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Synthesis of Homo and Block Copolymers of Norbornene with $W(CO)_6$ *via* Photo-initiation

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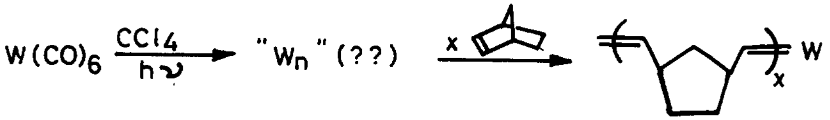
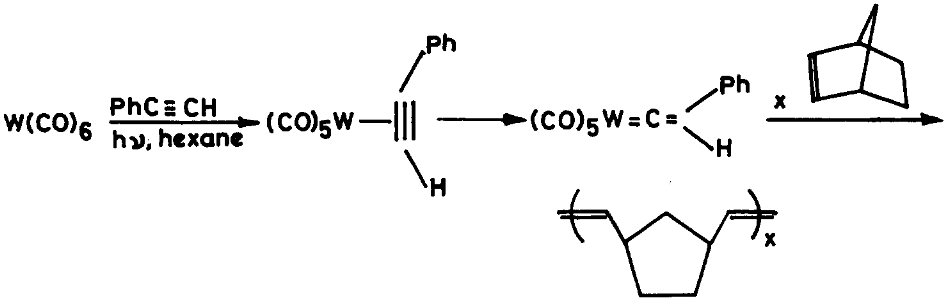
Abstract: Block copolymers of norbornene and phenylacetylene have been synthesised employing $W(CO)_6/CCl_4$ /hν system indicating formation of a metallacarbene as the active species.

Polymerisation *via* metathesis offers a good route for the preparation of conducting polymers like polyalkynes and specialty polymers like polyalkenamers. As the stability and processability of the polyacetylenes are poor, methods are sought to improve them. The most common techniques employed to alter the properties of the polymers are the preparation of either graft or block copolymers. In a block copolymer, if one of the blocks is an electrically conductive polymer, it could show better processability. Domain separated block copolymers have been synthesised *via* a precursor route[1]. The comonomer used most frequently with the acetylenes is norbornene. Usual metathesis catalysts involve elaborate syntheses and costly starting materials. Moreover, these catalysts are highly sensitive to air and moisture. Here, a few methods of preparation and characterisation of the homopolymer of norbornene (NBE) and the block copolymer of NBE and phenylacetylene (PA) involving the use of two simple photolytic systems will be discussed.

$W(CO)_6/CCl_4$ /hν[2] (System 1) has been used extensively for metathesis reactions and $W(CO)_6$/hexane/hν/PA(initiator)[3] (System 2) has been shown to be effective for synthesis of polyacetylene (albeit of low molecular weight). (See below)



Scheme 1. System 1

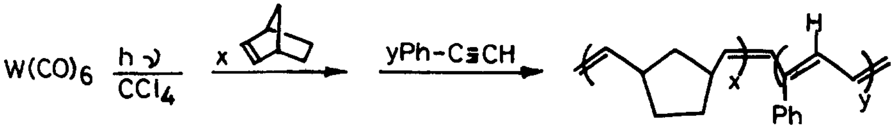


Scheme 2. System 2

The earlier formulation of the catalytically active species in 1, i.e., $W(CO)_3Cl_2{=}CCl_2$ [4] has been disproved in a recent report, wherein a polymeric material containing tungsten is allegedly the catalyst[5]. We have set out to compare the two systems towards synthesis of homo- and copolymers of NBE and review the above claim regarding the active species in 1 in the wake of these results.

For the preparation of PNBE, both 1 and 2 were employed. The yield in 1 was 28% whereas that in 2 was 19%. The PNBE prepared from both the systems is rubbery in nature and insoluble in all common organic solvents. PNBE from 1 was white in colour whereas that from 2 was light yellow in colour, probably because of the initiator (PA) employed. However IR spectra in the form of KBr pellets, the UV-Vis spectra (in CH_2Cl_2) could be obtained while it was not possible to get the NMR spectra. The molecular weight determination could not be carried out but we can be sure that they are above 10,000 since they are methanol precipitated[6].

