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POLYMERIZATION OF METHYL PROPIOLATE WITH PALLADIUM CHLORIDE, TRIPHENYLPHOSPHINE, AND PALLADIUM CHLORIDE TRIPHENYLPHOSPHINE COMPLEX

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ABSTRACT

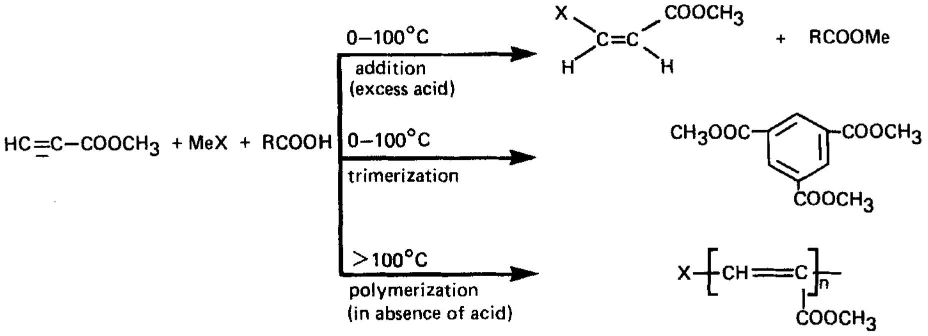
Some results of the bulk polymerization of methyl propiolate in the presence of $PdCl_2$, triphenylphosphine, and $[(C_6H_5)_3P]_2.PdCl_2$ complex are presented. From the polyconjugated polymers obtained, fractions based on their solubility in various solvents were separated. Subsequently, these products were characterized by IR and ^1H NMR spectroscopies and by thermal analysis. The data obtained indicate that polymerization assisted by $[(C_6H_5)_3P]_2.PCl_2$ proceeds faster, giving products with a lower cyclic oligomers content. The polymers possess good thermal stability and semiconducting properties.

INTRODUCTION

Esters of propynoic (propiolic) and acetylenedicarboxylic acids can polymerize under basic conditions to give mixtures of polyconjugated linear and cyclic structures. The following order of reactivity was established for such monomers [1, 2]: $CH_3OOC{-}C{\equiv}C{-}COOCH_3 > HC{\equiv}C{-}COOCH_3 > CH_3{-}C{\equiv}C{-}COOC_2H_5 > C_6H_5{-}C{\equiv}C{-}COOCH_3$. Moreover, it was found that an anionic mechanism is more common than free-radical or cationic ones for methyl propiolate. Thus, the literature data mention the polymerization of methyl propiolate with triethylamine, both in homogeneous and heterogeneous media [3, 4]. The mentioned monomers also form polymers vigorously under the influence of bis(acrylonitrile)- and bis(acrolein)nickel [5].

The attempts of Meriwether and coworkers to polymerize 35 mono- and disubstituted acetylenic monomers with $Ni(CO)_2(PPh_3)_2$ have revealed that ethyl and methyl propiolates are of the highest reactivity in the aromatization Reppe process. The latter gives 1,2,4-tris(carbomethoxy)benzene in 78% yield when it reacts in benzene solution at reflux temperature [6].

Dvorko, Soboleva, and Karpenko [1] established that the reaction of methyl propiolate proceeds in three directions in DMF or sulfolane solution and in the catalytic presence of carboxylic acids or their salts. By selecting the reaction conditions, one may obtain the desired product:



where MeX is a metal halide.

Polymerization of methyl propiolate in the presence of organometallic compounds (Pd, Co, Ni, and Pt arsines, stibines, or phosphines) showed the best yields with $PdCl_2$ complexes [7].

The electrochemical polymerization (up to $\overline{M}_n$ 7000) of methyl propiolate was studied recently, and its behavior toward cathodic reduction was evidenced by polarography [8, 9]. In most cases the cyclic trimer (1,3,5- and 1,2,4-trisubstituted benzene) was obtained besides linear polymers.

This paper presents a comparative investigation of methyl propiolate polymerization catalyzed by $PdCl_2$, $(C_6H_5)_3P$, and $[(C_6H_5)_3P]_2.PdCl_2$.

EXPERIMENTAL

Methyl propiolate (MP) was prepared as described in Ref. 10, dried over CaH_2, and vacuum distilled. Triphenylphosphine (TPP) was crystallized from $CHCl_3$

before use. The $[(C_6H_5)_3P]_2.PdCl_2$ complex (TPP-Pd) was prepared and purified as described in Ref. 11. All solvents were distilled before use.

