2060 *Macromolecules* 1992, *25*, 2060–2061

Metathetical Polymerization of Phenylacetylene with in Situ Generated (Arene)Mo(CO)$_3$ Complexes under Thermal Conditions and Electron Transfer Chain Catalysis: A Comparative Study

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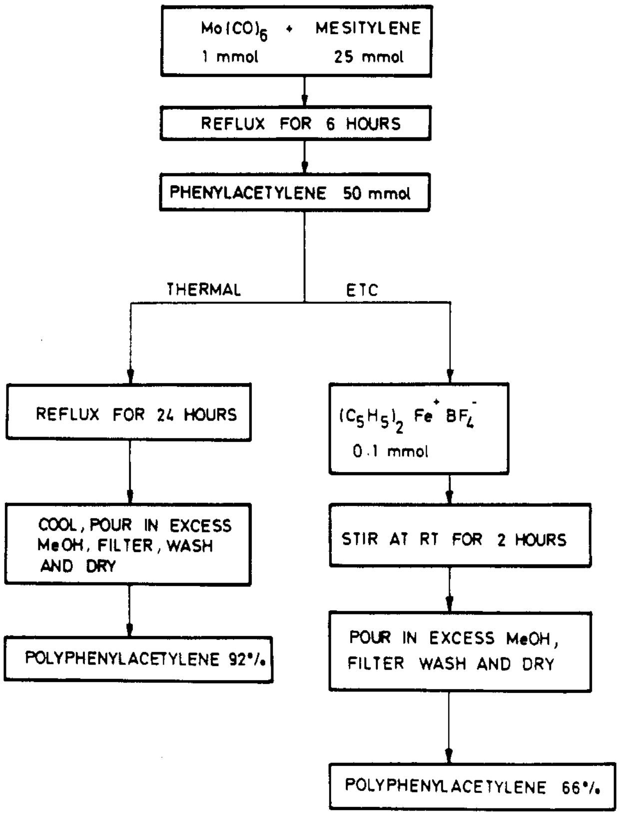
Received June 10, 1991
Revised Manuscript Received December 17, 1991

We recently reported[1a] that poly(phenylacetylene) (PPA) can be obtained in high yield from phenylacetylene (PA) under thermal conditions (i.e., reflux) by employing in situ generated (arene)M(CO)$_3$ (arene = toluene, *o*-xylene, or mesitylene; M = Cr, Mo, or W) complexes as catalysts and that the material obtained by this method shows significant non-linear-optical behavior.[1b,c] While, in general, reasonably high molecular weight PPA can be obtained in good yield by this method, the conformation of PPA obtained differed for different precursors used and at times was irreproducible for the same catalytic precursor. One reason for this anomaly would be the severity of the conditions employed for polymerization. So as we searched for milder ways of obtaining polyalkynes, the now well-established principle of electron transfer chain (ETC) catalysis[2a] as applied to organometallic catalysis[2b,c] came to our rescue. In this paper a comparative note will be struck between thermal and ETC catalytic polymerization of PA under catalytic metathetical conditions, employing in situ generated (arene)M(CO)$_3$ complexes as catalysts (see Scheme I).[3a]

The various conditions under which the polymerization was performed and the results obtained are detailed in Table I.[3b] As can be seen under reflux conditions, the PPA is obtained in reasonably high yield, and under ambient conditions the yields (of methanol-precipitated fractions) are uniformly poor. ETC catalysis, i.e., addition of 0.1–0.2 equiv of an oxidant,[3c] $Cp_2Fe^+BF_4^-$ (Cp = C_5H_5), seems to yield PPA in moderate amounts with certain catalyst precursors (W(CO)$_3$(CH$_3$CN)$_3$, Mo(CO)$_6$/toluene, Mo(CO)$_6$/*o*-xylene, and Mo(CO)$_6$/mesitylene) and fails with others (W(CO)$_6$/arene and Cr(CO)$_6$/arene). It is difficult to say anything now about the found success in polymerization with one catalyst precursor and the pronounced failure with another. We think that the clue might lie in the oxidation potentials of the corresponding complexes, and we hope to test this hypothesis in the future.

