Metathetical polymerization of substituted phenylacetylenes using in situ generated (arene)M(CO)$_3$ complexes (arene = toluene, o-xylene or mesitylene, M = Cr, Mo or W) as catalysts

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Abstract

Substituted phenylacetylenes are polymerized using in situ generated (arene)M(CO)$_3$ complexes as catalysts. The catalytic activity of the complexes is discussed with reference to the metals and arene ligands. A ladder polymer of phenylacetylene formed via cycloaddition mechanism as a possible precursor to linear polyphenylacetylenes, in bulk polymerization conditions, has been isolated and characterized. Some of the properties of the polymers are also described.

Keywords: Alkyl-vinylidene polyphenylacetylene; (Arene)M(CO)$_3$ complexes; Conductivity; Ladder polymer; Metathesis; Polymerization; Phenylacetylene derivatives; Vinylidene derivatives

1. Introduction

Metathetical polymerization of alkynes by employing transition metal complexes as catalysts is a promising area of research [1]. These polymers exhibit conductivity and show non-linear-optical behavior [2], which find applications in areas such as telecommunications and optical data storage. These materials can be tailor-made to suit the application parameters by introducing different pendent groups along the polymer backbone. Conventional methods of polymerization of phenylacetylene (PA) using preformed metal–carbene and carbyne complexes involve laborious syntheses and expensive procedures [3]. We have earlier reported a *one-pot synthesis* [4] involving in situ

generation of catalyst complex (arene)M(CO)$_3$ (arene = toluene, o-xylene or mesitylene, M = Cr, Mo or W) which polymerizes PA to polyphenylacetylene (PPA) in high yields. To evaluate the efficiency of the above mentioned catalyst system, and to study the effect of substituent groups on monomer reactivity, we synthesized various substituted phenylacetylenes and polymerized them by the in situ generated (arene)M(CO)$_3$ complexes.

2. Experimental

2.1. General procedures

All the reactions were carried out under pre-purified nitrogen atmosphere. The metal carbon-

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yls were bought from Aldrich and used as received. Arenes were dried by distillation and stored over sodium wire and degassed prior to usage. All transfers were performed in a glove box filled with nitrogen or via syringes in the case of liquids.

The IR spectra were taken as KBr pellets using Perkin Elmer (1760) FTIR spectrophotometer. NMR spectra were recorded with both Hitachi (R600) 60 MHz (^{1}H) NMR instrument and JEOL 400 MHz (GSX400) (^{1}H and ^{13}C) high resolution spectrometer. The spectra were recorded as parts per million (ppm) from TMS, with CDCl$_3$ as solvent. Gas chromatographic analysis was carried out in Nucon (5700) GC with ORACLE1 computing integrator in a OV-17 stainless steel column of 3 m length maintained at 160°C. Dodecane was used as internal standard. Molecular weight measurements were carried out in a Waters gel permeation chromatographic system (410), with an RI detector using three ultra Styragel columns (100 Å, 10^3 Å and 10^5 Å) connected in series with THF as eluent at 1 ml/min. Polystyrene was used as the calibration standard. Conductivity measurements were carried out at room temperature as pressed pellets in a Keithley (610) electrometer using silver foil as contact electrodes. Doping was done by mixing and grinding the polymer with iodine in a mortar. The pellets were made by pressing the polymer in a Shimadzu (SSP-10A) hydraulic press.

2.2. Monomer synthesis

(a) 4-Methoxy phenylacetylene (4-OMePA) was prepared from 4-methoxy benzaldehyde by a known procedure [5]. (b) 2-Methyl phenylacetylene (2-McPA) and 2-methoxy phenylacetylene (2-OMePA) were prepared by literature reported method [6] from corresponding iodobenzenes. (c) 4-Methyl phenylacetylene (4-MePA), 4-chloro phenylacetylene (4-ClPA), and 4-bromo phenylacetylene (4-BrPA) were prepared from corresponding acetophenones by a modified reported method [7]. All the monomers were characterized using IR and NMR spectra.