Bulk polymerization was adopted as a working technique and was carried out at 90 ± 1°C (close to the reflux temperature of MP) under magnetic stirring at various times and monomer/catalyst ratios. The polymerization was stopped by adding solvents with labile hydrogen. The products obtained were separated into fractions: one insoluble in acetone (I), two soluble in acetone but insoluble in diethyl ether (II) and petroleum ether (III), respectively, and a last one (IV) was isolated by removing solvents (i.e., soluble in all three solvents).

Characterization of polymers was done by elemental analysis, IR (KBr pellets, on a Perkin-Elmer instrument) and ^1H NMR (JEOL 60 MHz in $CDCl_3$ and TMS as internal standard) spectroscopy, and thermal analysis (Paulik-Paulik-Erdey MOM-Budapest apparatus). The softening range was established with a hot-stage microscope, while the viscosities were measured in acetone with an Ostwald viscometer.

RESULTS AND DISCUSSION

Polymerization of Methyl Propiolate with $PdCl_2$

The thermal bulk polymerization of MP was found to proceed under rather drastic conditions (200 ± 2°C and 48 h), and two fractions which melted at 100-125°C and 60-80°C, respectively, could be isolated from the polymers obtained. Faster polymerization and milder conditions were observed for $PdCl_2$-catalyzed reactions, so that the process was carried out at 90 ± 1°C. When the catalyst contacts the monomer, the system turns brown in color, which indicates a rapid onset of the reaction. However, results were poor for short times (15-25 min), so that the process was run for 5 h.

Table 1 and Fig. 1 summarize reaction conditions and some of the polymer characteristics. It is seen that the quantity of the first fraction increases slowly with catalyst concentration, while the other fractions do not show the same correlation. The overall yield of polymer depends on the catalyst concentration mainly at its lower levels. In the higher range of catalyst-to-monomer ratio, the polymer yield becomes almost independent of the catalyst concentration when conversion reaches 95-100%. The melting range varies within narrow limits for all the polymerization conditions. It was also found that Fraction IV contains tricarbomethoxybenzene as white crystals (1,2,4- or 1,3,5-trisubstituted derivative).

Polymerization of Methyl Propiolate with $(C_6H_5)_3P$

Although the bulk polymerization of MP catalyzed by TPP starts immediately, the results obtained show low yields and the absence of Fraction I

TABLE 1. Bulk Polymerization of MP Catalyzed by $PdCl_2$ [a]

Experiment no.	Catalyst/monomer molar ratio	Fraction	Polymer[b] g	Polymer[b] %	Softening range, °C
1	1:453	I	0.254	8.45	233-234
		II	0.147	4.91	177-181
		III	0.974	32.45	120-135
		IV	1.336	44.51	36-60
2	1:196	I	0.276	9.19	231-234
		II	0.108	3.59	162-168
		III	1.077	35.90	115-127
		IV	1.484	49.46	57-80
3	1:180	I	0.272	9.06	234-237
		II	0.090	3.00	170-182
		III	0.843	28.10	118-127
		IV	1.618	53.93	64-75
4	1:140	I	0.298	9.77	231-234
		II	0.055	1.81	189-197
		III	1.079	35.95	105-130
		IV	1.573	52.40	52-68
5	1:105	I	0.308	10.27	227-229
		II	0.136	4.53	168-180
		III	1.058	32.25	115-125
		IV	1.468	48.95	56-100

[a] Time, 5 h; temperature, 90 ± 1°C.

[b] State and color of products: I, yellow; II, brown; III, light brown; IV, an oily product + crystals.

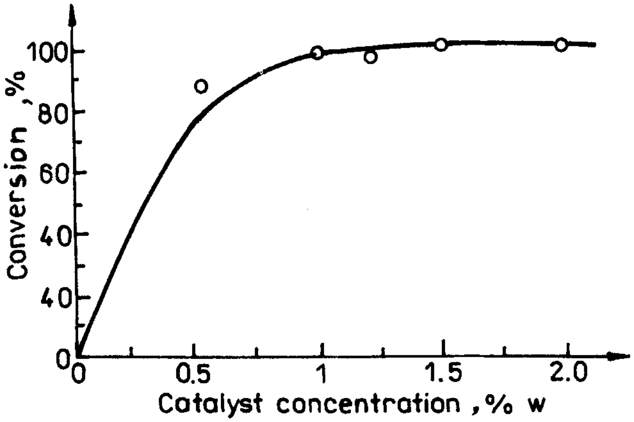


FIG. 1. Polymerization of MP with $PdCl_2$ at various catalyst concentrations. Time, 5 h.