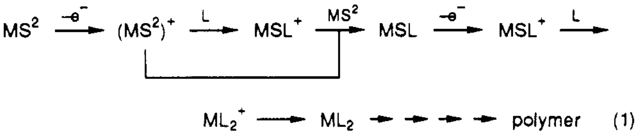
On examining the effect of solvent on the degree of polymerization in (Table I), we can see that the same trend is observed: i.e., Mo(CO)$_6$/arene proves to be a better catalytic system than either W(CO)$_6$/arene or Cr(CO)$_6$/arene combinations. It is to be noted that the molecular weights of PPAs obtained by ETC catalytic methods are high and the polymer samples are also uniformly light-colored, yellow to yellowish-orange, in strict contrast to the products of thermal polymerization, which are pale yellow to dark brown or even black. On adopting the method suggested by Simionescu[4] for fixing the conformation of PPA, we arrived at the following conclusion.

Scheme I
One-Pot Synthesis of PPA



The PPA obtained from thermal reactions yielded both cis-transoidal and trans-cisoidal polymers, and as mentioned earlier we have also failed to observe any reproducibility in the conformation of PPA obtained from the same catalyst precursor. In strict contrast, the ETC catalytic conditions, irrespective of the catalyst precursor used, consistently yielded PPA of cis-transoidal configuration (cf. Table I for the percent cis content in various PPA samples). The observation could be attributed to the ambient experimental conditions in ETC catalytic reactions, as opposed to the vigorous 24-h reflux for reactions under thermal conditions.

The ease with which alkynes are polymerized under ETC catalytic conditions owes to the fact that ligand substitution in 17-electron metal-centered radicals is a trillion times faster than those in corresponding saturated 18-electron complexes.[5] By oxidizing a fraction of the catalyst complex having a labile ligand (like CH$_3$CN or η^6-arene undergoing ring-slipping to η^4 or η^2), substitution by monomer alkyne becomes facile at the newly created radical center.[6] A redox reaction between the unoxidized catalyst and monomer-substituted odd-electron species followed by an exergonic cross-redox step for subsequent stepwise incorporation of monomer molecules would then lead to polymerization (eq 1).



(1)

$S^2 = \eta^6$-arene
$S = \eta^4$-arene
L = PA

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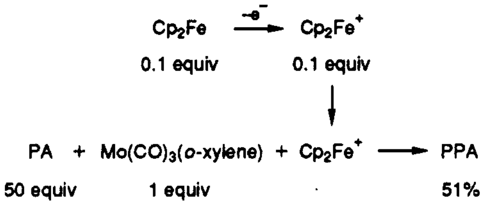
0024-9297/92/2225-2060$03.00/0

Table I
Percent Yield of PPA[a] (Percent Cis Content[b]) under Various Conditions

		conditions				
				ETC catal.[e]		
no.	cat. precursor	thermal,[c] arene solvent	ambient,[d] arene solvent	arene solvent	CH_2Cl_2 solvent	THF solvent
1	$W(CO)_3(CH_3CN)_3$[f]		13 (78) (toluene)	36 (73) (toluene)	42 (74)	45 (71)
2	$Cr(CO)_6$/toluene, *o*-xylene, or mesitylene		no methanol-insoluble fraction			
3	$Mo(CO)_6$/toluene	93	5 (84)	32 (83)	48 (82)	26 (83)
4	$Mo(CO)_6$/*o*-xylene	66	5 (88)	44 (87)	50 (86)	30 (88)
5	$Mo(CO)_6$/mesitylene	92	8 (86)	66 (85)	70 (90)	42 (86)
6	$W(CO)_6$/toluene	92	5 (85)	6 (90)	7 (84)	5 (90)
7	$W(CO)_6$/*o*-xylene	60	5 (90)	10 (84)	15 (80)	8 (87)
8	$W(CO)_6$/mesitylene	15	6 (87)	15 (88)	35 (88)	18 (88)

[a] As determined by GPC and viscosity measurements, the molecular weight of PPA ranged from 12 000 to 15 000 for both thermal and ETC reactions and was around 8000 for reactions performed at ambient conditions. [b] Calculated from the ratio of bands at 760 and 740 cm^{-1}. [c] Reflux, 24 h. [d] Room temperature, 10 h. [e] Addition of 0.1 equiv of $Cp_2Fe^+BF_4^-$, 2 h. [f] Taken from ref 2c.

