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# $W(CO)_6/CBr_4/h\nu$ – a new system for metathesis polymerisation<sup>1</sup>

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## Abstract

Metathesis polymerisation can be effected with many catalysts under a variety of conditions. The system described here, viz.,  $W(CO)_6/CBr_4/h\nu$ , induces polymerisation by in situ generation of the active species and has not been reported in the literature so far. In this paper, optimisation studies of this system, yields obtained with various monomers and characterisation of the active species are discussed. Variation of different parameters such as the ratio of  $W(CO)_6:CBr_4$ , the time of photolysis and the effect of solvents as well as that of the metal carbonyls have been studied. In addition, copolymers of phenylacetylene and norbornene have been synthesised. We have also attempted to characterise the active species responsible for the polymerisation by reaction with acetophenone.

*Keywords:* Metathesis polymerisation; Photo-induced; Block copolymer;  $W(CO)_6$ ;  $CBr_4$ ; Phenylacetylene; Norbornene; Norbornadiene

## 1. Introduction

A large number of transition element compounds, from Group IV (Ti) to Group VIII (Ir) either alone or in conjunction with a cocatalyst have been employed as catalysts for olefin metathesis polymerisations [1]. The most common among them are based on compounds of tungsten or molybdenum. Given the established tenet that the metathesis polymerisation is initiated and propagated by a metal carbene moiety, the catalyst systems can be classified into three general categories, i.e., (i) those possessing an actual metal carbene unit, (ii) a transition metal compound which on reaction with an alkyl or

allyl group containing compound such as  $C_2H_5AlCl_2$  generates a carbene ligand, or (iii) a compound that is lacking a preformed carbene or alkyl group but producing a metal carbene ligand by interaction with the monomer itself or by in situ generation.

In this paper, a new catalyst system of type (iii) generated by photo-induction is discussed. We had earlier reported the synthesis and characterisation of homo and block copolymers produced via the metathesis route employing the  $W(CO)_6/CCl_4/h\nu$  system [2,3]. As there seems to be some ambiguity in the literature with reference to the actual composition of the catalyst species [4,5], we investigated along similar lines leading to a new system i.e.,  $W(CO)_6/CBr_4/h\nu$ . We find this catalyst active for polymerisation of alkynes and also for ring-opening-metathesis-polymerisation (ROMP) of

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<sup>1</sup> Dedicated to Prof. K.J. Ivin on the occasion of his 70th birthday.

strained cyclic olefins. This observation contradicts an earlier report [6] which claims that halides like  $\text{CBr}_4$  and  $\text{FeCl}_3$  barely activate  $\text{W}(\text{CO})_6$  since they decompose easily to produce a catalytically inactive complex of the formula  $[\text{M}(\text{CO})_4\text{X}_2]_2$ . There could of course be a possibility that some of the  $\text{W}(\text{CO})_6$  is converted to such a catalytically inactive complex, since we do not seem to obtain polymers in comparable amounts to other systems though the yields are in general moderate to good. We report here the salient parts of our study on this new system.

## 2. Experimental

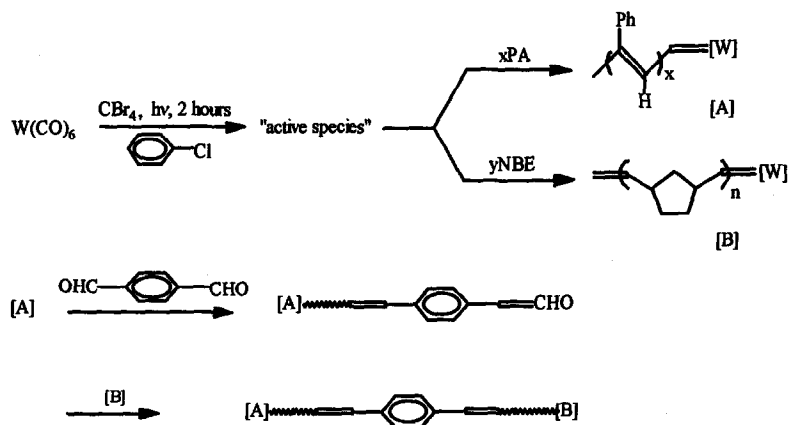
The photolysis reactions were carried out in a Rayonet reactor using light of 350 nm as the source. All procedures for catalyst preparation and polymerisation were carried out under dry, oxygen free nitrogen since the reactants are sensitive to water and oxygen. Transfers were performed in a nitrogen filled glove bag or by standard syringe techniques. The metal carbonyls were bought from Aldrich Chemical Co. and carbon tetrabromide from E. Merck and used as received. Phenylacetylene (PA), norbornene (NBE) and norbornadiene (NBD) were bought from Aldrich. PA and NBD were stored over molecular sieves prior to use while NBE

was refluxed over sodium, distilled and used. The hydrocarbon solvents were purified by washing first with acid then with water; dried over calcium chloride, distilled and stored over sodium wire. Acetonitrile was purified by refluxing and distilling over  $\text{P}_2\text{O}_5$  followed by  $\text{CaH}_2$  and storing over molecular sieves. Chlorobenzene was distilled and stored over molecular sieves.

