a terminal methyl ketone functionality has been used to initiate block copolymerization of acetylene in the presence of $Ti(OBu)_4/AlEt_3$ catalyst.[23] The mechanism of the process is unclear, but may involve a Grignard type of reaction.[24] Similar reactions leading to branched copolymers are unlikely for the following reasons. The titanium alkoxides are in reduced valence states and $AlEt_3$ had been converted to $AlEt_m(OBu)_{3-m}$. Also, the copolymer is insoluble and reactions of catalyst with the solid copolymer would be inefficient. However, the intensity of the 1132-cm^{-1} band in the copolymer may be due to the C–O stretching vibration of tertiary alcohol (after workup) at the branch point. But the close agreement of the copolymer composition obtained from the ^{13}C NMR resonances of the carbonyl carbons with the other determinations (vide supra) suggests the above-mentioned side reactions to be of minor significance.

The cis and trans contents in the copolymers can be calculated from the absorbances[25] at 740 and 1010 cm^{-1}. The values in Table III show that copolymer AC-41 has nearly the same cis content as polyacetylene freshly polymerized at −78 °C. However, this content decreases markedly with the increase of CO in the copolymer, which may be due to isomerization when the copolymers were brought to room temperature or even during the course of polymerization.

Heating of AC copolymers causes rapid cis–trans isomerization. For instance, heating of AC-11 at 150 °C for 10 and 25 min increases the percent trans from 63% to 80% and 92%, respectively. According to theory,[26] the presence of the C–C single bonds introduced by the incorporation of CO should significantly lower the energy barrier for cis–trans isomerization.

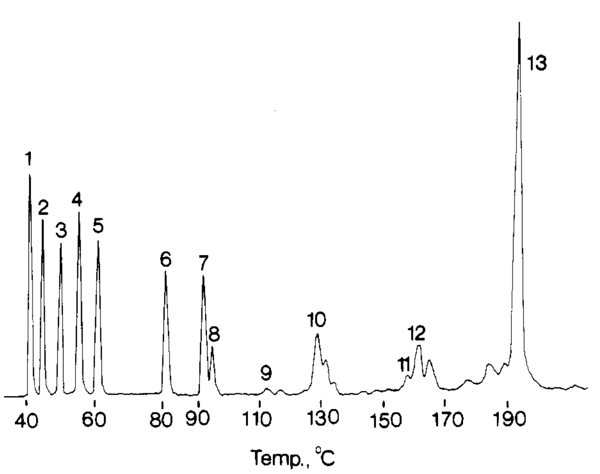
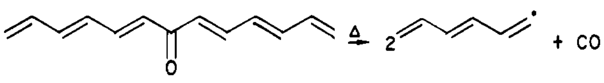


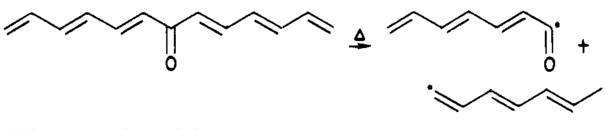
Figure 2. Low-boiling pyrogram of AC-11 copolymer; 66 μg was pyrolyzed at 650 °C in He for 20 s and separated on a Chromosorb 102 column (6 ft × $^1/_8$ in.) with a Varian 3700 GC. Peak assignments: (1) CO; (2) CH_4; (3) CO_2; (4) C_2H_4; (5) C_2H_6; (6) H_2O; (7) C_3H_6; (8) C_3H_8; (9) CH_3CHO; (10) butadiene-1,3; (11) pentadiene-1,3; (12) cyclopentadiene; (13) benzene.

Thermochemistry. The AC copolymers are thermally more unstable than polyacetylene; the instability increases with increasing CO content. Detectable weight loss in the TGA curve of polyacetylene did not begin until ca. 320 °C.[16,17] TGA weight loss for AC-11 copolymer commences at 50 °C; at 350 °C the sample had lost ca. 14% of weight. On the other hand, TGA weight loss for AC-41 begins at ca. 150 °C and loses about 5% in weight at 350 °C. These weight losses in TGA correspond almost exactly to the CO content in the copolymers. Therefore, the stability of the product CO governs the low-temperature degradations.



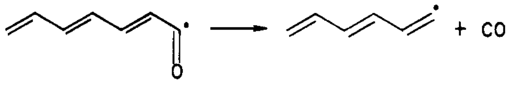
(11)

Flash pyrolysis GC-MS of AC copolymers was compared with that of $[CH]_x$. The pyrograms of the high-boiling fractions are identical for the two polymers (Figure 3 and Table II of ref 16). On the other hand, there are differences between the low-boiling-fraction pyrogram of AC-11 copolymer (Figure 2) and those of $[CH]_x$ (Figure 2 of ref 16). The former contains additional peaks due to CO, CO_2, H_2O, CH_3CHO (peaks 1, 3, 6, and 9 in Figure 2) which were not found among the pyrolyzates of $[CH]_x$. These products may be attributable to the CO conomoner produced by electron–atom exchange processes.[16,17] The initial chain scission occurs at a CO unit:



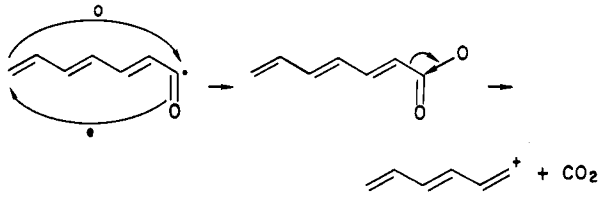
(12)

CO is produced by simple elimination:



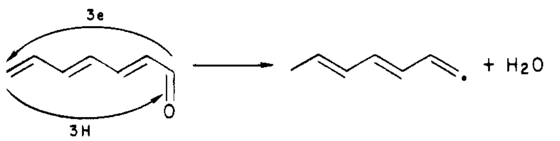
(13)

CO_2 could result from electron–oxygen exchange reaction



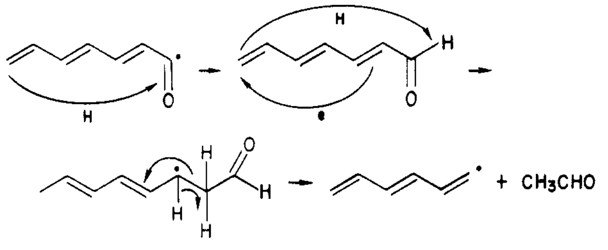
(14)

H_2O may be formed by electron–proton exchange processes



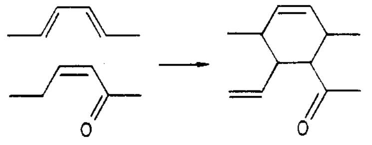
(15)

Processes leading to CH_3CHO may be postulated as



(16)

Apparently, some electron–atom exchanges occur even at low temperatures. For instance, heating the AC copolymer films at 150 °C produced new IR bands at 2860 and 2920 cm^{-1} attributable to C–H stretching vibration of sp^3 carbon atoms and a broad OH band at 3500 cm^{-1}. These bands may be due to the intermediates in reactions 15 and 16. Also, the electron-withdrawing effect of the carbonyl group may facilitate Diels–Alder reaction to form sp^3 carbon atoms.



(17)

Copolymerization. The general copolymerization reactions are

$$\text{Ti–A–P} + \text{A} \xrightarrow{k_{11}} \text{Ti–A–A–P} \quad (18)$$

$$\text{Ti–A–P} + \text{C} \xrightarrow{k_{12}} \text{Ti–C–A–P} \quad (19)$$

$$\text{Ti–C–P} + \text{A} \xrightarrow{k_{21}} \text{Ti–A–C–P} \quad (20)$$

$$\text{Ti–C–P} + \text{C} \xrightarrow{k_{22}} \text{Ti–C–C–P} \quad (21)$$

where P, A, and C denote copolymer chain, acetylene, and carbon monoxide, respectively. The addition of CO into a titanium acyl bond (eq 21) would be inconceivable for Ziegler–Natta catalysis. IR spectra contain no band due to α,β-diketones. Therefore, $k_{22} = 0$. With the limited data, one estimates the reactivity ratio r_1 to be approximately $s(9 \pm 1)$, where s is the ratio of solubility of C_2H_2 to CO, and $r_2 = 0$.

It is interesting that though the rates of CH≡CH and CO copolymerization are much slower than the rate of acetylene homopolymerization, their molecular weights differ only by threefold. This suggests that chain transfer to aluminum alkyls and bimolecular chain termination found in acetylene homopolymerization[6] for the Ti–P species do not occur as readily for the Ti–C(=O)—P species in the copolymerization.

Homogeneity of Copolymers. Since both AC copolymer and $[CH]_x$ are insoluble in any solvent, it is a matter of concern whether the latter was formed in the copolymerization. If reaction 19 is always followed by reaction 20, then the copolymers must contain random blocks of polyenes separated by CO units. There is on the average about one CO unit separating 19, 9, and 7 polyene sequences in AC-41, AC-21, and AC-11, respectively. The average degree of polymerization is ca. 150. Therefore, there are at least seven to eight CO in a AC-41 copolymer chain and correspondingly more CO comonomers in the other copolymers. The probability of having any homopolyacetylene is thus quite small.

Table IV
Magnetic and Electrical Properties of *trans*-AC Copolymers

	undoped		doped	
copolymer	$10^5[\text{S}\cdot]^a$	$10^5\sigma_{RT}$, $(\Omega\ cm)^{-1}$	y^b	σ_{RT}, $(\Omega\ cm)^{-1}$
AC-11	5.0	1.3–3.5	0.040	90
AC-21	8.3	1.7–4.5	0.047	49
AC-41	2.2	4.0–8.8	0.060	69
trans-$[CH]_x$	66–200	0.12–0.35	0.060	160

[a] Spin per repeat unit. [b] Mole fraction of I_3^-.

