Soluble Conducting Poly(acetylene) Block Copolymers

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Soluble conducting poly(acetylene)–poly(isoprene) block copolymers have been synthesized by using the polymeric catalyst formed by the reaction of poly(isoprenyl-lithium) with tetrabutoxytitanium in toluene at room temperature; an instantaneous polymerization of acetylene is observed leading to the formation of a block copolymer in which the poly(isoprene) chain length is the determining factor of the materials electrical behaviour.

Freestanding films of poly(acetylene), prepared by using concentrated Ziegler–Natta catalyst solutions,[1] are known to undergo a dramatic increase in electrical conductivity upon doping.[2] Most previous studies concentrated on the physical properties of the non-doped and doped polymer for it exhibits interesting electronic properties. However, some of the properties of poly(acetylene), such as the complete insolubility and the decomposition at high temperatures without melting, limits its use in many technological applications.

Attempts to render the polymer soluble, by synthesizing derivatives of poly(acetylene) have resulted in materials with poor electronic properties.[3]

The successful synthesis of graft[4] and block[5] copolymers involving poly(acetylene) has been reported recently by an anionic-to-Ziegler–Natta catalysis. These attempts resulted in soluble copolymers but truly insulating materials. The polymers which consisted of poly(styrene)–poly(acetylene) or poly(isoprene)–poly(acetylene) were synthesized by using very high molecular weight anionic poly(isoprene) or poly(styrene) (M_w 50 000—100 000). The relative amount of poly(acetylene) in the copolymers was very small, which is the reason for the insulating properties of the material.

One of the reasons for the insolubility of the Ziegler–Natta poly(acetylene) is the rigidity of its backbone. In order to bypass this problem without affecting significantly its electronic properties, block copolymers of poly(isoprene)–poly(acetylene) are prepared in which the carrier chain length [poly(isoprene)] is varied.

The anionic poly(isoprene) is prepared, under vacuum, by using n-butyl-lithium in toluene as a catalyst at room temperature. The chain length of this polymer can be varied easily by varying the concentration of the catalyst or the monomer. In all the experiments, the concentration of Bu^nLi is 2×10^{-2} mol l^{-1}, and the concentration of isoprene is varied. The polymerization of isoprene is monitored by using u.v. spectroscopy since the monomer absorbs at 250—260 nm and the live polymer chains absorb at 300—330 nm. The polymerization is maintained for several days until the monomer band disappears (completion of the reaction). Then an equimolar amount of $Ti(OBu)_4$, 2×10^{-2} mol l^{-1}, is added to the solution and reacts with the live polymer. The solution is stirred for 48 h and undergoes several changes in the colour indicating a change in the structure of the catalyst. This reaction can also be monitored by using u.v. spectroscopy. In fact, a band with a maximum absorption at 500 nm is observed after 48 h, and before then the band is observed at higher energies ($\lambda < 500$ nm). In this reaction one of the ligands of the titanium atom is replaced by the poly(isoprene) chain, and by aging the catalyst solution at room temperature the Ti^{IV} species which do not show any signal in the e.s.r. spectrum, are reduced to Ti^{III} species with the appearance of several e.s.r. peaks of g values in the range 1.96—1.98. When the acetylene gas is allowed into the reaction vessel at room temperature, a dark blue solution is formed characteristic of the *trans*-rich poly(acetylene) sequences in the copolymer. The reaction is maintained until no uptake of acetylene gas is observed. A large band is observed in the u.v.–visible region (500—700 nm) due to the conjugated backbone of poly(acetylene) sequences in the copolymer, and to the polymeric catalyst which has a maximum absorption at 500 nm.

The molecular weights of poly(isoprene)–poly(acetylene) copolymer are determined by using gel permeation chromatography. The copolymer chains are almost monodisperse ($I = M_w/M_n = 1.15$—1.20). The molecular weight of poly(acetylene) sequences is measured by the difference between the molecular weight of the copolymer and the molecular weight of poly(isoprene) before the copolymerization reaction. This study is limited to low molecular weights of poly(isoprene) ($M_w < 10\,000$). The molecular weight of the poly(acetylene) sequences depends upon the molecular weight of the carrier chain and ranges between 1 500 and 1 900 when the latter ranges between 7 000 and 10 000.

The fibrillar morphology characteristic of Ziegler–Natta poly(acetylene) films is non-existent in the copolymers as verified by scanning electron microscopy.

^{1}H N.m.r. and i.r. studies showed that the poly(isoprene) microstructure consists of 60% of 1,4 *cis*, 30% of 1,4 *trans*, and 10% of 3,4, and that poly(acetylene) sequences consist of 88% *trans* and 12% *cis*. The latter is transformed to 100% *trans* isomer when heated under vacuum at 90 °C for a few minutes.

Films of the copolymers can be cast from homogeneous solutions in toluene, benzene, tretrahydrofuran, chloroform, *etc.*, and doped with iodine. The four probe conductivity measurements show that the doped material exhibits metallic conductivity, 1—10 S cm^{-1}. Such a conductivity might be increased by synthesizing the poly(isoprene) carrier chain with lower molecular weights, a condition in which the copolymer can still be soluble.

The preliminary results obtained by using conductivity measurements at room temperature on the iodine doped samples while exposed to oxygen and moisture showed that the copolymers are not air stable. Therefore, the films are cast in an inert atmosphere and doped under vacuum.

In conclusion, the importance of this study resides in the generation of soluble poly(isoprene)–poly(acetylene) block copolymers in which the carrier chain length is easily controlled. This process may be extended to monomers other than isoprene, such as styrene and butadiene, yielding conducting copolymers, when doped, in which the carrier chain is long enough to make the material go into solution. The interest in such materials is due to the fact that they can be processed easily, a property which is very important for most technological applications, *i.e.*, electromagnetic interference shielding.

A detailed study on the main characteristics of the copolymers and the effect of the poly(isoprene) chain length on the poly(acetylene) chain length as well as a study of the electrical behaviour of the material will be reported.

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References

1 A. Shirakawa and S. Ikeda, *Polym. J.*, 1971, **2**, 231.
2 A. G. MacDiarmid and A. J. Heeger, *Synth. Met.*, 1979, **1**, 101; M. Rolland, M. Aldissi, and F. Schue, *Polymer,* 1982, **23**, 834; R. H. Baughman, J. L. Bredas, R. R. Chance, R. L. Elsenbaumer, and L. W. Shacklette, *Chem. Rev.*, 1982, **82**, 209.
3 J. C. W. Chien, G. E. Wnek, and F. E. Karasz, *Macromolecules,* 1981, **14**, 479.
4 F. S. Bates and G. L. Baker, *Macromolecules,* 1983, **16**, 704.
5 G. E. Wnek, Communication at Los Alamos Workshop on Synthetic Metals, Los Alamos, New Mexico, U.S.A., August 20—23, 1983.