The catalytically active species was generated by irradiating a mixture of  $\text{W}(\text{CO})_6$  and  $\text{CBr}_4$  in an appropriate solvent. The typical polymerisation procedure is as follows:

$\text{CBr}_4$  was weighed into a flask and dissolved in 10 ml of dry, degassed solvent. This solution was transferred via cannula into a quartz tube containing a weighed quantity of  $\text{W}(\text{CO})_6$  and photolysed for 2 h. The active species was cannula-transferred to a flask containing 50 eq. of the monomer (in 5 ml of solvent) and the flask was covered with aluminium foil to prevent photoinduced depolymerisation. The reaction mixture was stirred for 24 h in the dark, precipitated with excess methanol, filtered, washed and dried in vacuum.

For copolymerisation, the active species was generated as described above and this was cannula-transferred into a flask containing 30 eqs. NBE and stirred for 24 h. A solution of 30 eqs. PA was then cannula-transferred into the reaction mixture under nitrogen flow. This was



Scheme 1. Preparation of linked copolymers with terephthalaldehyde.

stirred for a further period of 24 h and then quenched by pouring into excess methanol. The polymer thus obtained was filtered, washed and dried. The yield of the copolymer was 34.65%. To prepare the linked copolymer [7], the active species was generated, PPA (1:50) and PNBE (1:50) were prepared in two reaction flasks. PPA was transferred into a solution of terephthalaldehyde (1 eq. in 5 ml of solvent) and stirred for 6 h. The polymer was precipitated in methanol, filtered, washed to remove excess terephthalaldehyde and dried. An appropriate amount of this polymer was weighed out, dissolved in chlorobenzene and then cannula-transferred into the active PNBE reaction mixture. This was stirred for 24 h and quenched by pouring into excess methanol. The polymer was then filtered, washed and dried (*vide* Scheme 1). The yield of the copolymer in this case was 52.48%. The ratio of  $W(CO)_6:CBR_4$  used for the copolymerisation reactions was 1:10 and the solvent used was dry, degassed chlorobenzene.

The polymers were characterised using spectroscopic techniques like  $^1H$  and  $^{13}C$  NMR, IR and TGA.  $^1H$  and  $^{13}C$  NMR spectra were recorded using JEOL model GSX 400 high resolution spectrometer (400 and 100.5 MHz respectively).  $CDCl_3$  was used as the solvent and the signals were obtained in parts per million (ppm) with tetramethylsilane as reference. The IR spectra were obtained using a Shimadzu (model-470) IR spectrophotometer and a Bruker IFS-66v FTIR spectrophotometer. The samples were analysed as KBr pellets or in solution form. Mass spectra were obtained using Finnigan-MAT (model 8230) high resolution mass spectrometer. Thermogravimetric analysis and DSC were done using a Stanton Redcrofts Simultaneous Thermal Analyzer (781 series) and a Perkin-Elmer Thermal Analyzer (model TGA-7) under nitrogen atmosphere. Samples were analysed for the determination of molecular weight using Waters GPC, with RI detector (model 410). The analyses were done using three ultrastragel columns (100 Å, 10 Å and 10<sup>5</sup> Å) connected in series, maintained at 32 ±

1°C with DMF as the eluant at the flow rate of 1 ml per min. The molecular weight was determined with polystyrene as the calibration standard.

### 3. Results and discussion

To obtain the optimal relative ratio of  $W(CO)_6/CBr_4$  needed to generate the catalytically active species, phenylacetylene (PA) and norbornene (NBE), two versatile monomers, were employed independently for metathesis polymerisation reactions. For all the reactions, hexane (dry, degassed) was used as the reaction medium. The dependence of polymer yield on the ratio of  $W(CO)_6/CBr_4$  used was not uniform for both polymers and the best yield of polyphenylacetylene (PPA) was obtained when the ratio of  $CBR_4/W(CO)_6$  was kept at 10:1 while that of polynorbornene (PNBE) was quantitative for a ratio of 40:1 as seen from Table 1. We are not able to explain why a 40:1 mole ratio of  $CBR_4/W(CO)_6$  leads to high yield of PNBE. In solutions containing other ratios, the low yields of the polymer might be due to the presence of other metal-containing species, whose specific concentration in the medium is not known, and which might be responsible for catalyst deactivation. Moreover, a preliminary analysis of the filtrate from the reaction mixture

