

Synthesis of highly conducting polystyrene–polyacetylene copolymers

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Polystyrene–polyacetylene block copolymers were synthesized, via an anionic-to-Ziegler–Natta catalysis, where the amount of polystyrene in the copolymer is well controlled by controlling the monomer concentration at a fixed anionic catalyst concentration. The iodine doped films of the copolymers exhibit very interesting electrical properties, and their electrical conductivities are in the metallic regime for a ratio of polystyrene/copolymer $\leq 20\%$. This can be understood as a percolation phenomena supporting a variable range hopping transport mechanism in metallic polyacetylene.

(Keywords: acetylene; styrene; block copolymer; doping; electrical conduction; percolation)

INTRODUCTION

Most studies on polyacetylene over the last decade have focussed on the films prepared with the Ziegler–Natta catalyst, $\text{Ti}(\text{OBu})_4/\text{AlEt}_3$.¹ Due to problems such as poor stability of the doped polymer², the research has been extended to the synthesis and study of blends prepared by impregnating a host polymer such as polyethylene or polystyrene, with the Ziegler–Natta catalyst solution and then polymerizing the acetylene³. Slightly superior mechanical properties to those of pure polyacetylene are achieved and the stability is relatively improved. Also, graft and block copolymers have been prepared via an anionic-to-Ziegler–Natta catalysis, respectively, by reacting $\text{Ti}(\text{OBu})_4/\text{AlEt}_3$ with a functionalized, high molecular weight anionic polystyrene ($\bar{M}_n \approx 1 \times 10^5$)⁴, and by alkylation of $\text{Ti}(\text{OBu})_4$ with the anionic polystyrene⁵. In both cases the acetylene reacts with the polymeric catalyst to form the soluble copolymers. Whilst the high molecular weight of the carrier chain, i.e. polystyrene, is responsible for the solubility of the copolymer, unfortunately it also makes it an insulating material.

In this paper we report the synthesis of polystyrene–polyacetylene copolymers in which the carrier chain length is varied, and the resulting electrical properties of the doped material are examined.

EXPERIMENTAL

The anionic polystyrene is prepared, under vacuum, by using *n*-butyllithium in toluene, as a catalyst, at room temperature. The chain length of this polymer can be varied by varying the concentration of the catalyst or of the monomer. In all the experiments the concentration of *n*-BuLi is $5 \times 10^{-2} \text{ mol l}^{-1}$, and the monomer's concentration is varied. The polymerization of styrene is maintained for 24 h to insure the completion of the reaction, with total consumption of the catalyst. Then an

equimolar amount of $\text{Ti}(\text{OBu})_4$ ($5 \times 10^{-2} \text{ mol l}^{-1}$) is added to the solution and reacts with the live polystyrene chains, $\text{PS}^- \text{Li}^+$, and the colour of the solution changes from yellow to dark brown. The solution is stirred for 24 h. In this reaction, one of the ligands of the titanium atom is replaced by the polystyrene chain. By ageing this catalyst solution the Ti^{IV} species are reduced to Ti^{III} species, similarly to what is observed in the case of tetrabenzyltitanium, as verified by e.p.r. measurements⁶. The acetylene gas is then allowed into the reaction vessel, at room temperature, forming the copolymer.

The amount of polystyrene in the material studied here is 0–40% of the copolymer's weight. The samples are obtained as gels, at the catalyst concentrations mentioned above, which are compressed to give flexible films. These films are doped with iodine in the vapour phase for 12 h at room temperature. These conditions are required for the saturation level in pure polyacetylene, which is used as a reference in every case. The samples are pumped at room temperature for 20 h, then washed repeatedly with pentane, under vacuum, to reach a stable doping level and to remove the iodine which might be absorbed by polystyrene sequences.

RESULTS AND DISCUSSION

The scanning electron micrographs (*Figure 1*) show that the fibrillar morphology of pure polyacetylene. *Figure 1(a)* is altered by the increase of the amount of polystyrene in the copolymer. The fibrils can still be detected in the copolymer shown in *Figure 1(b)* where PS=10% in weight. In the copolymer shown in *Figure 1(c)*, where PS=20% in weight, the characteristic fibrillar morphology of pure polyacetylene is already strongly affected. Upon increasing the amount of polystyrene in the copolymer to 40% in *Figure 1(d)*, the void space is almost completely filled and the fibrillar morphology has disappeared.