To substantiate the need for an ETC initiating oxidant for the polymerization of PA, a solution containing 0.1 equiv of Cp_2Fe in DMF was subjected to oxidation at 0.5 V for 10 min and was then treated with a freshly prepared broth containing $Mo(CO)_6$/*o*-xylene (1 equiv) and PA (50 equiv). The polymerization was very rapid, and in 2 h at ambient conditions more than 50% of the monomer was consumed (eq 2).[7]



(2)

In the absence of ferrocene, however, no polymerization is observed. This clearly demonstrates the initiation and propagation of ETC in the (arene)$Mo(CO)_3$-catalyzed polymerization of PA upon addition of 0.1 equiv of Cp_2Fe^+.

In conclusion, it has been shown that the ETC catalysis is a milder and viable alternative for metathetical polymerization of terminal alkynes. This technique also yields polymers of the same conformation independent of the catalyst precursor used.

Acknowledgment. G.S. thanks the Department of Science and Technology for a Young Scientist award and grant (SP/SY/022/86). We also thank R. Ramaswamy for helpful discussion.

References and Notes

(1) (a) Shivasubramanian, V.; Sundararajan, G. *J. Mol. Catal.* **1991**, *65*, 205. (b) Vijaya, R.; Murti, Y. V. G. S.; Sundararajan, G.; Prasada Rao, T. A. *Optics Commun.* **1990**, *76*, 256. (c) Murti, Y. V. G. S., et al. *J. Appl. Phys.* **1991**, *69*, 3429.

(2) (a) Astruc, D. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 643. (b) Desbois, M. H.; Astruc. D. *J. Chem. Soc., Chem. Commun.* **1988**, 472. (c) Astruc, D., et al. *New J. Chem.* **1989**, *13*, 595.

(3) (a) A part of this paper was presented in the 10th National and 4th Indo-Soviet Symposium on Catalysis, Dec 18–21, 1990. See Proceedings: Viswanathan, B.; Pillai, C. N., Eds.; Narosa Publishing House: New Delhi, 1991; p 616. (b) Typical reaction procedures are as follows. The parent metal carbonyl $M(CO)_6$ was refluxed with 25 mmol of the corresponding arene for 6 h under an inert atmosphere of nitrogen. The monomer, PA (50 mmol), was added to the cooled solution. For polymerization under thermal conditions, the mixture was refluxed under nitrogen for an additional 24 h. For polymerization under ETC catalytic conditions, a solution of 0.1 mmol of $Cp_2Fe^+BF_4^-$ in CH_3CN was added, and the mixture was stirred for 2 h at room temperature in the dark. Polymers were precipitated by pouring the reaction mixture into excess methanol and were later filtered, washed, and dried. (c) This ratio was found to yield the optimal amount of PPA. Increasing the amount of $Cp_2Fe^+BF_4^-$ added decreased the yield of PPA. Thus Cp_2Fe^+/catalyst and percent yield of PPA varied as follows: 0, 7.6; 0.1, 69.5; 0.2, 47.2; 0.4, 24; 0.74, 7.2; 10, 0.

(4) Simionescu, C. I.; Persec, V.; Dimitrescu, S. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 2497. The PPA obtained by us displayed not only identical IR and ^1H-NMR spectra as suggested herein but the XRD patterns also corresponded well.

(5) Magnuson, R. H.; Meirowitz, R.; Zula, J.; Giering, W. P. *Organometallics* **1983**, *2*, 460.

(6) For ligand substitution reactions assisted by ETC catalysis, see: Hershberger, J. W.; Klinger, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1982**, *104*, 3034.

(7) Facile reductive elimination at oxidized metal centers via the homogeneous electron-transfer mechanism can be aided by similar in situ electrochemical oxidation of ferrocene to ferricenium ion. See: Burk, M. J.; Tumos, W.; Ward, M. D.; Wheeler, D. R. *J. Am. Chem. Soc.* **1990**, *112*, 6133.

Registry No. PPA, 25038-69-1; $Cp_2Fe^+BF_4^-$, 1282-37-7; $(W(CO)_3(CH_3CN)_3)$, 13939-06-5; MePh, 108-88-3; MeC_6H_4-*o*-Me, 95-47-6; mesitylene, 108-67-8.