2.3. Polymerization

To a flame dried 50 ml flask, capped with a rubber septum and equipped with a Teflon-coated magnetic stirring bar, Mo(CO)$_6$ (0.145 g, 0.54 mmol) was added, inside a nitrogen filled glove bag. The monomer/catalyst ratio was kept at 50, after assuming a partial conversion of Mo(CO)$_6$ to (arene)Mo(CO)$_3$ [8]. The flask was fitted with a reflux condenser, capped with a septum and degassed toluene (6 ml) was injected. The suspension was refluxed for 6 h in an oil bath with stirring. To the resulting yellow colored solution, 2-methyl phenylacetylene (1.27 g, 10.9 mmol) was added and refluxed for 24 h. The dark brown reaction mixture was poured into excess methanol. The precipitated polymer was filtered, washed with methanol and dried under vacuum. The dark red polymer obtained, 0.86 g (yield 70%), was reprecipitated from CCl$_4$.

2.4. Ladder polymer: synthesis and isolation

(Mesitylene)W(CO)$_3$ (0.0424 g, 0.109 mmol), and phenylacetylene (0.56 g, 5.5 mmol,) were taken in a long stemmed round bottomed flask and heated in nitrogen atmosphere at 70°C for two hours. Excess PA was removed under reduced pressure and the red residue was then subjected to column chromatography over freshly activated neutral alumina, with CCl$_4$ as eluent. The polarity of the mobile phase was increased with portions of ether. The first fraction contained low molecular weight oligomers and the second fraction yielded the ladder polymer. Subsequent elutions gave linear polyphenylacetylenes. Evaporation of solvent from the second fraction resulted in an orange solid 0.01 g (Yield = 1.7%).

3. Results and discussion

3.1. Catalysis and reactivity

The catalyst was generated in situ by refluxing the metal carbonyl with arene until all the carbonyl

Table 1
Polymerization of substituted phenylacetylenes by in situ generated (arene)M(CO)$_3$ catalyst complexes

Yield of polymer (%) [a,b]

No.	Monomer	Cr(CO)$_6$			Mo(CO)$_6$			W(CO)$_6$		
		tol.	o-xyl.	mesit.	tol.	o-xyl.	mesit.	tol.	o-xyl.	mesit.
1.	2-MePA	c	c	c	70	65	40	52	28	5
2.	4-MePA	c	c	c	33	28	40	5	15	c
3.	2-OMePA	c	c	c	46	10	16	5	c	c
4.	4-OMePA	30	c	c	33	28	40	5	15	c
5.	4-ClPA	5	5	c	42	20	21	20	61	c
6.	4-BrPA	24	12	c	51	43	23	46	88	c

[a] According to M(CO)$_6$/arene used.

[b] Calculated based on the weight of methanol insoluble fraction. Catalyst/monomer ratio 1/50, monomer conversion was more than 80% except for chromium and (mesitylene)W(CO)$_3$ catalysts.

[c] Negligible amount of methanol insoluble polymer fraction.

reacted to give a yellow colored solution. It is proposed that the active species generated is (arene)M(CO)$_3$ complex which catalyzes the polymerization. Formation of this complex, in the reaction medium was confirmed by IR spectroscopy, which showed two strong bands in the region of 1900–2000 cm^{-1}. These absorptions correspond to the stretching vibrations of terminal carbonyl group of (arene)M(CO)$_3$ complex and were shown to compare well with those of the respective isolated complexes. Also, polymerization of 4-MePA monomer both by using in situ generated M(CO)$_6$/toluene system as well as by isolated (toluene)M(CO)$_3$ complexes gave comparable yields of the polymer [1]. We feel that the premise about the (arene)M(CO)$_3$ complex as the active catalytic species is quite justified [4].

