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Copolymerization of 2,4-dichlorophenylacetylene with disubstituted acetylenes by metathesis catalysts

Mikhail A. Tlenkopatchev[1,*], **Yuri V. Korshak**[2], **Edmundo Miranda**[1], **Takeshi Ogawa**[1]

[1] Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, Apdo. P. 70-360, 04510-México, D.F., México
[2] Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Leninskii Pr. 29, Moscow, 117912, Russia

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Summary

Polymerization and copolymerization of 2,4-dichlorophenylacetylene and 3-heptyne was carried out using tungsten-containing catalysts. The monomer reactivity ratios showed that the phenylacetylene was more reactive than 3-heptyne by a factor of 3.2. Relationships between the monomer composition, gas permeability and selectivity were investigated, and it was found that the incorporation of 2,4-dichlorophenylacetylene decreases the permeability, but increases selectivity for the gas mixtures tested in this work. The electrical conductivities of the polymers were also determined.

INTRODUCTION

The polymerization of alkynes has been studied by many researchers in last decades in search of new materials especially as electrical conductors[1] and gas permeable membranes[2]. The polymerization of phenylacetylenes has been reported by many workers. Katz and coworkers have extensively studied the polymerization with W and Mo catalysts[3], and Masuda et al. [4] have obtained high molecular weight polymers of various substituted phenylacetylenes using Mo and W based catalysts. Sen et al.[5] used Pd based catalysts, and Furlani et al. have used Ni[6] and Pt[7] catalysts. Rh compounds are particularly useful for polymerization of phenylacetylenes and many studies have been reported by Furlani et al.[8], Tabata et al. [9], and Ogawa et al. [10]. The present authors have previously studied the polymerization of 2,4-dichloro-[11], p-bromo-[12], and p-methoxy-[13] phenylacetylenes using W, Mo and Nd based catalysts. 2,4-Dichlorophenylacetylene gave an air stable, high molecular weight, conjugated polymer soluble in toluene and chloroform.

Disubstituted acetylenes, i.e., inner alkynes, are known to polymerize to give nonconjugated high polymers by metathesis catalysts[14,15]. These polyacetylenes

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[*] Corresponding author

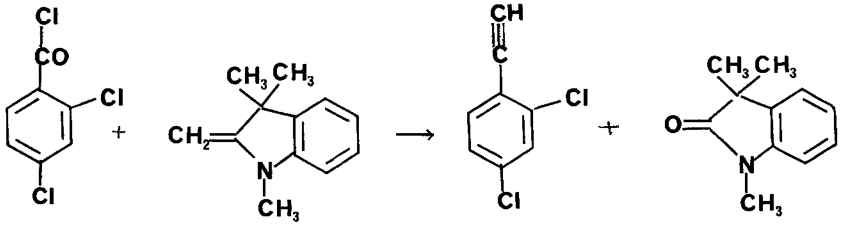
are colourless because their main chains take twisted conformations due to the steric hindrance of substituted groups. The polymers are soft and ductile.

Little study has been reported about copolymerization of acetylenes. Masuda et al.[16] have studied the copolymerization of phenylacetylene with alkynes using metathesis catalysts, and reported monomer reactivity ratios. The present authors are interested in studying the relationships between the comonomer compositions, polymer structure and properties of copolymers obtained by the copolymerization of phenylacetylenes with inner alkynes. In this work, 2,4-dichlorophenylacetylene, Cl2PA, was chosen as the comonomer because it gives high molecular weight polymer by W catalyst. 3-Heptyne and diphenylacetylene were used as inner alkyne monomers.