Random copolymerisation of NBE and PA in 1 was reported recently[7]. Here, we have carried out block copolymerisation of these two monomers in the ratio 1:20:30 ($W(CO)_6$:NBE:PA). These block copolymers have been prepared by the sequential addition of monomers to the active species[8].



Scheme 3.

The IR spectra compared well with those of both the homopolymers. They show absorbance around 1590 cm^{-1}, 1350 cm^{-1} and 960 cm^{-1} as in PNBE and the characterestic bands of PPA around 690 and 750 cm^{-1}. PPA shows a λ_{max} at 240 nm and a shoulder at 340 nm. PNBE has a λ_{max} at 230 nm. All the copolymers show a λ_{max} at 235 nm and a shoulder between 330-350 nm. As the solubility of the copolymer is high compared to the homopolymer of NBE, the high resolution NMR spectra of the copolymer in $CDCl_3$ was most informative. The ^{13}C NMR spectrum of PPA shows a broad peak around 130 ppm which is seen in the spectra of the copolymers. The aliphatic region compares very well with the spectra of PNBE (% cis = 50%) reported in the literature[9]. Thus from the ^{13}C spectra of these copolymers, we were able to say unequivocally that the polymers obtained are indeed block copolymers and not random copolymers.

It was also found that the χ^3 (third-order-susceptibility constant) of PPA increased by an order of magnitude when block copolymerised with NBE [10].

In conclusion, PNBE from 2 has been reported for the first time, block copolymerisation of NBE and PA has also been reported for the first time. This copolymerisation improved the solubility and thus enabled complete characterisation of the PNBE backbone in this system. The ready formation of PNBE from 1 shows that the active species may contain a metallacarbene. Furthermore, the synthesis of the block copolymer also points in the same direction!

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REFERENCES AND NOTES:

1. Stelzer, F.; Leitner, O.; Pressel, K.; Leising, G.; Grubbs, R. H. *Syn. Met.*, 1991, *41-43*, 991-994.
2. Szymanska Buzar, T.; Ziolkowsky, J. J. *J. Mol. Catal.*, 1987, *43*, 161-170.
3. Landon, S. J.; Shulman, P. M.; Geoffroy, G. L. *J. Am. Chem. Soc.*, 1985, *107*, 6739-6740.
4. Garnier, F.; Krausz, P.; Rudler, H. *J. Organometal. Chem.*, 1980, *186*, 77-80.
5. Schilder, P. G. M.; Stufkens, D. J.; Oskam, A.; Mol, J. C. *J. Organomet. Chem.*, 1992, *426*, 351-359.
6. Masuda, T.; Takahashi, T.; Yamamoto, K.; Higashimura, T. *J. Polym. Sci., Polym. Chem.*, 1982, *20*, 2603-2610.
7. Masuda, T.; Yoshida, T.; Makio, K.; Rahman, M. Z. A.; Higashimura, T. *J. Chem. Soc., Chem. Commun.*, 1991, 503-504.
8. The active species was generated by irradiation of 1 using 354 nm Hg lamps in a Rayonet reactor with 0.07g (0.21 mmole) of $W(CO)_6$. NBE (0.39g. 4.11 mmole) dissolved in deaerated CCl_4 (5 ml) was injected into the reaction flask and stirred for 24 hours. An aliquot of 2 ml was withdrawn and quenched with excess methanol to yield rubbery PNBE of similar characteristics as before. Then PA (0.63 g, 6.16 mmole) was injected into the reaction flask followed by stirring for 24 hours. The viscous brown solution was poured into methanol and a fibrous copolymer was obtained.
9. Ivin, K. J. *Olefin Metathesis*; Academic Press: New York, 1983; pp.202-204.
10. Vijaya, R.; Murti, Y. V. G. S.; Gita, B.; Sundararajan G. submitted for publication.

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