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Microwave assisted polymerisation of phenylacetylenes

K. Dhanalakshmi, G. Sundararajan*

Department of Chemistry, Indian Institute of Technology, Madras – 600 036, India

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Summary

Metathesis Polymerisation of phenylacetylenes using *in situ* generated (arene)M$(CO)_3$ complexes under unconventional microwave energy condition was achieved successfully. The reaction time was reduced to 1 hour in contrast to refluxing conditions of 24 hours.

Introduction

Among the class of conjugated polymers, polyphenylacetylene(PPA) has gained special attention due to its interesting optical[1] and electrical properties[2]. PPA is generally obtained by metathesis polymerisation of phenylacetylene(PA)[3]. It has earlier been demonstrated in our laboratory, that PA can be polymerised by *in situ* generation of (arene)M$(CO)_3$ complex (M = Cr, Mo & W) under reflux conditions for 24 hours[4]. However, it is known that the reaction time for many thermal reactions can be reduced drastically by the use of microwave[5]. A variety of organic[6], organometallic[7] and polymerisation[8] reactions have been carried out using this unconventional energy source very successfully. The observed rate enhancement in these reactions is attributed to the pressure development inside the vessel due to the interaction of microwave energy with polar solvent molecule and concomitant superheating of the solvent molecule[9]. Hence, we decided to study the effect of microwave irradiation for the polymerisation of PA by *in situ* generated (arene)M$(CO)_3$ complexes.

Experimental

Chemicals

The metal carbonyls were purchased from Aldrich Fine Chemicals and used as received. 1,2-dichloroethane was purified by distilling over P_2O_5 and dried over molecular sieves. Arenes were purified by distilling over sodium benzophenone ketyl and stored over sodium wire. Phenols were purified by the standard method[10].

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* Corresponding author

Monomer synthesis

Phenylacetylene, 4-methoxyphenylacetylene[11], 4-methylphenylacetylene, 4-chlorophenylacetylene[12] and 4-bromophenylacetylene[13] were prepared according to reported methods.

Polymerisation

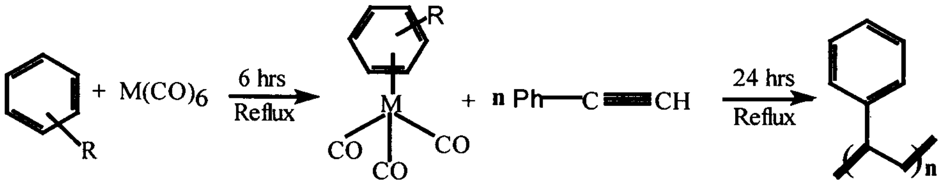
Microwave irradiations were carried out in a Batliboi Eddy kitchen microwave oven. Polymerisation reactions were carried out under dry, oxygen free nitrogen atmosphere. All transfers were performed in a nitrogen filled glove bag or by standard syringe techniques. Specially designed long necked round bottom flasks which can withstand the pressure were used for carrying out the reaction. $W(CO)_6$(0.199 mmol), phenylacetylene(5.975 mmol), toluene(0.5 ml) and 1,2-dichloroethane (5 ml) were taken in the dry round bottom flask. The catalyst:monomer ratio was kept at 1:50. The flask was sealed before irradiation. Irradiation was carried out for 5 min at time intervals of 10 min to cool the reaction mixture. The progress of the reaction was easily seen from colour change (colourless to red). After 60 min the polymer was poured into excess methanol and the precipitated polymer was filtered, washed with methanol and dried under vacuum. Yield (67%).

Polymer characterisation

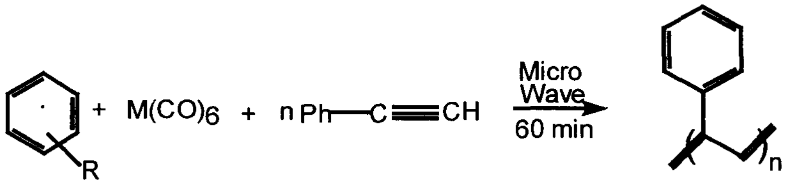
All polymers were characterised by IR, ^1H,^{13}C NMR and thermal analysis. The IR spectra were recorded as KBr pellets using Shimadzu (model470) IR spectrometer. ^1H and ^{13}C NMR were recorded using JEOL model GSX 400 high resolution spectrometer. $CDCl_3$ was used as the solvent and the signals were obtained in parts per million (ppm) using tetramethylsilane as reference. Thermogravimetric analysis was done using a Perkin - Elmer Thermal Analyser (model TGA-7) under nitrogen atmosphere. The molecular weight of the polymers were analysed using Waters gel permeation chromatography with RI detector. The analyses were done using three ultrastyragel columns (100A, 10^3A and 10^5A) connected in series. THF was used as the eluant at the flow rate of 1ml/min and narrow molecular weight polystyrene samples were used as calibration standards.