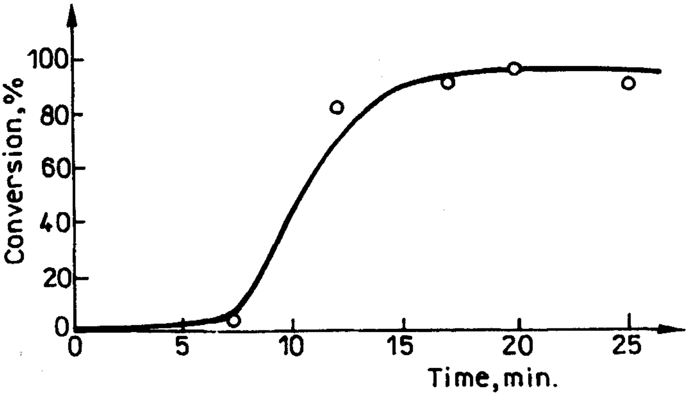


FIG. 2. Time-conversion curve for MP polymerization. Catalyst: TPP-Pd complex.

(Table 2). Consequently, this process was carried out only at one monomer/catalyst ratio.

Polymerization of Methyl Propiolate with $[(C_6H_5)_3P]_2.PdCl_2$

The ability of MP to polymerize with the palladium chloride-triphenylphosphine complex contrasts with its behavior in reactions assisted by other catalysts. The process is more rapid, so that after an induction period of 7-8 min the polymerization starts at a high rate and with high yields of polymer (81-93%) (Fig. 2 and Table 3).

TABLE 2. Bulk Polymerization of MP Catalyzed by TPP[a]

Experiment no.	Catalyst/monomer molar ratio	Fraction	Polymer yield		Color	Softening range, °C
			g	%		
6	1:252	II	0.102	3.38	Dark brown	173-210
		III	0.077	2.56	Brown	140-152
		IV	0.181	6.00	Brown oil	35-85

[a] Time, 5 h; temperature, 90 ± 1°C.

TABLE 3. Bulk Polymerization of MP with TPP-Pd[a]

Experiment no.	Reaction time, min	Fraction	Polymer yield[b] g	%	Softening range, °C
7	12	II	0.601	20.02	–
		III	0.672	22.38	135-141
		IV	1.164	38.78	55-110
8	17	II	0.479	15.95	–
		III	0.938	31.25	135-147
		IV	1.186	39.54	55-109
9	20	II	0.648	21.61	–
		III	0.917	30.55	142-145
		IV	1.219	40.65	45-80
10	25	II	0.562	18.71	–
		III	0.919	30.64	132-145
		IV	1.131	37.69	40-90

[a] Temperature, 90°C; catalyst/monomer, 1:410 molar ratio.
[b] State and color of products: II, dark; III, brown, IV, oily brown.

The $(Ph_3P)_2.PdCl_2$-catalyzed polymerization of MP results in a complex product with a distribution of the polymer fractions different from that obtained by $PdCl_2$-catalyzed reactions. The complete absence of Fraction I, the substantial increase of Fraction II, and the decrease of the fraction containing cyclic trimer (IV) (Table 3) are worth mentioning, as is the fact that Fraction II does not show any softening.

The polymerization of acetylenic derivatives with palladium complex catalysts is taken to imply acetylide intermediates [6, 12-14]. Thus, one may assume that the $(C_6H_5)_3P$ ligand facilitates removal of HCl and formation of the mentioned promoters. This effect may also explain the short induction period and higher reaction rates.

Polymer Characterization

IR spectra were recorded for the polymer fractions obtained under various polymerization conditions with $PdCl_2$ (Fig. 3) and TPP-Pd (Fig. 4) as catalysts.

Unlike the spectrum of the monomer, the IR spectra of polymer fractions show no absorption at 2100 cm^{-1} ($\nu_{C\equiv C}$) but exhibit a new peak at 1620 cm^{-1} ($\nu_{C=C}$). These modifications are less noticeable for Fraction IV (Fig. 4) since it contains mainly cyclic oligomer. Fraction I reveals strong absorption at 700 cm^{-1}, which is specific to *cis* unsaturation [15, 16]. It is missing in the other spectra, and the presence of a 950 cm^{-1} band suggests that the *trans* structure dominates in these fractions. The 720 and 730 cm^{-1} bands exhibited by Fraction IV (Fig. 4) confirm the formation of cyclic tricarbomethoxybenzene during the polymerization process.

