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Acetylene-cyclopentene copolymers

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Summary

Cyclopentene (CP) and 7,8-bis(trifluoromethyl)tricyclo-[4,2,2,$0^{2,5}$]-deca-3,7,9-triene (p-A) were copolymerized. The copolymers were thermally converted to acetylene-cyclopentene copolymers ACP-13, ACP-11, and ACP-31 containing 60.3%, 48.3% and 39.4% of CP, respectively. Infrared spectroscopy showed the copolymers to have increasing sequence length of conjugated double bonds with increasing acetylene contents. The copolymers have only small amounts of unpaired spins which are only one-tenth to one-hundredth of that found in normal trans-poly(acetylene). The copolymers absorb large quantities of iodine, which on the basis of sp^2-carbon atoms are comparable to iodine doped poly(acetylene). Doped ACP-copolymers acquire some increase of conductivity up to 10^{-4} $(\Omega\ cm)^{-1}$ for ACP-31 copolymer and evacuation returned the materials to their insulating states even though the samples retained a few mole % of I_3^-. The results are attributed to low carrier concentration and mobility.

Introduction

There have been several reports of copolymerizations of acetylene such as with methylacetylene (1) and carbon monoxide (2,3). However, polyacetylene even having MW as low as 480 is insoluble (4-7) though it has undiminished doped conductivity as compared to higher MW polymers. It is possible that during these reactions the precipitation of the copolymer may alter the cause or stop the copolymerizations. As a result it is difficult to ascertain the uniformity of the copolymer microstructure.

An important question concerning all conducting polymers is the length of conjugation required for electronic transport. There is now ample evidence that very short conjugations of say 7 - 10 would suffice. For instance acetylene-carbon monoxide copolymer with 15 mole % of CO, (2,3) trans-poly(acetylene) of MW 480,(4-7) and hydrogenated poly(acetylene) having 17% sp^3 carbons (8) have almost as high doped conductivity as high MW trans-poly(acetylene) itself. Nevertheless, the uncertainty about the uniformity of microstructure continue to cloud the issue.

In this study metathesis catalyst is used to copolymerize an acetylene precurosr (p-A = 7,8-bis(trifluoromethyl)tricyclo[4,2,2,$0^{2,5}$]deca-3,7,9-triene) and cyclopentene, CP. Since the copolymers of all compositions are soluble and the copolymerizations are not complicated by precipitation, they should have uniform microstructures. Results of the synthesis, characterization, and electrical conductivity of the ACP copolymers are presented in this paper.

Experimental

Materials. Cyclopentene was purified by distillation from CaH_2. Chlorobenzene was dried over P_2O_5, distilled under argon and stored over 4A molecular sieves. WCl_6 was used as received (Aldrich). Me_4Sn was purified by distillation over CaH_2 and stored in a Schlenk tube. Cyclooctatetraene, COT, was distilled under vacuum prior to use. p-A was synthesized from COT and hexafluoro-2-butyne by previously reported procedure (9).

Copolymerization. All chemicals were degassed and stored under argon. All operations were performed either in a dry box or using Schlenk techniques. Comonomers of different ratios totaling 2 M are weighed into vials with septum caps. WCl_6 (1 mol %) was weighed into the polymerization vessel, required quantity of chlorobenzene added, and the vessel covered with a butyl rubber liner and a metal cap with holes was crimped over the crown top. Me_4Sn (2 mol %) was added to the WCl_6 solution and the mixture aged for five minutes during which the colour changed from dark purple-blue to reddish brown. The catalyst solution was cooled to between 0 - 15°C then the monomer mixture was injected into it and agitated using a vortexer to affect efficient mixing at high viscosity. The polymerization was terminated by addition of an excess of methanol. The polymer was redissolved in cold acetone/chloroform and reprecipitated into cold methanol. A low temperature was maintained throughout the work-up to avoid premature elimination of hexafluoroxylene. The polymer samples were then dried under a high vacuum (10^{-4} torr) at low temperature. The copolymer compositions were determined by both thermogravimetric analysis, TGA and elemental analysis.

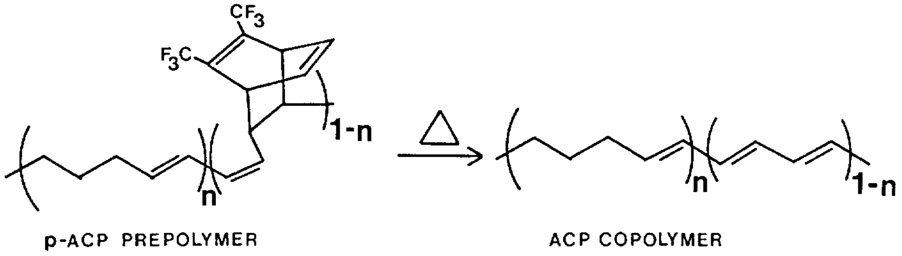
Film casting and thermal conversion. The solvents used for casting copolymer films were deoxygenated by bubbling with high purity argon and stored over molecular sieves. Polymers with high p-A content were cast from acetone while those with a lower content were cast from a methylene chloride solution. The films were dried under a slow flow of argon and then further dried under a high vacuum (10^{-4} torr). Thermal elimination of hexafluoroxylene were performed by heating the copolymer films under vacuum in an oil bath at a temperature between 80 - 90°C for 12 - 15 hrs. The casting dishes were pretreated with Me_3SiCl to facilitate removal of the films. The thickness of the resulting copolymer film varied from 20 to 40 microns.