Results of the polymerization studies are listed in the Table 1, with reference to the metal and the ligand employed. It can be seen that irrespective the monomer or ligand employed, in most cases, molybdenum-based catalysts gave consistently higher yields of the polymer compared with those of tungsten. On the other hand, chromium-based catalysts exhibited consistently poor catalytic

activity. This anomaly can be explained on the basis of the stability of the (arene)chromium carbonyl complexes compared to molybdenum and tungsten complexes. The heat of formation of (mesitylene)M(CO)$_3$ complexes, from microcalorimetric studies [9] is found to be the highest for Cr and the lowest for W (ΔH_f Cr: -571, Mo: -533, W: -477 kJ/mol). Thermal decomposition studies also show a positive enthalpy of decomposition for (mesitylene)Cr(CO)$_3$ complex, whereas molybdenum and tungsten analog show a negative value (ΔH_d = Cr: $+17.6$, Mo: -25, W: -66.5 kJ/mol). Thus the strong ligand–metal bonding in chromium complexes prevents coordination of alkyne and hence no,polymerization occurs. Therefore chromium seldom act as a catalyst. We could also infer that (arene)tungsten carbonyl complex shows moderate activity, probably because of the ease with which the arene ligand departs from the metal. The high efficiency of molybdenum complex could thus lie in the fact that they are of intermediate stability.

From Table 1 it is observed that arene ligands do influence the reactivity of a particular metal. Among the arenes, toluene seems to be a better ligand than mesitylene for most of the metal complexes. If we assume ring-slipping of arene to accommodate the alkyne as essential for the polymerization of the alkyne, then the arene ligand should affect the reactivity of the complex both by ease of ring-slipping (depends upon the strength of the arene–metal bond) and by steric hindrance. Kinetic studies on the ligand substitution reactions of (arene)Mo(CO)$_3$ complexes [10] show that the rate of substitution decreases for change in arene in the order toluene $\geq$ xylene $\gg$ mesitylene. Thus mesitylene, an electron-rich and bulky ligand, reduces the reactivity by forming a stronger metal–arene bond and also obstructs the monomer approach by steric hinderance while toluene enhances the catalytic activity with o-xylene falling in between. This trend is a near generality as evinced from the entries in Table 1.

[1] Polymer yield (%): in situ generated catalyst (isolated complex): Cr: 0 (0), Mo: 33 (28), W: 5 (3).
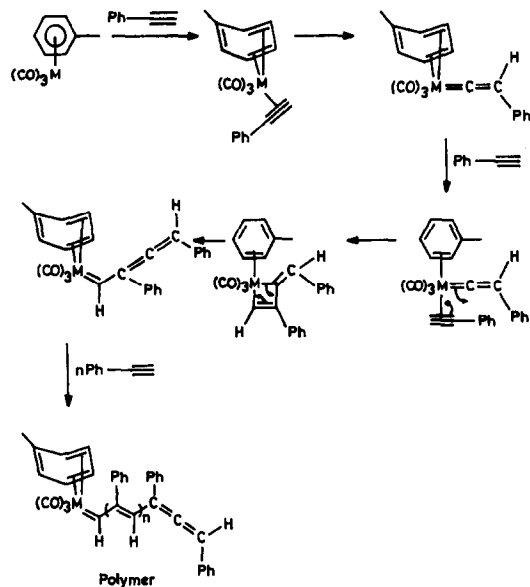
Scheme 1. Proposed mechanism of polymerization using in situ generated (arene)M(CO)₃ complexes as catalysts.

3.2. Mechanism of polymerization

In situ generated (arene)M(CO)₃ catalyst system polymerizes terminal alkynes, but fails to produce any polymer for internal alkynes such as 1-phenyl-1-propyne and 1,2 di(trimethylsilyl)acetylene. Gas chromatographic analysis shows the absence of any cyclized products, trimers or oligomers, in the reaction mixture. However, polymerization can be achieved in this case by adding five equivalents of terminal alkyne such as phenylacetylene. This establishes the necessity of terminal alkyne for the initiation of polymerization. Also, co-polymerization studies revealed that only random co-polymerization proceeds smoothly but there is no block co-polymerization implying the non-living nature of the catalyst system [11].