The four-probe conductivity measurements performed at room temperature on the samples saturated with iodine

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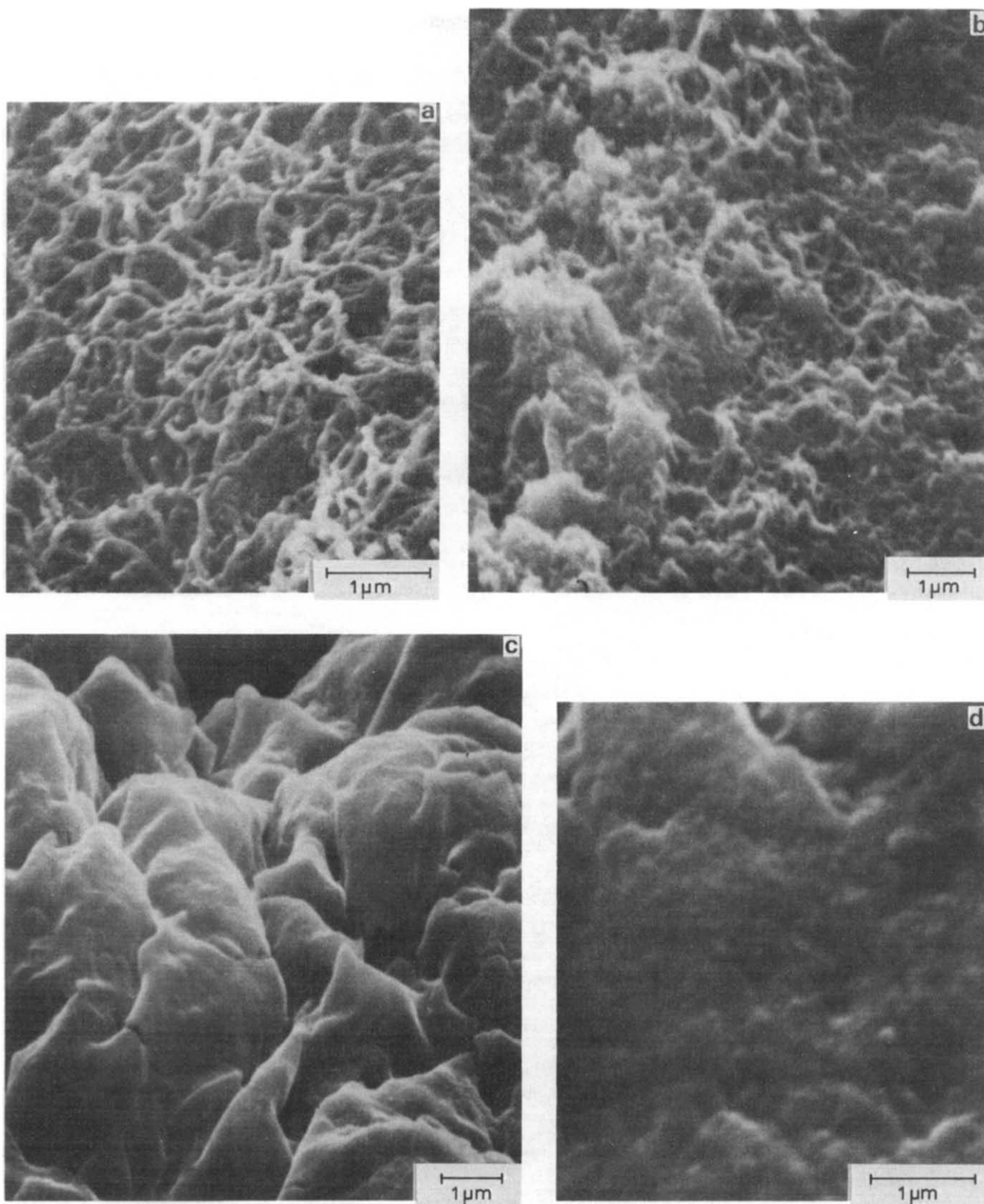


Figure 1 Scanning electron micrographs of pure polyacetylene (a), polystyrene–polyacetylene copolymer with (b) polystyrene=10% in weight (c), polystyrene=20% in weight and (d), polystyrene=40% in weight

(17% molar, based on the amount of the active material, polyacetylene) in the procedure described above show that the electrical properties of the doped copolymer are similar to those obtained for the doped homopolymer, polyacetylene, and can be doped to a metallic regime with activation energies varying between 20 meV and 40 meV

when the amount of polystyrene ranges from 0 to 20% in weight. The electrical conductivity decreases when the amount of the non-active material, polystyrene, increases (*Figure 2a*). At 40% of polystyrene the electrical properties of the doped copolymer become quite poor. At a higher percentage of polystyrene, the carrier chain is long enough