Doping. Doping was carried out by exposing the films to iodine at a slow controlled rate (10), by varying the vapour pressure affected by changing the temperature of the iodine reservoir.

Characterization. The IR spectra of the polymer films were recorded with a Mattson Cygnus 100 spectrophotometer. The EPR spectra were obtained with an IBM ESP-300 spectrometer. The g values were calculated using diphenylpicrylhydrazyl as a marker and the spin concentrations were determined using tetramethylpiperidinoxyl as a standard. The electrical conductivity was measured by either the two probe or the four probe technique as required by the resistance of the material (10). The dopant concentration determined by weight uptake and the EPR spectra of the samples were taken after the doped samples were pumped to attain constant conductivity.

Results and Discussion

Copolymerization. The p-ACP and ACP copolymers had the following general structures



The conversion during all the polymerizations was kept below 50% to minimize the formation of homopolymers. The composition of the copolymers are most readily measured by thermogravimetric analysis of the polymers (Figure 1). The weight loss corresponds to the amount of hexafluoroxylene eliminated from which the mole fractions of the two comonomers can be calculated (Table I).

Table I. Acetylene-Cyclopentene Copolymers

Copolymer	p-A/P[a] mole ratio in feed	Mole % of CP in copolymer		Elemental Analysis, %		Mole % of acetylene in copolymer by TGA[c]
		from C/H	from TGA	C	H	
ACP-13	0.34	58.8	60.3	89.0	10.3	58.6
ACP-11	1.0	42.1	48.3	89.1	9.6	68.2
ACP-31	3.17	20.8	39.4	88.9	8.6	75.5

[a] P is cyclopentene; [b] calculated from TGA; [c] Calculated giving consideration to the fact that each p-A unit contributes two acetylenic units.

The compositions were obtained from C/H ratios, but the CP contents are markedly smaller than obtained with TGA and the discrepancies increase with increasing p-A content suggestive of systematic errors in elemental analysis.

<u>IR spectra</u>. IR spectra were done on completely eliminated films with thicknesses ranging from 20 - 40 μm. The spectra clearly show an increase in the intensity of the trans out-of-plane vibration and the C-H stretching vibrations corresponding to the conjugated trans double bond with increasing acetylene content. The WCl_6/Me_4Sn catalyst system produces poly(pentenomer) with high trans content as seen from the ratio of the 966 cm^{-1} and the 720 cm^{-1} bands that correspond to the <u>trans</u> and <u>cis</u> double bond, respectively (Figure 2a). In the case of the ACP copolymers there is a gradual shift of the <u>trans</u> C-H out-of-plane bending vibration from 988.6 cm^{-1} in ACP-13 to 1009.2 cm^{-1} in ACP-31 and an increase in its relative intensity (Figure 2). This behaviour indicates an increase in the <u>trans</u> double bond conjugation length (13). The ACP-13 film has a reddish-yellow color while ACP-11 is dark reddish-black in color and the ACP-31 film has a shiny appearance very much like polyacetylene indicating increasing conjugation with the increase of acetylene units in the copolymers.

<u>Electron spin resonance</u>. The copolymers have weak ESR signal at g = 2.0026. The unpaired spins, S·, per gm of copolymer are given in Table II column 3. Since S: can be only found on <u>sp</u>^{2} carbon atoms, the number of the latter per S: are calculated from the copolymer compositions and listed in column 4. Even for ACP-31 with about 75% of acetylene units the [S·] is only about one-tenth of that in normal <u>trans</u>-poly(acetylene) (14).