Based upon these observations, the proposed mechanism of polymerization is shown in Scheme 1. Here we suggest ring slipping of η^6 (arene)M(CO)₃ complex to η^4 for coordinating with the alkyne followed by 1,2 *hydrogen migration* to form an alkyl vinylidene complex [12]. Further ring slipping occurs to give a η^2 complex with the coordination of one more alkyne unit and subsequent cyclization to give a metallacyclobu-

tene complex. This complex can then rearrange metathetically to yield metal carbene complex thus initiating the polymerization process. The polymerization then proceeds by repeated metathesis to give the polymer (Scheme 1). However, absence of terminal hydrogen, in the case of internal alkynes rules out the possibility of hydrogen migration to form vinylidene complexes and therefore retards polymerization.

3.3. Monomer reactivity

Among the monomers, 2-MePA and 4-OMePA polymerize better than the others (Table 2) and

Table 2
Molecular weight and conductivities of the substituted polyphenylacetylenes

No	Polymer[a]	Molecular weight 10⁻³			Conductivity/ S·cm⁻¹×10⁻¹²	
		M_n	M_w	M_w/M_n	0% I_2	20% I_2
1.	poly(PA)	6.00	11.6	1.5	4.20	5800
2.	poly(2-OMePA)	12.9	20.5	1.6	16.5	14000
3.	poly(4-OMePA)	2.30	3.29	1.4	0.065	25000
4.	poly(2-MePA)	15.0	22.9	1.5	260	97000
5.	poly(4-MePA)	7.79	11.2	1.4	450	27000
6.	poly(4-ClPA)	2.51	3.87	1.5	540	26000
7.	poly(4-BrPA)	1.86	3.99	2.1	570	6200

[a] Synthesized using the (toluene)Mo(CO)₃ catalyst system.
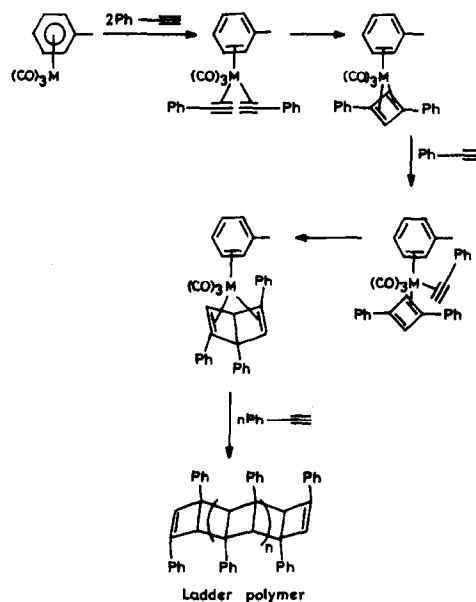
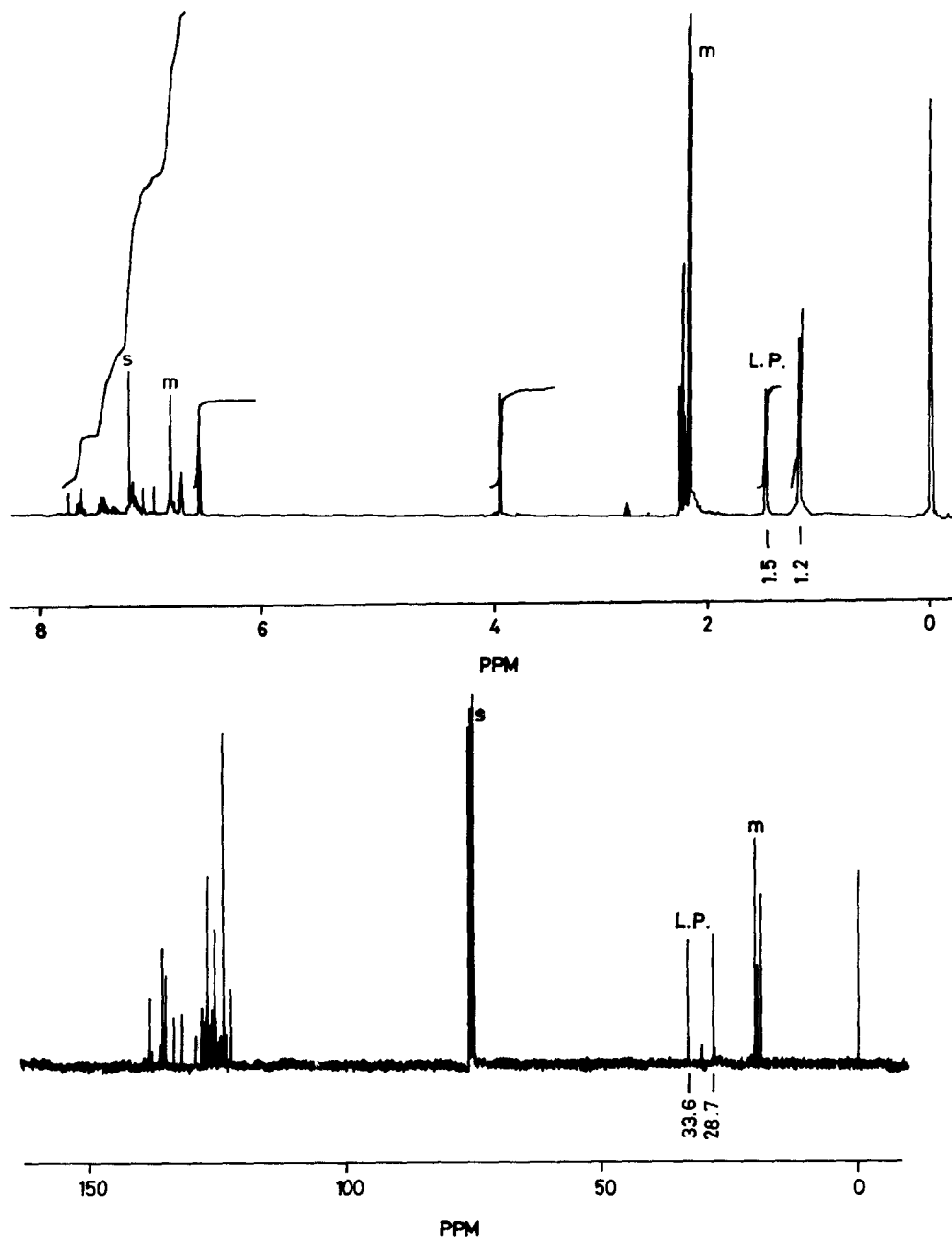Scheme 2. Proposed mechanism for the formation of ladder polymer.