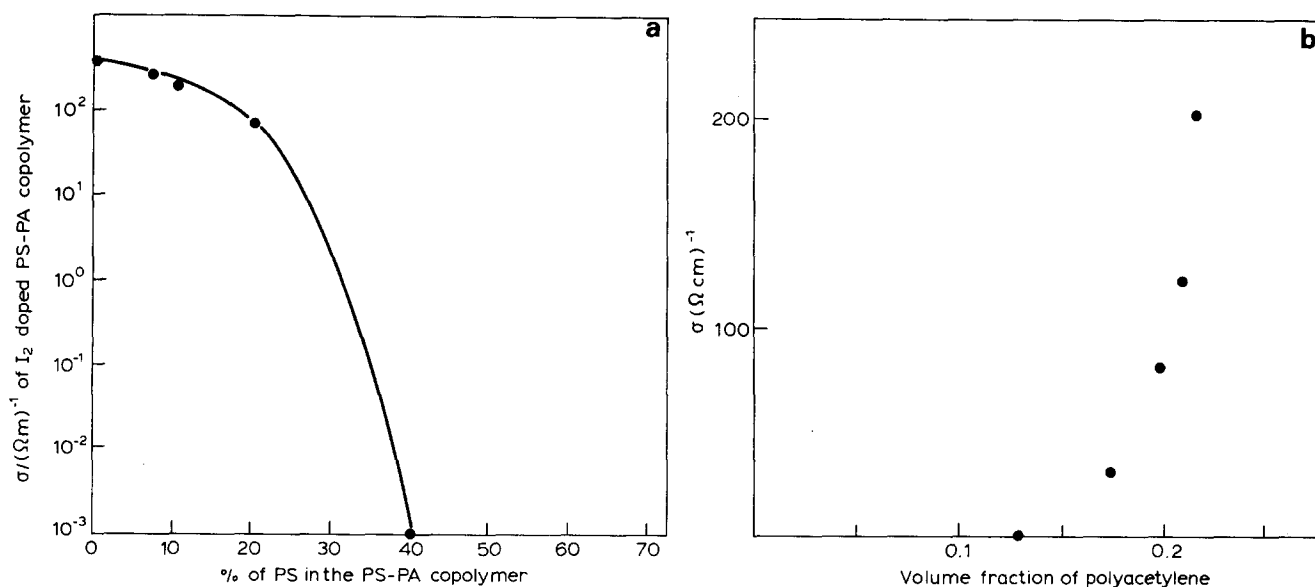


Figure 2 Electrical conductivity of polystyrene-polyacetylene block copolymer films saturated with iodine, (a) as a function of the relative amount of polystyrene, and (b) as a function of the estimated volume fraction of Polyacetylene in the copolymer. (Note the 'percolation' threshold at $\approx 16\%$; see text)

to allow the material go into solution, and yields a perfectly insulating material.

Popular 'solution' theories⁷ of transport in polyacetylene, do not seem to us appropriate in the heavily doped regimes and the morphological changes as a function of polystyrene content further mitigate against simple diffusive soliton mechanisms. Rather, we favour variable-range or polaron hopping mechanisms⁸ both along and between chains. The situation in our case, is then very similar to that of hopping transport in amorphous semiconductors where percolation concepts have frequently been invoked⁹. In Figure 2b, we have plotted conductivity versus volume fraction of polyacetylene. Here we have assumed (i) that the polyacetylene regions are essentially unchanged (in density) by the polystyrene content, (ii) that the heavily doped polyacetylene is saturated, i.e. the dopant regions on each chain are fully overlapping, and (iii) that there are only two mediums (conducting polyacetylene and insulating polystyrene or vacuum). The striking threshold at approximately $16 \pm 2\%$ volume fraction of polyacetylene is in excellent agreement with estimates of the percolation threshold in 3-dimensional random networks⁹. This picture is further supported by the effects observed upon compression. For example, the maximum conductivity under doping of the 40% polystyrene sample increases to $\sim 1 (\Omega \text{ cm})^{-1}$ under 10 Kbars pressure.

CONCLUSIONS

The copolymerization of acetylene with styrene (this can

be extended to other monomers than styrene), has proven to be an interesting way of synthesizing conducting polymers, with conductivities in the metallic regime. The amount of the dopable material, polyacetylene, affects the electrical conductivity of the iodine doped copolymer in a percolation-like manner. The results discussed in this paper favour a hopping conduction mechanism in the metallic regime in polyacetylene. It will be very instructive to study the temperature- and frequency-dependence of the conductivity for our block copolymers to further elucidate this mechanism.

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