EXPERIMENTAL

MATERIALS

Cl2PA was synthesized by the method reported previously[11,17] using 1,3,3-trimethyl-2-methyleneindoline, as shown in scheme 1. Cl2PA thus obtained was purified by flash-chromatography on silica gel. Yield was 72 %, and it had a purity of 99 % determined by gas chromatography and a melting point of 58 °C. Commercial 3-heptyne was destilled twice over calcium hydride before use. Diphenylacetylene was recrystallized from ethanol. Tungsten (VI) chloride, diethylaluminum chloride and tetraphenyltin, all supplied by Aldrich, were used as received. Diepichlorohydrin tungsten tetrachloride was prepared by the reaction of tungsten (VI) chloride with epichlorohydrin in toluene [18]. Benzene and toluene, used as solvents for polymerization were purified by the usual methods. The synthesis of catalysts and polymerizations were carried out under a dry nitrogen atmosphere.



SCHEME 1

CHARACTERIZATION

^1H and ^{13}C NMR spectra were recorded by a Bruker AM-300 spectrometer. IR spectra were taken using a Nicolet 510P FT-IR spectrometer. UV-VIS absorption spectra were taken in chloroform using a Shimadzu UV 260 spectrophotometer. Intrinsic viscosities were determined in toluene at 25 °C. The average molecular weights were measured using a Waters GPC Model 510 in chloroform with polystyrene standard. Thermogravimetric analysis (TGA) was performed with a heating rate of 10 °C/min under nitrogen using a Du Pont 2100 thermoanalyzer. Wide angle X-ray diffractometry (WAXD) was carried out using a Siemens D-500 diffractometer. Electrical conductivity was measured by the four-point probe DC method. Gas permeability coefficients were determined by a chromatographic method as described in detail [19]

RESULTS AND DISCUSSION

Table 1 shows results of homo- and copolymerization of Cl2PA, 3-heptyne and diphenylacetylene(DPA) in toluene at room temperature using the W catalysts. Cl2PA polymerized almost quantitatively with these catalysts giving high molecular weight, soluble polymers. The polymerization of 3-heptyne was somewhat slower but it also gave high molecular weight, colourless, fibrous polymer. Diphenylacetylene gave an insoluble polymer which precipitated during polymerization, but other polymers were soluble in common solvents such as chloroform, benzene and toluene and flexible transparent films were obtained by casting their solutions.

The copolymer obtained from Cl2PA and 3-heptyne were coloured indicating that the conjugation in the polymer chain increases by the introduction of Cl2PA. ^{1}H NMR spectrum of a copolymer obtained from an equimolar mixture of Cl2PA and 3-heptyne, are shown in Fig. 1. The peaks in the region of 6.2 - 7.85 ppm are assigned to the trans olefinic and aromatic protons form the Cl2PA monomer; a weak signal of cis- olefinic protons is observed at 5.95 ppm. The signals in the regions 1.8 - 2.07, 1.45 and 1.0 ppm correspond to the protons on the carbons adjacent to the double bond, methylene and methyl protons of 3-heptyne,

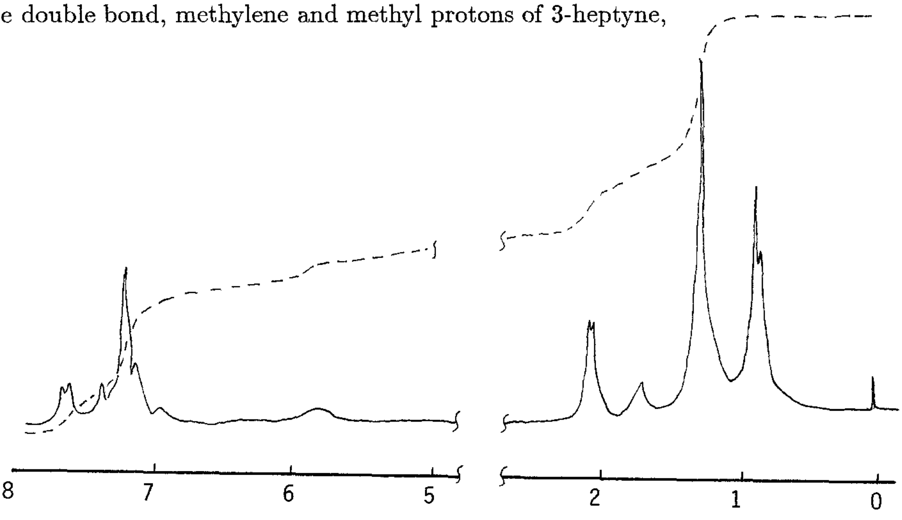


Fig. 1. ^{1}H NMR spectrum of Poly(Cl$_2$PA-co-3-Heptyne): Equimolar monomer feed.

