

A Novel Route for producing Soluble Polyacetylene–Polyisoprene Block Copolymers

S. P. Armes,^a B. Vincent,^{a*} and J. W. White^b

^a *Department of Physical Chemistry, University of Bristol, Bristol BS8 1TS, U.K.*

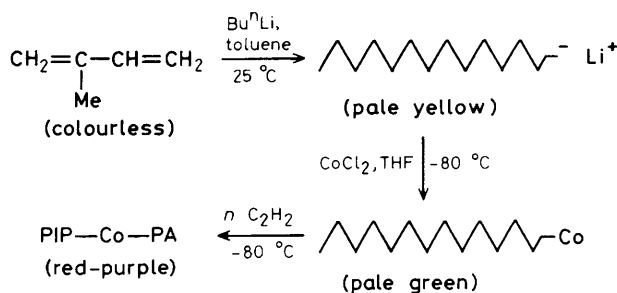
^b *Research School of Chemistry, Australian National University, Canberra, ACT 2601, Australia*

A novel cobalt catalyst system for the synthesis of soluble polyacetylene–polyisoprene block copolymers, *via* the anionic to Ziegler–Natta route is reported; preliminary experiments indicate that this catalyst is less susceptible to impurities and more versatile than the polymeric titanium catalyst route reported previously.

Polyacetylene has a complex fibrillar morphology when prepared as a film, using either the titanium-based Shirakawa catalyst or the cobalt-based Luttinger catalyst.¹ The intractability of the resulting material has severely restricted technological applications of its highly conducting doped state. Recently, however, soluble block copolymers have been synthesised in which the rigid polyacetylene chain is solubi-

lised by a carrier polymer such as polystyrene or polyisoprene.^{2–8} Furthermore, it has been shown that films cast from solutions of the block copolymers prepared by an anionic to Ziegler–Natta route may still be doped to the metallic régime, despite the presence of the electrically insulating carrier polymer.³

Attempts by ourselves to prepare polyacetylene–



Scheme 1. PIP = polyisoprene; PA = polyacetylene.

polyisoprene block copolymers by this method were not effective, probably owing to the high sensitivity of the polyisoprenyl titanium intermediate to deleterious impurities. In view of this, an alternative catalyst system was sought. The Lutinger catalyst is known to be less air-sensitive than the Shirakawa catalyst¹ but the cobalt species normally used in this method is $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. This is unsuitable for the present purpose since water would kill the living polymeric carbanion before carbon-cobalt bond formation could take place. The chosen cobalt species therefore was anhydrous CoCl_2 in dry tetrahydrofuran (THF). The decomposition temperature of the Lutinger catalyst is $\sim -30^\circ\text{C}$ so the polymeric cobalt intermediate was synthesised and used at -80°C to prevent possible degradation. The carrier polymer molecular weight was controlled by the monomer/initiator ratio and chosen to be ~ 8000 , a similar value to that used by other workers.³ The reaction scheme is summarised in Scheme 1.

Isoprene was polymerised anionically at 25°C in toluene by standard techniques using a high vacuum apparatus. The initiator was Bu^nLi injected *via* a Suba-Seal using a syringe pre-purged with dry argon. The living polymer solution was left to react for 24 h, before being cooled to -80°C in a solid CO_2 -ethanol bath. A stoichiometric amount of CoCl_2 with respect to the living polymer was placed in a pre-weighed Schlenk tube and flushed with dry argon. The cobalt salt was then dissolved in dry THF, freshly distilled over sodium-benzophenone. The solution was injected *via* a syringe, pre-purged with dry argon, into the reaction vessel. An immediate colour change to light green was observed. The resulting cobalt intermediate was stored at -80°C for *ca.* 8 h. A sample of this polyisoprenyl-cobalt species was abstracted under argon for subsequent analysis by Fourier transform i.r. spectroscopy. Acetylene was then introduced to the stirred solution at an initial monomer pressure of ~ 700 Torr. A red-purple colouration was observed instantaneously and the viscosity of the reaction solution increased. ~ 86 Torr of acetylene reacted in *ca.* 1 h. This corresponds to an average polyacetylene molecular weight of 1200, based on the assumption that each Bu^nLi molecule produces one living polyisoprenyl carbanion, which is then converted into the active polymeric cobalt intermediate. The reaction solution was then allowed to warm to ambient temperature with continuous stirring. The low-temperature nature of the reaction resulted in an all-*cis*-polyacetylene portion of the block copolymer as indicated by visible absorption spectroscopy (Figure 1a).