Most of the properties of AC copolymers cited above can be rationalized for an AC polymer–$[CH]_x$ blend such as IR, ^{13}C NMR, composition, TGA, pyrolysis GC-MS, etc. However, if there are appreciable amounts of $[CH]_x$ present, there may be expected phase separation to form some fibrils or crystallites. But they are both not found.

Perhaps the most conclusive evidence that only random copolymers were formed is the following. Many laboratories have reported that *trans*-$[CH]_x$ has unpaired spin concentration of one per 1000–3000 CH units[25] or (0.7–2) × 10^{-3} spin per repeat unit. In contrast the *trans*-AC copolymers have (2–8) × 10^{-5} spin per repeat unit (Table IV). Therefore, even assuming the copolymers to possess no unpaired spin and that all the unpaired spins are due to the *trans*-$[CH]_x$ in the copolymer, then the maximum amounts of the homopolymer lie between 0.1% and 1%.

Conclusions

Acetylene–carbon monoxide copolymers have been synthesized. The mechanism of copolymerization is probably the same as that proposed for the homopolymerization of acetylene, i.e., cis opening of the triple bond and cis insertion of the acetylene monomer.[6] The cis-transoid sequences in copolymers more easily undergo cis–trans isomerization than that in polyacetylene because of the presence of those C–C single bonds of the CO unit and the absence of crystallinity. For the AC-41, AC-21, and AC-11 copolymers, there is on the average one CO unit separating 19, 9, and 7 —CH=CH— sequences. However, this frequent interruption of backbone conjugation resulted in no decrease in room-temperature electrical conductivity, σ_{RT}. In fact, the undoped trans copolymers have higher values of σ_{RT} than undoped *trans*-$[CH]_x$ (Table IV, column 3). Even upon being doped the copolymers have σ_{RT} values within a factor of 3 of similarly doped *trans*-$[CH]_x$. In conclusion, polyene sequence length of ~7 is sufficient for a conducting polymer.

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Registry No. Iodine, 7553-56-2; (acetylene)·(carbon monoxide) (copolymer), 56993-49-8.

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Isotactic Polymerization of Propene: Initiation at Titanium–Phenyl Bonds

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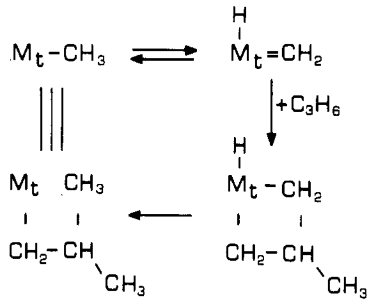
ABSTRACT: The structure of the end groups coming from initiation in the presence of active sites carrying phenyl substituents has been elucidated. Insertion of propene into the phenyl bonds of the isotactic-specific sites appears to be enantioselective.

Heterogeneous Ziegler–Natta catalytic systems for isotactic-specific polymerization of α-olefins are usually prepared by contacting a transition-metal halide and an organometallic compound, e.g., AlR_3, ZnR_2, BeR_2 (where R is an alkyl, aryl, or aralkyl group). According to the literature the isotactic-specific active sites are surface transition-metal atoms carrying one active R group and several halide ligands, i.e., X_n*Ti*–R. Isotactic polymerization involves sequential enantioselective insertions, e.g., of propene into the active Mt–R bonds of the active sites. In fact the isotactic-specific sites are chiral and, depending on the configuration, preferentially attack either one or the other enantioface of prochiral α-olefins. The enantioselectivity of propene insertion has been determined on active sites of different composition (Mt = Ti, X = Cl or I, R = CH_3 or C_2H_5 or i-C_4H_9 or growing polymer chain).[1-3] In particular for X = Cl it has been observed that the enantioselectivity of the insertion of propene into Ti–CH_3 bonds is negligible if it exists.[2,3] The enantioselectivity of the insertion into Ti–CH_2–CH_3 is appreciable and becomes very high for Ti–i-C_4H_9 and Ti–growing chain bonds.[2,3]

These findings, particularly the lack of enantioselectivity of the insertion into Ti–CH_3 bonds, have been rationalized by Corradini and co-workers[4-6] by means of a model of chiral active sites. According to these authors the stereochemical control of the insertion comes from the nonbonded interactions between the methyl of the incoming propene and the carbon of R ligands in the β position with respect to the transition metal. The isospecificity of the reaction should be mainly due to the fixed chiral orientation of the first C–C bond of the growing polymer chain. Therefore, the presence of a bulkier R group bearing two carbons instead of one carbon in the β position could in principle produce a decrease or even a change of the nature of the steric control in the insertion of the first monomer unit.

Scheme I



The lack of enantioselectivity for the insertion of the monomer into Ti–CH_3 bonds could be as well rationalized considering the possibility that the insertion might occur via a mechanism involving reversible migration of H from the α carbon to the transition metal, and carbene metallacyclobutane intermediates as proposed by Ivin[7] and by Casey.[8] (See Scheme I.)

The use of active sites carrying aryl groups could verify (i) the influence of the presence of two β carbons on the steric control of the first monomer insertion and (ii) the likelihood that propene insertion into the metal–aryl bonds

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