Table 1. Copolymerization of Cl_2PA with 3-heptyne and diphenylacetylene at room temprature in toluene for 18 hrs. using W-containing catalysts. $[\text{monomer}]_0$ = 2 mol/l, [Cat]/[M] = 0.5 (mol %)

Exp. #	Catalysts[a]	Comonomer ratio: (mol.%.)	Yield[b] (%)	$[\eta]$[c] (dl/g)	λmax[d] (nm)	colour
1	WCl_6	Cl_2PA(100)	91	0.5	490	dark violet
2	$W(OR)_2Cl_4$/ $5AlEt_2Cl$	"	94	1.25[e]	510	" "
3	$W(OR)_2Cl_4$/ $5AlEt_2Cl$/ THF	"	85	1.54	510	" "
4	$W(OR)_2Cl_4$/ $5AlEt_2Cl$	3-heptyne (100)	58	4.16[f]	275	colourless.
5	$W(OR)_2Cl_4$/ $5AlEt_2Cl$/ 5THF.	"	45	4.28	280	"
6	WCl_6/ $5SnPh_4$	diphenyl acetylene	15	---	385[h]	yellow
7	$W(OR)_2Cl_4$/ $5AlEt_2Cl$	Cl_2PA/3-heptyne 80/20	87	1.46	365	dark orange.
8	"	50/50	89	1.81[g]	350	orange
9	"	30/70	75	2.05	340	yellow orange.
10	"	Cl_2PA/ diphenyl acetylene 70/30	82	1.26	470	red
11	"	50/50	84	1.16	450	red

a) R = $-OCH(CH_2Cl)_2$. b) methanol-insoluble fraction.
c) in toluene at 25°C. d) in $CHCl_3$, e) $M_n = 5 \times 10^4$, $M_w = 1.23 \times 10^5$
f) $M_n = 3.5 \times 10^5$, $M_w = 8.5 \times 10^5$, g) $M_n = 1.2 \times 10^5$, $M_w = 3.0 \times 10^5$.
h) chloroform soluble fraction.

respectively. IR spectra of these polymers showed bands at 3000 - 3100 cm^{-1} and 1600 - 1610 cm^{-1} characteristic to the double bonds, instead of the bands at 3300 and 2100 cm^{-1} corresponding to the acetylenic proton and acetylenic stretching, respectively, which are seen in the IR spectra of the monomers.

The monomer reactivity ratios were determined for the copolymerization of Cl2PA with 3-heptyne using $W[OCH(CH_2Cl)_2]_2Cl_4$-$Al(C_2H_5)_2Cl$ catalyst at room temperature 25 °C. Copolymer compositions were measured by ^{1}H-NMR spectroscopy using relative intensities of the peaks of the olefinic, aromatic and allylic protons. The method of Fineman and Ross [20] was employed for calculation of r_1 and r_2. The yields of copolymerization were kept below 10 % by stopping the copolymerization in 10 minutes. The monomer reactivity ratios were $r_{(Cl2PA)} = 2.9$ and $r_{(3-hep)} = 0.9$. Fig. 2 shows the monomer-copolymer composition curve for this system, which shows that more Cl2PA units are incorporated in copolymers than 3-heptyne units.

