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Polymerization of phenylacetylene catalyzed by $Mo(CO)_6$

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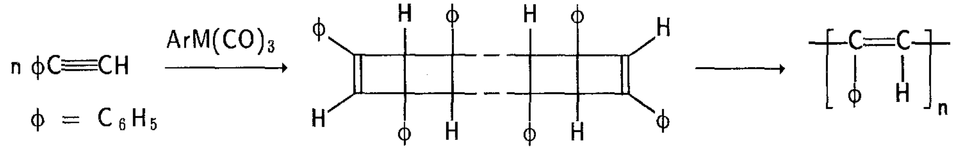
SUMMARY

Phenylacetylene was polymerized by the homogeneous alkyne metathesis catalytic system $Mo(CO)_6/C_6H_5OH$ in C_6H_5Cl at 120 °C. The polymer was characterized by IR, NMR and UV spectroscopy, and thermal methods. The stable polymer formed under these conditions was polyphenylacetylene with an alternating carbon–carbon double bond system with limited conjugation in the backbone and a mainly *trans*–configuration.

INTRODUCTION

Phenylacetylene (PA) has been reported to polymerize in the prescence of Group VIA metal carbonyls to yield high molecular weight (> 10^4) polyphenylacetylene (PPA). Complexes of the type $ArM(CO)_3$ (Ar = toluene or mesitylene; M = Cr, Mo or W) were used to synthesize linear PPA via a ladder polymer intermediate (1,2):



The best results were obtained with $(tol)Mo(CO)_3$ that yielded PPA with $\overline{M}_w = 1{,}2 \times 10^4$ in benzene at 80 °C or at 25 °C in the absence of any solvent.

PA was also polymerized by the active olefin metathesis catalyst $W(CO)_6/CCl_4/h\nu$ (3,4,5) and the analogous molybdenum catalytic system $Mo(CO)_6/CCl_4/h\nu$ (4,6). $W(CO)_6$ showed very high activity with a conversion of 93 % after 24h at 30 °C yielding a *trans*–rich conjugated dark brown polymer with $\overline{M}_n = 7{,}7 \times 10^4$. $W(CO)_6$ was also found to yield a dark red polymer with $\overline{M}_n = 14{,}9 \times 10^4$ (5). Under similar conditions $Mo(CO)_6$ exhibited a higher activity (conversion = 63 %) at higher catalyst concentrations and a reaction temperature of 60 °C (4). The yield of PPA was somewhat lower than the corresponding

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monomer conversion while a lower $\overline{M}_n$ value ($\overline{M}_n = 7,1 \times 10^3$) was also obtained.

According to Masuda and Higashimura (4,7,8) $Mo(CO)_6$ and $W(CO)_6$ are active polymerization catalysts only if CCl_4 is used as solvent and if the catalyst solution is irradiated by UV. However it has been shown that PA polymerized in the presence of the $W(CO)_6$/hexane/$h\nu$ system at 25 °C to yield red PPA after 24h (9). The thermal polymerization (100 – 150 °C) of terminal alkynes by $Mo(CO)_6$ and $W(CO)_6$ was also reported (9,10).

In the present study the polymerization of PA in the presence of $Mo(CO)_6/C_6H_5OH$ (11) at 120 °C was further investigated (12).

EXPERIMENTAL

Phenol, methanol (Holpro), molybdenum hexacarbonyl and phenylacetylene (Aldrich) were used as received. Chlorobenzene (Merck) was dried and distilled over $CaCl_2$.

The polymerization procedure was conducted under a dry nitrogen atmosphere in a closed glass reactor. The glass reactor with Mininert valve (Supelco) was placed in a glove bag in a nitrogen atmosphere and the catalyst $Mo(CO)_6$ (5×10^{-5} mol) and the cocatalyst C_6H_5OH (5×10^{-3} mol) added to the reactor. The reactor was then placed in a heating block at 120 °C, and the solvent C_6H_5Cl (2 cm^3) and PA (5×10^{-3} mol) added with a gastight syringe. Monomer consumption was determined by gas chromatography. A gradual change in colour from yellow to yellow–brown was observed. The reaction mixture was kept at 120 °C until the reaction ran to completion after which it was cooled. The polymer was precipitated in methanol, filtered off, washed with methanol and dried to constant weight. The consumption of the monomer determined by gas chromatography was in agreement with the polymer yield determined by gravimetry.

Gas chromatograms were obtained with a Varian gas chromatograph (3m x 3,2mm 10 % OV 101 on Supelcoport stainless steel column; isothermal at 120 °C; 25 $cm^3\ min^{-1}$ nitrogen carrier gas; flame ionization detector). The number average molecular weights ($\overline{M}_n$) were measured by GPC using a Waters/Pye Unicam combination gel permeation chromatograph (10^5, 10^3 and 10^2 Å PLGel columns; 0,7 $cm^3\ min^{-1}$ THF; refractive index detector) and polystyrene standards. UV (in CH_2Cl_2), IR (thin film) and NMR (in C_6D_6) spectra were recorded on Shimadzu UV–240, Shimadzu FTIR–2400 and Varian 60 MHz spectrometers, respectively. Thermal analysis curves were obtained with a Perkin Elmer Series II TG and DSC (heating rate 10 °C min^{-1} under nitrogen and medical oxygen).