Table II

Electron spin resonance of acetylene-cyclopentene copolymers

Copolymer	Spins per gm x 10^{-18}	<u>sp</u>^{2} carbons per spin x 10^{-4}	ΔH_{pp}, gauss
ACP-13	0.16	17.0	15.6
ACP-11	0.86	3.5	14.6
ACP-31	1.44	2.3	12.8

The unpaired spin wavefunction is said to be delocalized over six to eight monomer units in <u>trans</u>-poly(acetylene) (15). It is not known what the minimum number of conjugated carbon atoms is required to stabilize an unpaired spin by delocalization. The unpaired spin concentrations in the ACP-31, -11 and -13 copolymers are in the ratios of 0.1:0.07:0.01. Based on probability considerations of reaction of <u>p</u>-A monomer, the relative probabilities of <u>p</u>-A-<u>p</u>-A diads are in the ratios of 0.1:0.05:0.01. The correlation suggest that unpaired spins in the copolymers require the delocalization of its wavefunction over four acetylene units since each p-

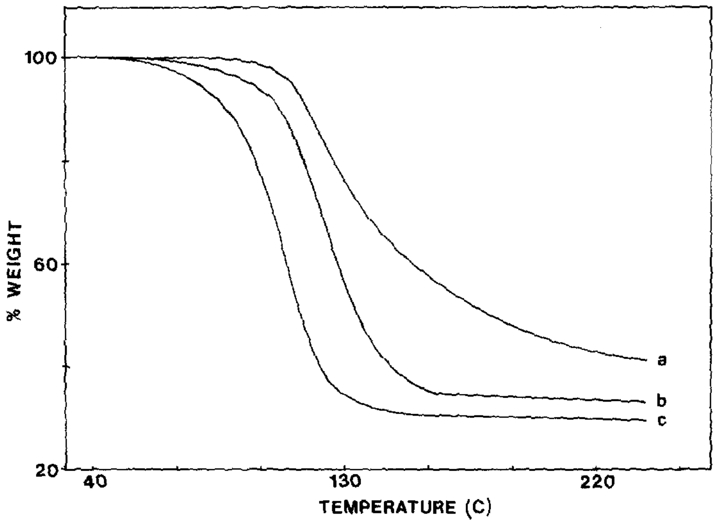


Figure 1. Thermogravimetric curves for copolymers: (a) p-ACP-13; (b) p-ACP-11; (c) p-ACP-31.

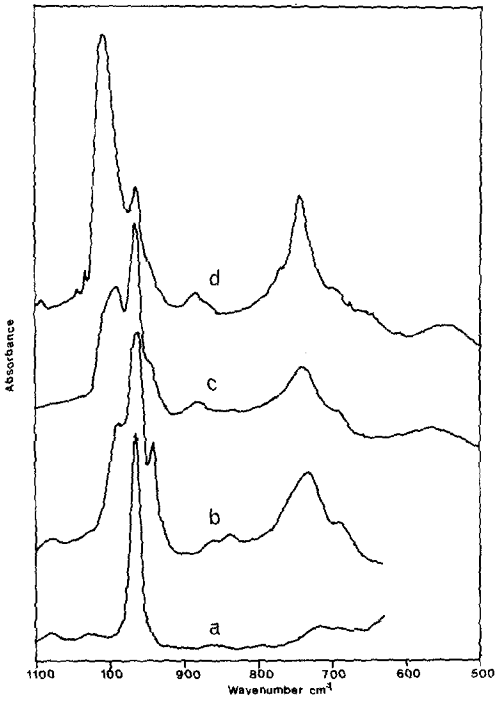


Figure 2. IR spectra of:
(a) poly(pentenomer);
(b) ACP-13; (c) ACP-11;
(d) ACP-13.

A is thermally converted to two acetylene units. Similar conclusions are reached from the room temperature ΔH_{pp} = 12.8 G for ACP-31 as compared to 8.5 G for *cis*-poly(acetylene). According to the theory that ΔH_{pp} is due to unresolved hyperfine structure and

$$\underline{a}_{eff} = \underline{a}_0 \, |\psi(\underline{n})|^2 \tag{2}$$

where $\underline{a}_{eff}$ is the observed ΔH_{pp}, $\underline{a}_0$ is the isotropic proton hyperfine coupling constant, and $\psi(\underline{n})$ is the wavefunction for a non-bonded single-electron state located at the center of domain of $\underline{n}$ lattice parameters (15), then S· is delocalized over four to five acetylene units.

Electrical conductivity. Undoped ACP-copolymers have low semiconductivity within experimental accuracy (Table III 2nd row). *Cis*-poly(acetylene) has room temperature conductivity, σ_{RT}, in the same range.