Table 1  
Dependence of polymer yield on  $W(CO)_6/CBr_4$ <sup>a</sup>

No.	$W(CO)_6$	$CBR_4$	Yield PPA (%) <sup>b</sup>	Yield PNBE (%) <sup>b</sup>
1	1	1	7.4	15.4
2	1	2	8.7	7.2
3	1	5	16.9	9.4
4	1	10	34.7	17.7
5	1	20	26.0	29.4
6	1	30	12.5	21.4
7	1	40	6.1	100.0
8	1	50	–	14.2

<sup>a</sup> The reaction was carried out using 1:50 equivalent of  $W(CO)_6$ : monomer by stirring at room temperature for 24 h followed by work-up.

<sup>b</sup> The yields are calculated based on the methanol insoluble fraction.

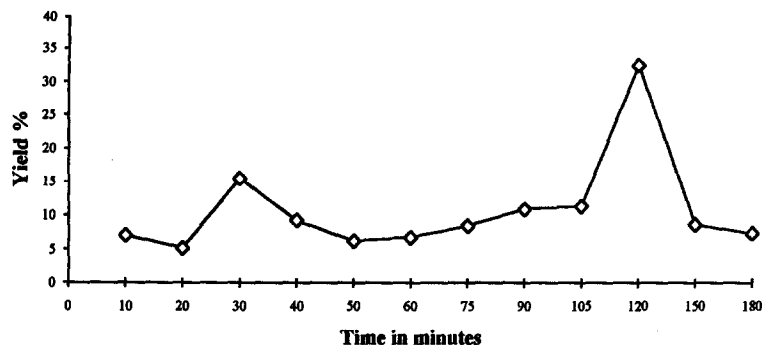


Fig. 1. Yield of PPA as a function of irradiation time (in percent).

indicates that besides the ring-opening reactions of norbornene, no other side reactions like oligomerisation by addition, take place and the unreacted monomer is recovered.

We are also at present unable to explain the anomaly of different ratios of  $W(CO)_6/ CBr_4$  for PA and NBE for obtaining the highest yields, but this observation may be due to the obvious difference in the reactivity of the two monomers. The time of irradiation to generate the active species is also crucial and maximum yield of PPA is obtained when the time of irradiation is 2 h (Fig. 1). It has been noted by others that  $W(CO)_6$  upon irradiation in presence of  $CCl_4$  generates a short lived and very active initiating species and another long lived less active species and that one or both of these may have a dichlorocarbene ligand [8,9]. A very similar

trend is observed in this new system also, as evinced from the higher yields of PPA with catalyst species obtained after irradiation times of 30 min and 120 min (Fig. 1).

Various solvents including hydrocarbons (aliphatic, aromatic and alicyclic) and coordinating solvents were employed in order to optimise the condition of polymerisation as well as to examine the effect of solvent on the degree of polymerisation. The results are presented in Table 2. While toluene as a reaction medium gives the highest polymer yield for PA, chlorobenzene seems to be the near ideal solvent for the polymerisation of all three monomers. As expected, coordinating solvents like acetonitrile and diethylether retard polymerisation with the exception of PA in the latter (entry #6, Table 2).

In order to investigate the use of other metal carbonyls for the photo-initiated olefin metathesis,  $Cr(CO)_6$  and  $Mo(CO)_6$  were also employed for polymerisation and the comparative efficiency is shown in Fig. 2 which indicates that

Table 2  
Effect of solvent on polymer yield<sup>a</sup>

No.	Solvent	Yield PPA (%) <sup>b</sup>	Yield PNBE (%) <sup>b</sup>	Yield PNBD (%) <sup>b</sup>
1	hexane	34.7	17.7	8.8
2	cyclohexane	42.4	20.6	22.6
3	benzene	34.4	18.0	13.0
4	toluene	51.7	20.8	19.6
5	chlorobenzene	32.0	52.6	19.2
6	diethylether	29.2	0	0
7	acetonitrile	0	0	0

<sup>a</sup> The reaction was carried out using 1:10 equivalents of  $W(CO)_6:CBr_4$  and 1:50 equivalents of  $W(CO)_6$ : monomer by stirring at room temperature for 24 h followed by work-up.

<sup>b</sup> The yields are calculated based on the methanol insoluble fraction.