The NMR spectra of the soluble fractions are presented in Figs. 5 and 6. All spectra reveal two large signals, i.e., one centered at δ = 3.75 ppm, assigned to $-CH_3$ protons, and the other at 7.2-7.3 ppm, corresponding to olefinic protons on the main chain. The structures of the analyzed fractions differ. Fraction IV (Fig. 6) contains large quantities of cyclic trimer and presents two additional signals at δ = 4 and 8.85 ppm. The broadening of the signal from δ = 3.75 to 2 ppm (Fig. 6, Fraction II) might be due to the cyclic structures formed

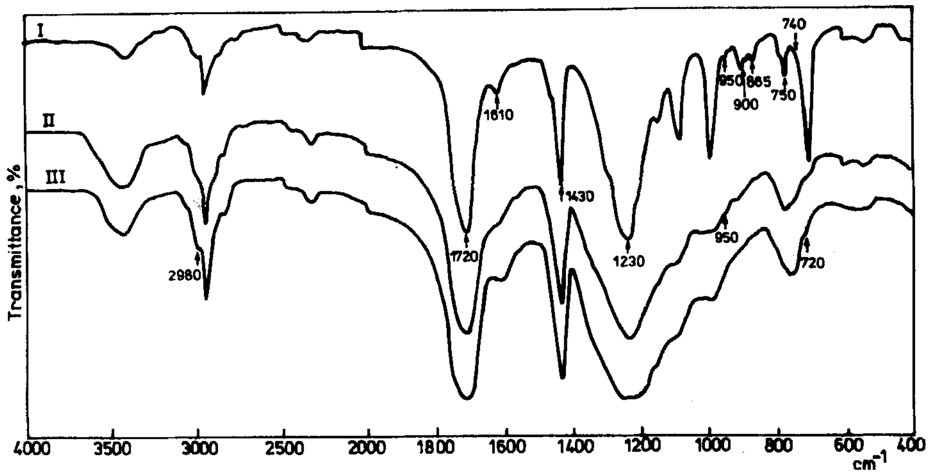


FIG. 3. IR spectra of polyMP Fractions I, II, and III. Catalyst: $PdCl_2$.

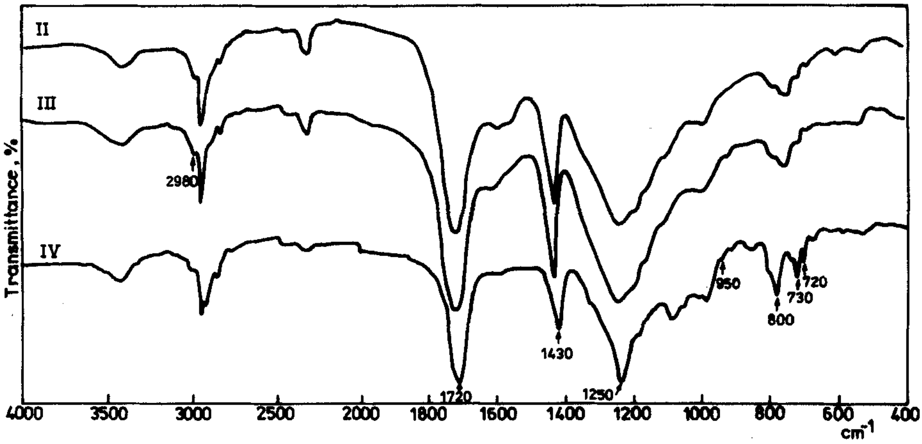


FIG. 4. IR spectra of polyMP Fractions II, III, and IV. Catalyst: TPP-Pd complex.

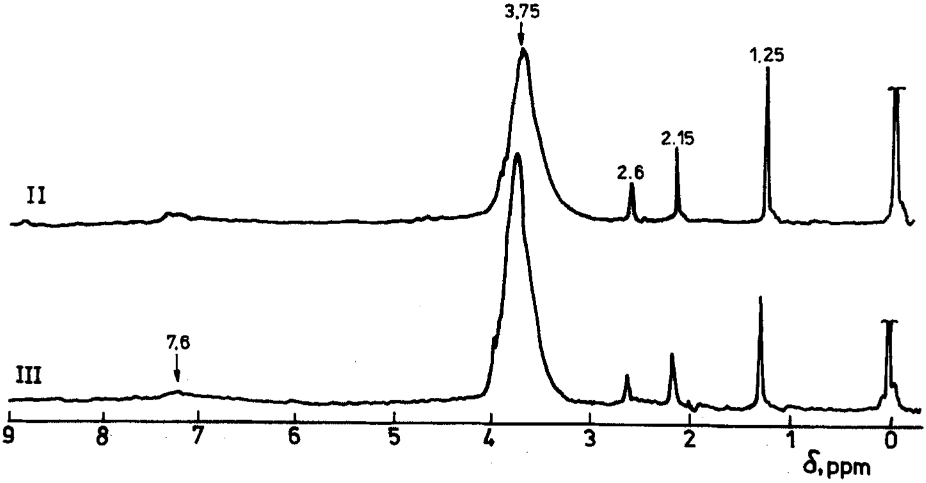


FIG. 5. ^{1}H NMR spectra of polyMP soluble Fractions II and III. Catalyst: $PdCl_2$. Room temperature in $CDCl_3$.