Fig. 1. ^{1}H and ^{13}C NMR spectra of isolated ladder polymer. Signals marked in ppm, correspond to cyclobutyl proton and carbon respectively. (m – residual mesitylene signals, s – solvent signal).

this observation is attributable to the electron-rich nature of the monomers. Moreover, 2-MePA also affords better yields than 4-MePA and this is in good agreement with the reported observation that sterically hindered monomers gave better yields (for example: t-butyl acetylene [13]). Strangely this was not found to be true for 2-OMePA. Here

we suspect a possible ligation of the methoxy oxygen to the metal template resulting in a cyclic five-membered chelate blocking a coordination site and hence preventing chain propagation. Halogen substituted monomers, 4-ClPA and 4-BrPA, also show good yields for the tungsten-based catalyst system.

3.4. Ladder polymer synthesis and characterization

A rather surprising observation in all the ^{1}H NMR spectra of the polymers is the persistent appearance of a signal at 1.25 ppm, which was ascribed by Woon and Farona [14] to the proton of the cyclobutyl ring of a ladder polymer, supposedly an icosomer of PPA. Formation of this ladder polymer was reasoned out via a $2+2$ cycloaddition of monomers at the metal template to give a cyclobutene complex, which eventually lead to ladder polymer by repeated $2+2$ cycloaddition (Scheme 2). The ladder polymer may at a later stage ring-open to give linear PPA, by the action of the metal catalyst. Thus the ladder polymer was suggested as an intermediate or precursor to linear PPA. We *also* observed that in bulk polymerization using (mesitylene)M(CO)$_3$ (M = Cr or W) catalysts isolable amounts of ladder polymer were formed, but not so in solution polymerization conditions. Thermogravimetric analysis shows that the decomposition temperature was 220°C for the ladder polymer whereas for linear PPA it was 410°C. Appearance of signals at 1.2 and 1.5 ppm in ^{1}H and signals at 28.7 and 33.6 ppm in ^{13}C NMR are evidence for the presence of ladder polymer structure (Fig. 1) [2]. Ladder polymer which has no extended conjugation like linear PPA absorbs in shorter range in the UV spectrum than PPA which shows rather broad range of absorption (Fig. 2). These clearly describe the ladder polymer structure as that shown in scheme 2 and provide an alternative reaction pathway for PPA synthesis, apart from metathesis. It may be noted that of the two competitive reaction mechanisms possible to give the polymer, the $2+2$ cycloaddition mechanism occurs only in bulk polymerization conditions to give isolable quantities of the ladder polymer. Also, in solution polymerization and in (arene)Mo(CO)$_3$-catalyzed reactions (which