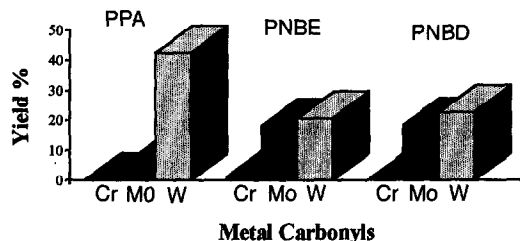


Fig. 2. Efficiency of Group VI carbonyls as catalysts.

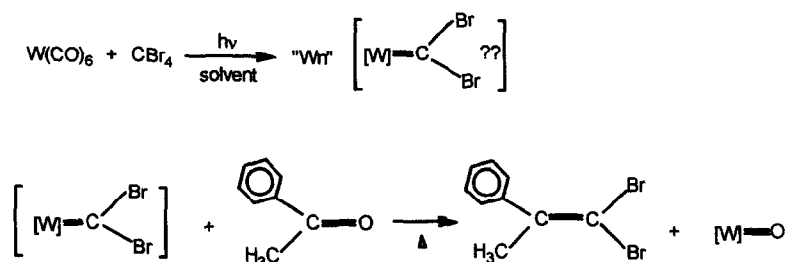
$W(CO)_6$  is by far a better catalyst precursor than its counterparts.

The 'living nature' of metathesis polymerisation was tested in this system by investigating the synthesis of block copolymers of PA and NBE using a 1:30:30 ratio of  $W(CO)_6$ :NBE:PA. The Gel Permeation Chromatogram shows a single peak with an  $M_w$  of 5200 and a polydispersity of 1.37. The  $^{13}C$  NMR spectrum of this polymer clearly indicates the presence of both polymer blocks, PPA and PNBE. A linked copolymer was synthesised according to Scheme 1 using a 1:50:50 ratio of  $W(CO)_6$ :NBE:PA (endcapped and linked with terephthalaldehyde). This polymer also showed a single peak in the Gel Permeation Chromatogram with an  $M_w$  of 5948 and a polydispersity of 1.37.  $^1H$  and  $^{13}C$  NMR were used to confirm the presence of two blocks.  $^1H$  and  $^{13}C$  Hetero COSY-NMR spectra very clearly show the presence of the PNBE block. However, the PPA block does not show any cross peaks since the signals in the one dimension spectrum are extremely broad. In the case of the end-capped and linked block copolymers, cross peaks showing the linkage between the two blocks with the *p*-phenylene divinyl unit of terephthalaldehyde can be clearly seen. These peaks are absent in the copolymer prepared via the sequential addition of monomers. Thus, the formation of the block copolymers can be clearly inferred from the 2D-NMR spectra. These are some initial results which suggest that photochemically initiated olefin metathesis reactions may have the potential to lead to 'living' polymerisations. Moreover, the facility with which such olefination reactions occur with

carbonyl compounds (see below, as well) indicate that the metal–carbene unit generated in these reactions, must be predominantly nucleophilic in nature [10].

To further investigate the nature of the catalyst system, which we presume is a metal carbene, direct reactions with an aromatic ketone were investigated. The active species generated as described earlier on reaction with acetophenone (reflux for 2 h) gave a product which showed a single spot in TLC (r.f. = 0.73, eluant hexane). The corresponding product did not contain any ketone functionality as shown by the IR spectrum which was devoid any of  $C=O$  stretching but displayed a strong  $C-Br$  stretching frequency at  $669\text{ cm}^{-1}$ . The reaction mixture was filtered using a Schlenck filter to remove the solid particles and the solvent was removed under reduced pressure. Since the compound rapidly decomposed in solution, characterisation by NMR proved to be elusive. The decomposition could be catalysed due to the presence of other metal complexes in solution (as mentioned in the Introduction) which could be the cause for the low yields of the polymers as well. But the EI mass spectrum ( $E = 70\text{ eV}$ ) suggested the presence of  $Ph-MeC=CBr_2$  with three molecular ion peaks at  $m/z$  274, 276 and 278 in the ratio 1:2:1 confirming the presence of two geminal Br atoms. The reaction could be described as shown in Scheme 2.

To conclude, we have demonstrated the viability of a new system  $W(CO)_6/CBr_4/h\nu$  to initiate and propagate metathesis polymerisation and have also given some insight into the proba-



Scheme 2. Reaction of the active species with carbonyl compounds.

ble structure of the active species. We may also surmise from the above results that the behaviour of  $W(CO)_6/CBr_4/h\nu$  system parallels that of  $W(CO)_6/CCl_4/h\nu$  though the  $W(CO)_6$  is not fully consumed during photolysis as in the latter case, and the active species in both cases is a metal dihalocarbene.

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