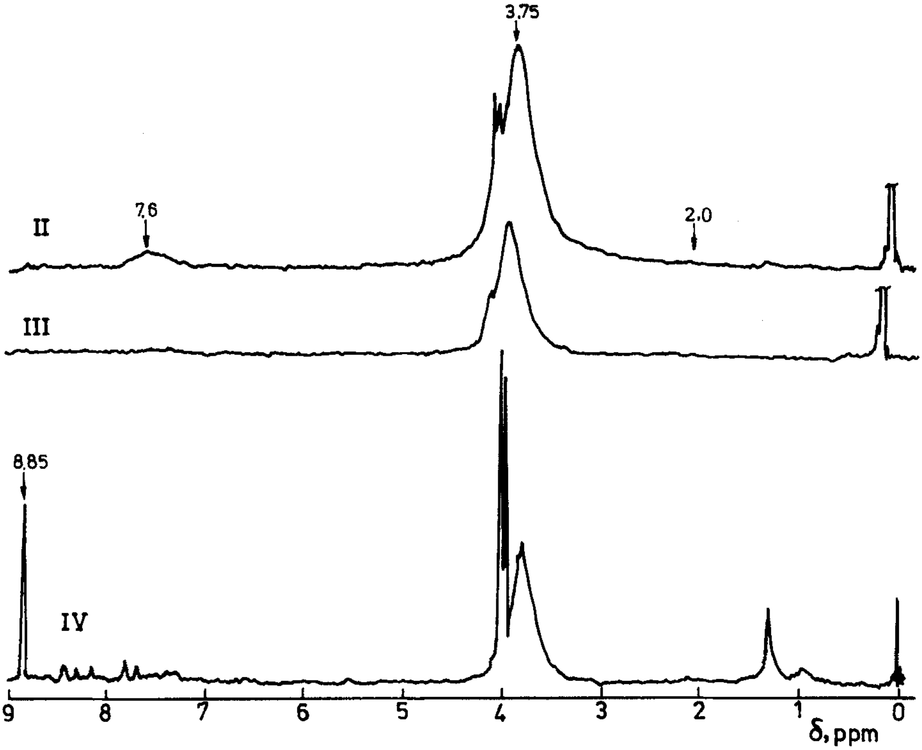


FIG. 6. ^{1}H NMR spectra of polyMP soluble Fractions II, III, and IV. Catalyst: TPP-Pd complex. Room temperature in $CDCl_3$.

by isomerization occurring in the propagating step [17]. The polymer obtained in $PdCl_2$-catalyzed reactions (Fig. 5) shows some signals specific to aliphatic domains, but their nature has not been clarified.

Elemental analyses for polyMP's obtained in various conditions are in good agreement with the calculated values and together with spectral information indicate the polyenic linear or cyclic structure of the synthesized products (Table 4).

Properties of the Polymers

The polyMP products are fusible or infusible colored powders and are soluble in polar organic solvents (except Fraction I), but insoluble or par-

TABLE 4

Catalyst	Fraction	C, %	H, %
$PdCl_2$ (Exp. 3)	I	56.80	4.86
	II	57.50	4.85
	III	57.01	4.92
$[(C_6H_5)_3P]_2.PdCl_2$	II	56.92	4.90
	III	57.20	4.86
	IV	56.90	4.92
Calculated		57.14	4.76

tially soluble in aromatic solvents. They also reveal good thermal stability.

Table 5 collects some physical properties of polyMP. The electrical resistance measurements show comparable values for Fractions II and III, but much higher resistances (R_{20}) for Fraction I. This might be an indication of a branched structure if one also considers its reported solubility.

TABLE 5. Properties of Poly(Methyl Propiolate) Fractions

Catalyst	Fraction	η_{red}, dL/g	Thermal stability,[a] °C	R_{20},[b] ohm
$PdCl_2$ (Exp. 1)	I	–	195	1.07×10^{15}
	II	0.103	160	3.71×10^{12}
	III	0.11	160	3.06×10^{13}
$[(C_6H_5)_3P]_2.PdCl_2$ (Exp. 9)	II	0.13	200	1.47×10^{13}
	III	0.106	170	1.31×10^{14}

[a] Temperature at which the sample starts to lose weight in air.
[b] Reference 3 gives $R_{20} = 7.58 \times 10^{16}$ ohm.

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