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[2] Here, the appearance of a number of signals in the aromatic region could probably be due to the occurrence of isomeric forms of the ladder polymer as well as isomerization of some of the ladder polymer to linear PPA.
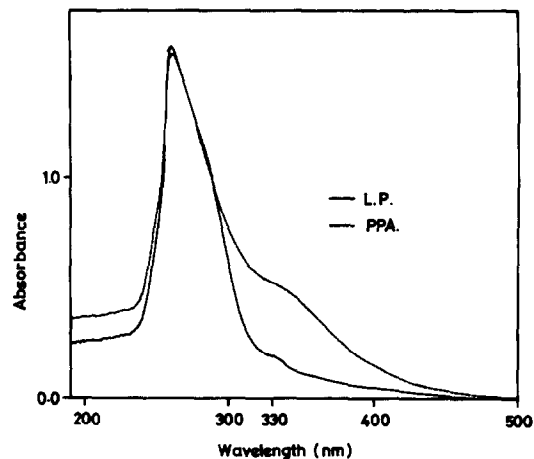

Fig. 2. UV spectrum of both (- - - - -) ladder polymer and (———) linear PPA. In ladder polymer spectrum, very poor absorption in higher wavelength regions shows absence of extended conjugation.

exhibit better reactivity) no isolable amount of ladder polymer is formed. Cycloaddition type polymerization, occurs only when less reactive catalysts are employed like (mesitylene)M(CO)$_3$, (M = Cr or W) but the yield of the ladder polymer was found to be still considerably less than that of the linear polymer. Moreover if this were to be the sole mechanism operating in our catalyst system, internal alkynes should also yield the linear polymer, which we find is not true (vide infra). Interestingly Woon and Farona [14] observe the formation of the trimer, hexamethylbenzne, as the major product when 2-butyne was treated with (arene)M(CO)$_3$ complexes. Thus we conclude that in our case polymerization occurs predominantly via the metathesis route.