Appreciable isomerisation to the *trans*-isomer over a period of 23 h at room temperature was observed to occur, as evidenced by the increased absorption in the 650 nm region of the visible spectrum (Figure 1b). Although the low reaction temperature precluded *in situ* visible absorption spectroscopy, a small sample of the polyisoprenyl cobalt intermediate was

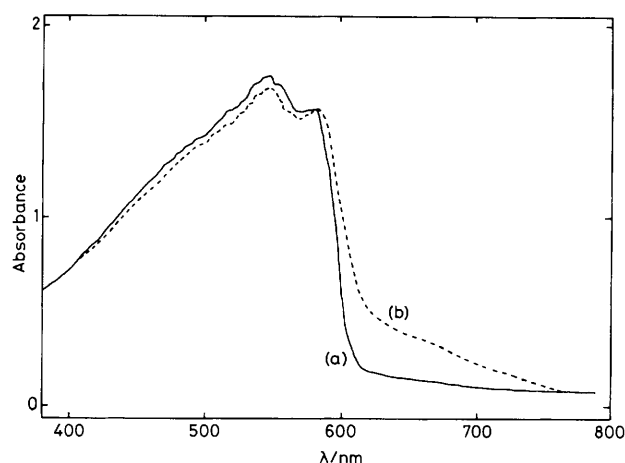


Figure 1. Visible absorption spectrum for polyisoprene-polyacetylene block copolymer in toluene: (a), after reaction at -80°C ; (b), after 23 h at ambient temperature.

extracted under a positive argon pressure prior to acetylene polymerisation and a spectrum recorded under ambient conditions. Three peaks were observed at ~ 550 , 612, and 640 nm. This contrasts with the spectrum reported by Aldissi^{3,5} for the polymeric titanium intermediate, for which a single peak at ~ 500 nm was observed.

I.r. spectra of the block copolymer and the polyisoprenyl-cobalt intermediate were recorded in the $500\text{--}1500\text{ cm}^{-1}$ range on a Perkin-Elmer 1800 Fourier transform i.r. instrument. Spectral subtraction revealed a peak at 1010 cm^{-1} characteristic of *trans*-polyacetylene. Unfortunately the 740 cm^{-1} peak due to *cis*-polyacetylene was completely obscured by the strong solvent absorbance in this region. Thus a *cis/trans* ratio measurement for the block copolymer was not possible.

It was subsequently shown that low-temperature conditions are not in fact necessary to carry out the synthesis of the block copolymer from the polyisoprenyl-cobalt intermediate. Reaction occurs even at room temperature, although a mixture of the *cis*- and *trans*-polyacetylene isomers is obtained (visible absorption spectroscopy), the ratio depending on the temperature. Although acetylene polymerisation at ambient temperatures has been carried out previously using the Shirakawa catalyst system, no similar successful acetylene polymerisation at ambient temperature has previously (as far as we are aware) been reported using a cobalt-based system.

It has been claimed that polyacetylene films prepared by the Lutinger catalyst have poorer crystallinity, more extensive cross-linking and a higher proportion of sp^3 carbons than those obtained using the Shirakawa catalyst.¹⁰ If the resulting inferior conduction properties are due to these defects then the polyisoprenyl cobalt intermediate may be more effective than the normal Lutinger catalyst since it probably promotes single polyacetylene chain formation.

Preliminary experiments have indicated that the polystyryl cobalt intermediate may also be used to initiate polymerisation of acetylene. Certain nickel compounds have been shown to be effective catalysts for normal acetylene polymerisation.¹¹ It is expected that the analogous nickel-based block copolymer could be synthesised by a similar reaction scheme and that the anionic to Ziegler-Natta route is of wider applicability than previously considered.

S. P. A. and B. V. acknowledge the Research School of Chemistry, the Australian National University, for providing

funds to enable them to carry out this work in that laboratory. We thank Dénes Bogsányi for assistance with the i.r. studies and analysis.

Received, 19th May 1986; Com. 675

References

- 1 J. C. W. Chien, 'Polyacetylene: Chemistry, Physics and Material Science,' Academic Press, New York, 1984.
 - 2 M. E. Galvin and G. E. Wnek, *Mol. Cryst. Liq. Cryst.*, 1985, **117**, 33.
 - 3 M. Aldissi, *J. Chem. Soc., Chem. Commun.*, 1984, 1347.
 - 4 M. Aldissi and A. R. Bishop, *Polymer*, 1985, **26**, 622.
 - 5 M. Aldissi, preprint *Synth. Met.*, 1986 (to be published).
 - 6 F. S. Bates and G. L. Baker, *Macromolecules*, 1983, **16**, 704.
 - 7 F. S. Bates and G. L. Baker, *Macromolecules*, 1984, **17**, 2619.
 - 8 A. Bolognesi, M. Catelloni, and S. Destri, *Mol. Cryst. Liq. Cryst.*, 1985, **117**, 29.
 - 9 T. Ito, H. Shirakawa, and S. Ikeda, *J. Polym. Sci., Polym. Chem. Ed.*, 1974, **12**, 11.
 - 10 H. Haberkorn, H. Naarmann, K. Penzien, J. Schlag, and P. Simak, *Synth. Met.*, 1982, 51.
 - 11 L. B. Luttinger, *J. Org. Chem.*, 1962, **27**, 1591.
-