RESULTS and DISCUSSIONS

Figure 1 shows the polymerization results. In the presence of the $Mo(CO)_6/C_6H_4OH$ catalytic system PA was found to polymerize easily. Only methanol insoluble polymers formed. The polymerization proceeded at a relatively high initial rate but slowed down after 2h until all the monomer was consumed after approximately 5h. Seeing that $W(CO)_6$ is more active than $Mo(CO)_6$ in the UV irradiated systems (4) and that the polymerization by thermally activated $Mo(CO)_6$ was also reported (9,10), the polymerization of PA in the presence of $W(CO)_6/C_6H_5OH$ and of $Mo(CO)_6$ under the same reaction conditions than the $Mo(CO)_6/C_6H_5OH$ system, were also performed. It is interesting to note that $Mo(CO)_6$ is more active than $W(CO)_6$ in the $M(CO)_6/C_6H_5OH$ catalytic systems when compared to the UV irradiated systems. It is also important to notice that the addition of an excess amount of C_6H_5OH to $Mo(CO)_6$ gives rise to a highly active polymerization catalytic system.

In all three cases a light yellow to yellow polymer formed which were highly soluble in nonpolar organic solvents. $\overline{M}_n$ values were found to be 4,07 x 10^4 ($Mo(CO)_6/C_6H_5OH$), 2,52 x 10^4 ($W(CO)_6/C_6H_5OH$) and 3,4 x 10^2 ($Mo(CO)_6$).

The characteristics of the PA obtained from the $Mo(CO)_6/C_6H_5OH$ catalyzed reaction were determined. Figure 2 shows the IR spectrum of this polymer. The strong absorption at 1510 cm^{-1} is due to the stretching vibration of a polyconjugated double bond while the absorption

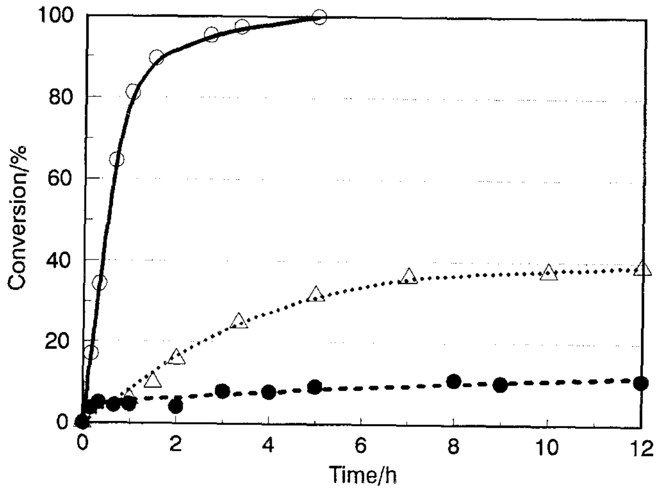

FIGURE 1. Polymerization of PA in the presence of various catalysts in C_6H_5Cl at 120 °C
(○ $Mo(CO)_6/C_6H_5OH$; △ $Mo(CO)_6$; ● $W(CO)_6/C_6H_5OH$)

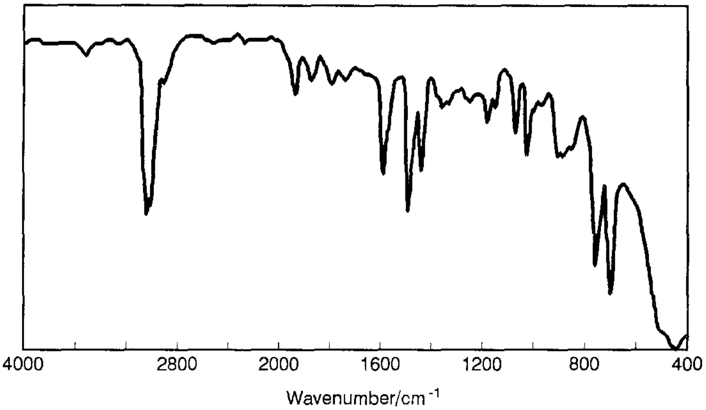

FIGURE 2. IR spectrum of PPA obtained from $Mo(CO)_6/C_6H_5OH$

at 1610 cm^{-1} is due to the stretching vibration of a trisubstituted double bond. The strong absorption at 3020 cm^{-1} is the typical C–H stretching vibration of an olefinic proton and those at 755 cm^{-1} and 693 cm^{-1} are due to C–H out–of–plane bending vibrations of monosubstituted benzene compounds which is confirmed by the characteristic pattern of the overtone absorptions at 1800 – 2000 cm^{-1}. This IR spectrum is identical to the reported IR spectrum for PA (13). The measure of *cis*–structure content as derived from the absorbance ratio A_{870}/A_{910} is 0,989. No indication that C_6H_5OH is part of the polymer chain is evident from the IR spectrum.