Reaction profile

Thermal Condition



Microwave Condition



Where M = Cr, Mo and W, Reaction time = 60 min, Solvent = 1,2-dichloroethane

TABLE-1

% Yield of PPA by arene/M(CO)$_6$ under microwave irradiation

S. No	Monomer	W(CO)$_6$			Mo(CO)$_6$		
		tol	o-xyl	mes	tol	o-xyl	mes
1	phenylacetylene	67	30	13	23	16	18
2	4-methoxyphenylacetylene	22	37	30	32	25	17
3	4-methylphenylacetylene	5	13	15	5	11	5
4	4-chlorophenylacetylene	27	5	c	c	c	c
5	4-bromoponhenylacetylene	17	46	35	28	30	22

TABLE-2

% Yield of PPA using phenol/M(CO)$_6$ under microwave irradiation

S. No	Monomer	W(CO)$_6$			Mo(CO)$_6$		
		phe	res	qui	phe	res	qui
1	phenylacetylene	75	65	52	43	24	27
2	4-methoxyphenylacetylene	23	21	28	9	c	26
3	4-methylphenylacetylene	17	24	29	13	5	10
4	4-chlorophenylacetylene	36	c	c	5	c	c
5	4-bromophenylacetylene	26	24	18	24	19	24

a. The catalyst to monomer ratio was kept at 1: 50

b. Cr(CO)$_6$ was inefficient for the polymerisation reaction

c. Negligible amount of polymer

Results and discussion

1,2-dichloroethane was used as the solvent for all the reactions because it is a non-coordinating solvent with high dielectric constant. Tungsten-based catalysts gave consistently higher yields than the molybdenum counterparts, while chromium based catalysts found to be inactive. This may be explained on the basis of lability of the complexes[14] towards the substitution of the monomer. Generally (arene)$W(CO)_3$ complexes are more labile than the molybdenum complexes . Phenol, having high dielectric constant was found to give higher yield. However, it should also be noted that phenols are capable of acting as a cocatalyst with simple metal carbonyls, the mechanism of such activation being unclear[15]. Bulkiness of the ligand also plays a definite role in the polymerisation reaction as seen from the polymer yield which decreases in the order (toluene>o-xylene>mesitylene). Halogen substituted monomers gave higher polymer yields compared with the methyl and methoxy substituted monomers.

TABLE-3

GPC and TGA Values of PPA using toluene/$W(CO)_6$

S. No	Polymer	Molecular weight Mn	 Mw	 Mw/Mn	TGA°C
1	poly(PA)	4005	4646	1.1	386
2	poly(4-MeOPA)	5046	6628	1.3	450
3	poly(4-MePA)	8041	12272	1.5	410
4	poly(4-BrPA)	12722	19062	1.4	430
5	poly(4-ClPA)	9904	15823	1.5	440

Polymer properties

All the polymers were yellow-orange coloured amorphous solids. They are highly soluble in common organic solvents like $CHCl_3$, CCl_4, THF, etc. The polymers are air-stable in solid as well as in solution form. The infrared spectrum showed only the presence of 760 cm^{-1} band and the band at 740 cm^{-1} was absent indicating that the polymer microstructure is predominantly of *trans* geometry. NMR spectrum of poly(4-MeOPA) showed a broad signal around 3-4 ppm corresponding to the MeO group and signal between 6-8 ppm corresponding to olefinic and aromatic protons. Other than these two broad signals the sharp peak at 1.16 ppm is seen, which may be due to the cyclobutyl hydrogen of the ladder polymer, supposedly an isomer of PPA formed in minor but parallel pathway that undergoes further polymerisation to give the linear polymer[16]. This also implies that the mechanism operating under microwave irradiation is similar to that suggested for polymerisation under thermal condition. Table-3 summarises the results of molecular weight measurements and TGA values. Compared to thermal conditions the molecular weight is found to be high . Number average molecular weight of the polymer varied from 4000-20,000. The polymers show low polydispersity value. TGA analysis showed that the decompositon temperature varied from 386-450 degrees.

Conclusion

Our . procedure using microwave energy is extremely simple for polymerising phenylacetylenes . Among the groupVIB metal carbonyls, $W(CO)_6$ was found to be the best catalyst precursor. Among the arenes, phenol showed the highest activity. To achieve high pressure and temperature easily and consequently to reduce the reaction time as well as to obtain good yields of the polymer, microwaves have been successfully utilised.

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