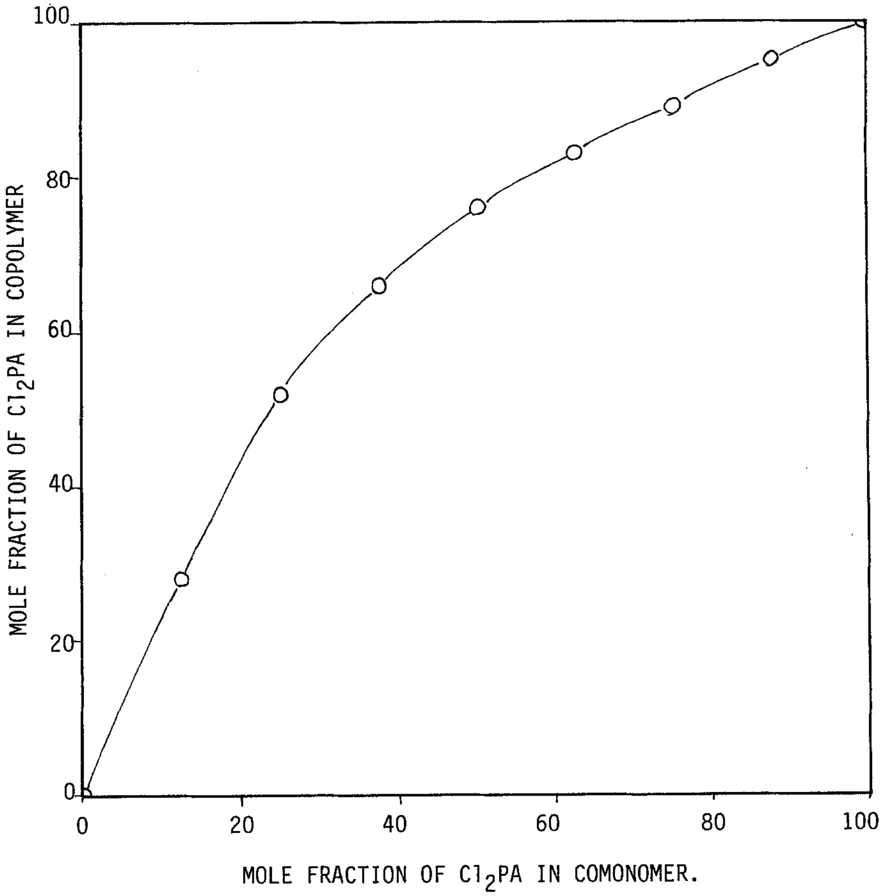


Fig. 2. Composition curve for copolymerization of Cl_2PA with 3-Heptyne at 25°C in toluene.

X-ray diffractometry indicated that both homopolymers and copolymers were amorphous. This is attributed to the bulky side groups which inhibit crystallization of polymer chains. The electric conductivity measurement indicated that the products are insulators. The conductivities increased to 10^{-9} - 10^{-8} Scm^{-1} when doped with iodine. TGA showed that the Cl2PA/3-heptyne copolymer with equimolar monomer feed started to lose weight at around 300 °C and lost 50 % of its weight at 410 °C under nitrogen. Poly(Cl2PA) started to lose weight at 360 °C and lost 50 % at 560 °C. The tensile strength of the above copolymer was 18 MPa.

Gas permeability of poly(Cl2PA-co-3-heptyne) was investigated and the results are shown in Table 2. It can be seen that the incorporation of Cl2PA units decreases the permeability for all the gases employed. However, increase in permeability generally leads to decrease in selectivity. As expected, selectivity increased by the introduction of Cl2PA units.

Table 2. Permeability coefficient, Pi(Ba)[a] and separation factors of poly(Cl_2PA-co-3-heptyne)s.

Mole % Cl_2PA in copolymer	O_2	N_2	CO_2	O_2/N_2	CO_2/N_2
0	69	---	---	2.2	---
15	58	27.6	202	2.1	7.3
25	41	17.8	174	2.3	9.8
40	7.5	2.2	36.6	3.4	16.6
75	5.1	1.37	20.8	3.7	15.2

[a] 1 Barrer (Ba) = 10^{-10} cm^3(STP) cm/cm^2 sec cm Hg.

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