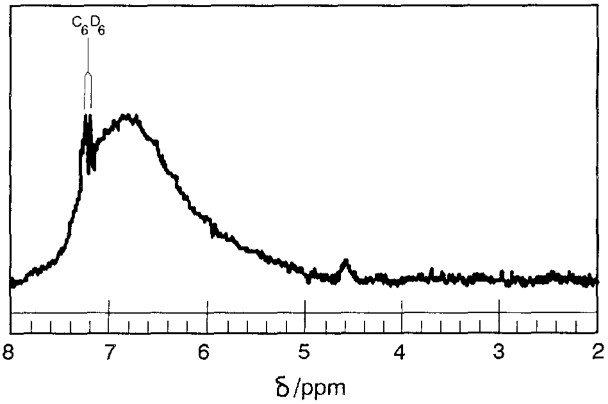

FIGURE 3. NMR spectrum of PPA obtained from $Mo(CO)_6/C_6H_5OH$

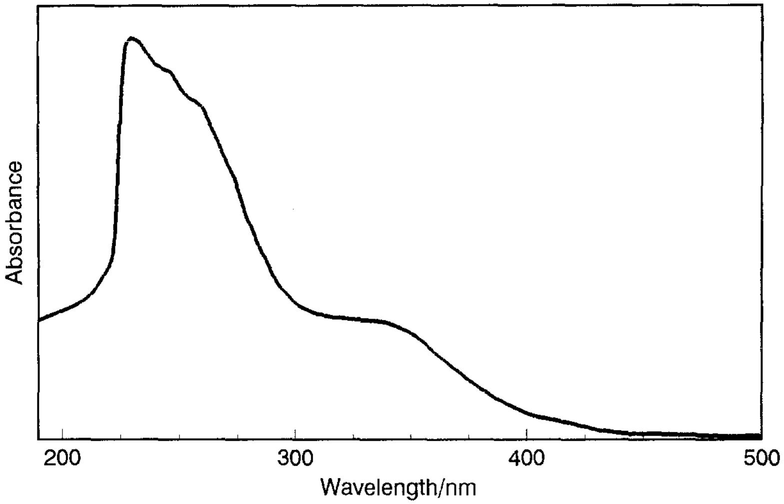

FIGURE 4. UV spectrum of PPA obtained from $Mo(CO)_6/C_6H_5OH$

The ^1H–NMR spectrum of the PA obtained on a 60 MHz instrument is shown in Figure 3. The broad resonance at 6,3 ppm is characteristic of olefinic and aromatic protons, and suggest a polymer of low steric purity (5,14). The absence of a well–defined resonance at 5,82 ppm is usually taken as evidence for a *trans*–rich polymer (13).

The UV spectrum of the polymer, shown in Figure 4, possesses a maximum absorption at 240 nm and a broad shoulder at 343 nm. No absorption above 400 nm was observed. The UV data indicates limited conjugation in a linear twisted structure (8).

The DSC and TG curves of the polymer are shown in Figure 5. An exothermic peak at 243 °C followed by polymer degradation are observed in the DSC curve. The degradation is confirmed by the mass loss at 260 °C in the TG curve. The initial mass loss (~ 5 %) at 130 °C is most probably due to the loss of light fractions, e.g. solvent, in the polymer. In an oxygen atmosphere the weight loss due to oxidation occurs at about 220 °C while the oxidized product decomposes at about 500 °C.

From this study it is clear that $Mo(CO)_6/C_6H_5OH$ is a highly active and selective catalytic system at 120 °C for the polymerization of PA. The PPA formed under these conditions is a stable, high polymer with a *trans*–rich structure in which the alternating double bonds exhibits limited conjugation due to twisting of the polymer chain.

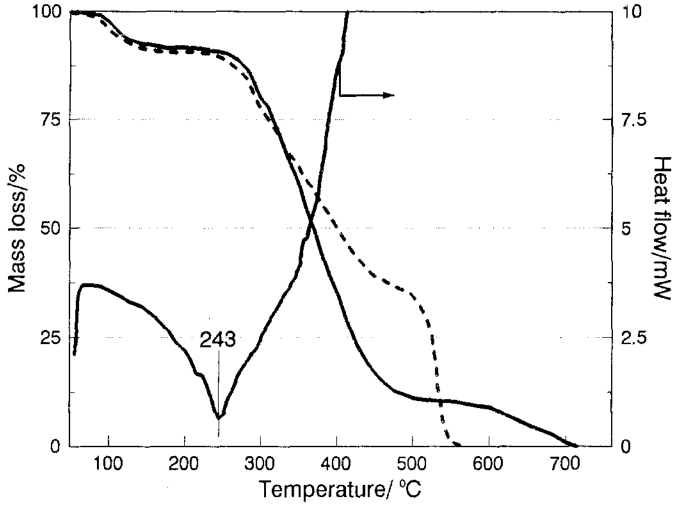

FIGURE 5. DSC and TG curves of PPA obtained from $Mo(CO)_6/C_6H_5OH$ (——— under N_2; – – – under O_2)

ACKNOWLEDGEMENT

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