3.5. Polymer properties

All the polymers were dark-colored amorphous solids, soluble in common organic solvents like benzene, acetone, CCl$_4$, THF, etc. Table 2 summarizes the results of molecular weight measurements. Number average molecular weight of the polymers, M_n, varied from 2,000–15,000. The polymers were found to be monodisperse in nature with an M_w/M_n values less than two. Undoped polymers except poly(4-OMePA) exhibit higher conductivity than PPA. Evidently, doping with
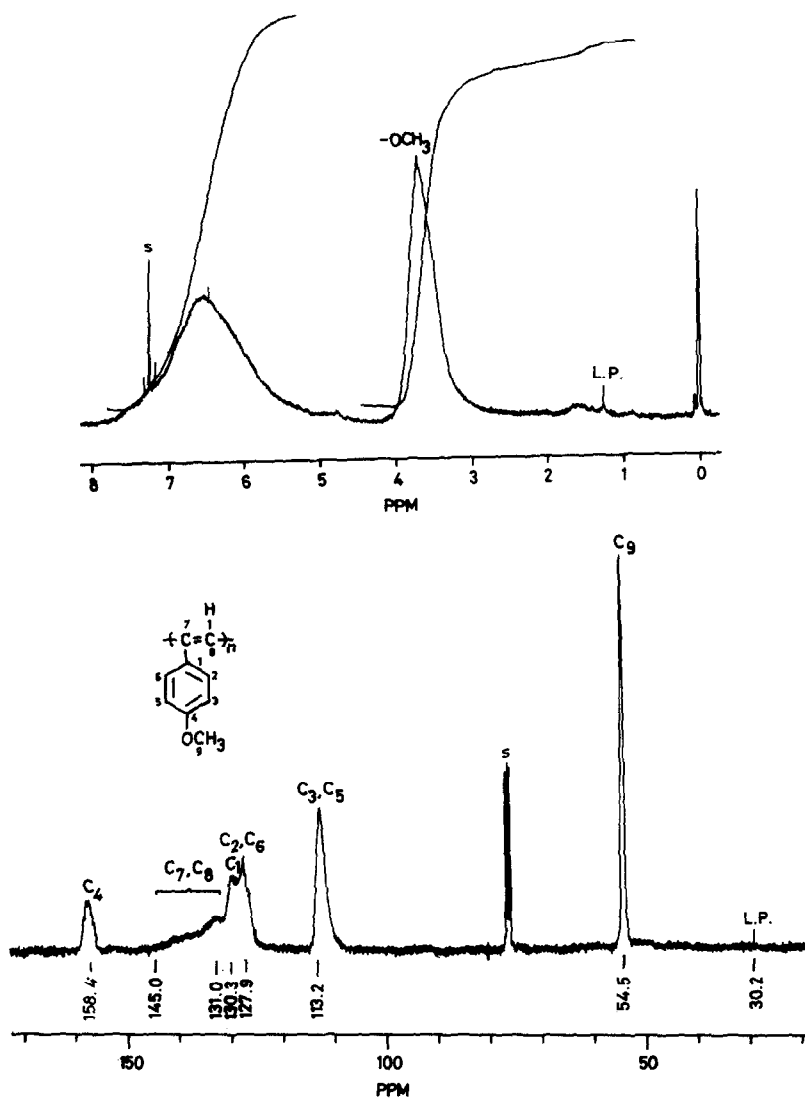
Fig. 3. ¹H and ¹³C NMR spectrum of poly(4-OMePA). Signals denoted as L.P. corresponds to ladder polymer. (s – solvent signal).

20% iodine increases the conductivity by three orders of magnitude. It is inferred from Table 2 that polymers with electron donating substituents show higher conductivity than PPA. 4-BrPA show higher dispersity value which probably means more branching of the polymer which reduces the effective conjugation length of the polymer backbone which in turn reduces the conductivity. The NMR spectra of poly(4-OMePA) are shown in Fig. 3. ¹H NMR showed two broad peaks between δ 3–4 and between δ 5.6–7.8 for methoxy and olefinic and aromatic protons respectively. ¹³C NMR signals were assigned on the basis of both

reported [15] and calculated ¹³C-δ values and shown in the spectra presented in Fig. 3.

4. Conclusions

Substituted phenylacetylenes were synthesized and subjected to polymerization by in situ generated group VI (arene)M(CO)₃ complexes as catalysts. All catalysts derived from Mo(CO)₆ and W(CO)₆ performed well barring (mesitylene)W(CO)₃ complex. Most of the (arene)Cr(CO)₃ complexes were not effective as

polymerization catalysts. This observation was explained on the basis of stability of the complex. Among the monomers high reactivity has been observed for 2-MePA, 4-OMePA and 4-BrPA. Reactivity of 2-OMePA was considerably less than that of 2-MePA and 4-OMePA. This may be due to the chelation by *ortho* methoxy group. Ladder polymer of PPA formed by the proposed 2 + 2 cycloaddition mechanism was synthesized, isolated and characterized by spectral methods. In our case metathesis predominates more than the 2 + 2 addition mechanism for the polymerization of phenylacetylene.

The polymers were characterized by both ^{1}H and ^{13}C NMR and M_n of the polymers varies from 2,000 to 15,000. Conductivity of the polymers were found to be in the semiconductor range, when doped with iodine. 4-OMePA shows maximum conductivity, upon doping.

Acknowledgements

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