Table III. Electrical conductivity of AP-copolymers

Copolymer	ACP-13	ACP-11	ACP-31
Undoped σ_{RT}, $(\Omega\ \mathrm{cm})^{-1}$	1.6×10^{-10}	5.3×10^{-12}	1.8×10^{-11}
I_2 uptake, wt %	27.5	93.5	121
sp^2-carbons, wt %	58.9	66.0	71.6
Mole I_3^- per mole *sp*^{2}-carbon	0.015	0.046	0.054
Maximum doped σ_{RT} $(\Omega\ \mathrm{cm})^{-1}$	5.5×10^{-10}	3.5×10^{-7}	5.9×10^{-4}
σ_{RT} after evacuation $(\Omega\ \mathrm{cm})^{-1}$	3.3×10^{-11}	2.3×10^{-11}	7.0×10^{-9}

Doping increases σ_{RT} as expected. But the maximum doped values (Table III, row 6) are without meaning, because evacuation can significantly reduce σ_{RT}. In the case of ACP-13 and -11 copolymers these σ_{RT} returned to undoped values after pumping off excess iodine. It is known that polymers saturated with iodine can exhibit ionic conductivity. The really meaningful conductivity for polymers having a low degree of conjugation is that measured after removal of all absorbed iodine. Then all the doped ACP copolymers have σ_{RT} much less than undoped *trans*-poly(acetylene) (Table III, row 7). In the case of ACP-31 doping increases σ_{RT} by 10^2 fold to a value of 7×10^{-9} $(\Omega\ \mathrm{cm})^{-1}$.

An interesting observation *ca*. 5% I_3^-/*sp*^{2}-carbon after evacuation. This level of doping is about the same as that found for iodine doped poly(acetylene). This implies that the complexation of iodine with olefin is insensitive to its conjugation length.

It is interesting to speculate why ACP-31 copolymer which contains 75% acetylene units and doped to 5 mole % I_3^- has only conductivity of 7 x 10^{-9} $(\Omega\ cm)^{-1}$. This result can be best explained by low carrier concentration and carrier mobility. In the case of poly(acetylene) there is complete charge transfer for each dopant (16-18). The degree of charge transfer may be very much smaller for very short sequences of acetylene units. The wavefunction of the iodine doped ACP-copolymers may be written as,

$$\psi_i = a_i \phi_a (CH^+ I_3^-) + b_i \phi_b (CH \rightarrow I_2) \qquad (3)$$

where i = 2, 4 ... is the number of *sp*^{2} carbon atoms in a conjugate sequence, ϕ_a is the wavefunction of the charge transfer state, and ϕ_b is that for contribution from induced dipolar interactions. The effective fractional charge transfer is a_i^2, where $a_i^2 + b_i^2 = 1$. For the ACP-copolymers a_i is very small while b_i approaches unity. Consequently the carrier concentration is very small even though there are large amounts of iodine bound to the polymer.

A second factor is the low carrier mobility. Charge transport in materials such as ACP copolymers can occur only if there is overlap of ψ_i's. Because the fractional charge is confined by small conjugated domains, there is very little overlap. Therefore, the electrical properties of ACP copolymers are qualitatively different from those of poly(acetylene). In the latter case, there are high carrier mobilities when the coulombic fields become shielded for high carrier concentrations which reduces greatly the pinning potential according to the model of carrier mobility transition (2).

Yaniger *et al*. (8) and Soga and Nakamura (19) had introduced methylene units into poly(acetylene) by *n*-doping followed by hydrogenation. The purposes here are to introduce CH_2 insulating units to alter the conjugation length l, where l is the average number of CH's in a sequence. Yaniger *et al*. (8) doped the materials with AsF_5 and reported $\sigma \propto l^{3.2}$ for $l \geq 3$. The latter workers used iodine doping to obtain a similar σ versus l dependence. However, the conductivities observed by Yaniger *et al*. are about 10^5 greater than those of Soga and Nakamura (19). By comparison the ACP-31 has even lower conductivity. ACP-31 has σ_{RT} = 7 x 10^{-9} $(\Omega\ cm)^{-1}$ for $l = 8$. For the same conjugation length for hydrogenated poly(acetylene), Yaniger *et al*. (8) and Soga and Nakamura (19) found doped conductivities of 6 and 10^{-5} $(\Omega\ cm)^{-1}$, respectively, the latter value was estimated by extrapolation.

The hydrogenated polyacetylene contains only CH_2 between conjugated sequences. The length of the latter is susceptible to increase due to isomerization by the dopant. The different conductivities of similarly prepared polymers may be due to more double bond isomerization by AsF_5 than by I_2. Furthermore, AsF_5 is a stronger oxidizing agent and the degree of charge transfer is greater for the former than the latter to a conjugation sequence of same 1. Isomerization may also partly account for the lower σ_{RT} for the ACP-copolymers than the hydrogenated polyacetylene. In the latter there are a minimum of three methylenes separating acetylene units and it is unlikely that 1 will be affected by isomerization. Finally, it is not stated by Soga and Nakamura (19) whether σ_{RT} was the value measured before or after removal of excess iodine by pumping.

Conclusions. Copolymers containing acetylene and pentene units have been prepared. Even at 75 mole % of the former having an average conjugation of four double bonds, the unpaired spins are not stabilized and only weak charge transfer occurs on doping. Synthesis and characterization of copolymers having high acetylene contents would be of both interest and significance.

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