Synthesis and characterization of a comb-like polyacetylene copolymer

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Graft copolymers were synthesized via lithiation of a polybutadiene backbone, transmetallation with titanium alkoxides and subsequent polymerization of acetylene. The products obtained were characterized by ultra-violet/visible spectroscopy, infra-red spectroscopy, wide-angle X-ray scattering and transmission electron microscopy. The I_2 doped copolymers exhibit interesting electrical conductivity. The proposed percolation model accounts for the properties of these materials.

(Keywords: synthesis; polyacetylene; polybutadiene; graft copolymers; morphology; conductivity)

INTRODUCTION

Recently some efforts have been devoted to the synthesis of copolymers and blends of polyacetylene (PA) with the aim of obtaining a material having good electrical properties and improved air stability by comparison with the homopolymer[1]. Moreover the synthesis of a PA copolymer can lead, in principle, to a soluble material which can be studied in more detail with the conventional spectroscopic techniques, namely ultra-violet/visible (u.v.–vis.), Raman, infra-red (i.r.) and nuclear magnetic resonance (n.m.r.).

Three different synthetic approaches have been reported for the formation of PA copolymers[1–3]. In this work we report on another synthetic route to obtain a comb-like copolymer made up of PA side chains grafted onto polybutadiene (PB) matrix and on its characterization by i.r., u.v.–vis., wide-angle X-ray scattering (WAXS) and transmission electron microscopy (TEM) techniques.

EXPERIMENTAL

A solution of *cis*-1,4-polybutadiene was prepared by dissolving 180 mg of polymer in 150 ml of dry cyclohexane. In a typical run only 5% of repeating units of butadiene in the *cis*-1,4-polybutadiene were lithiated, in the allylic positions, with the corresponding amount of sec-butyllithium (s-BuLi)[4]. Tetramethylethylenediamine (TMEDA) was added just after the addition of s-BuLi in a 1:1 ratio with respect to it. The solution was stirred for 2 h at room temperature, its colour changing from yellow to dark orange. Subsequently a given amount of $Ti(OBu)_4$ was added to the stirred solution. The dark orange solution change its colour to dark yellow-green. Acetylene was bubbled into this solution for 4 min at $4\,l\,h^{-1}$ flux. The colour of the solution immediately became dark blue. The polymerization was stopped by bubbling nitrogen instead of acetylene.

All the operations were performed in an inert atmosphere. s-BuLi was a commercial product; TMEDA was distilled prior to use and stored over molecular sieves. Cyclohexane was distilled over Na/K alloy in an inert atmosphere, *cis*-1,4-Polybutadiene was a commercial product (Janssen) (M_w 200 000). I.r. spectra were performed on a Perkin–Elmer 457 instrument; u.v.–vis. spectra were recorded on a Perkin–Elmer 920 instrument. WAXS experiments were carried out both on a Weissenberg camera and on a powder diffractometer (Siemens D-500). TEM and electron diffraction (ED) observations were performed on a Jeol 200B instrument. For the X-ray, ED and TEM characterizations and d.c. measurements see ref. 5.

RESULTS AND DISCUSSION

This synthetic route can be summarized as follows:

Step 1 Reaction of s-BuLi with *cis*-1,4-polybutadiene in dry cyclohexane. The presence of TMEDA favours the formation of carbanions in the allylic positions of the polymeric matrix[4].

Step 2 Exchange reaction between $Ti(OBu)_4$ and the polymeric lithiated compound to obtain a Ti–C bond on the polymer backbone. Meanwhile the Ti(IV) atoms bonded to the polymer are reduced to Ti(III) species[6].

Step 3 Polymerization of acetylene leading to a comb-like polymer which colours the solution dark blue.

The scheme of these reactions is reported in *Figure 1* while our main results are summarized in *Table 1*.

A long period of catalyst ageing does not produce acetylene polymerization. Probably the active centres are not stable in this system for such a long period. In a series of runs (e.g. run 2) in which the 1:1 Li/Ti ratio was used, the precipitation of copolymer as a gel was observed. At present we cannot give an explanation of this phenomenon. The reaction between Li-polymer and $Ti(OR)_4$ leads to substitution of at least one of the butoxy groups of $Ti(OBu)_4$ with a polymer chain and, subsequently to a reduction of Ti(IV) to Ti(III). One can suppose that a larger amount of $Ti(OR)_4$ with respect to s-BuLi can favour the formation of crosslinked polymer. In fact when acetylene polymerizes on these matrices, the

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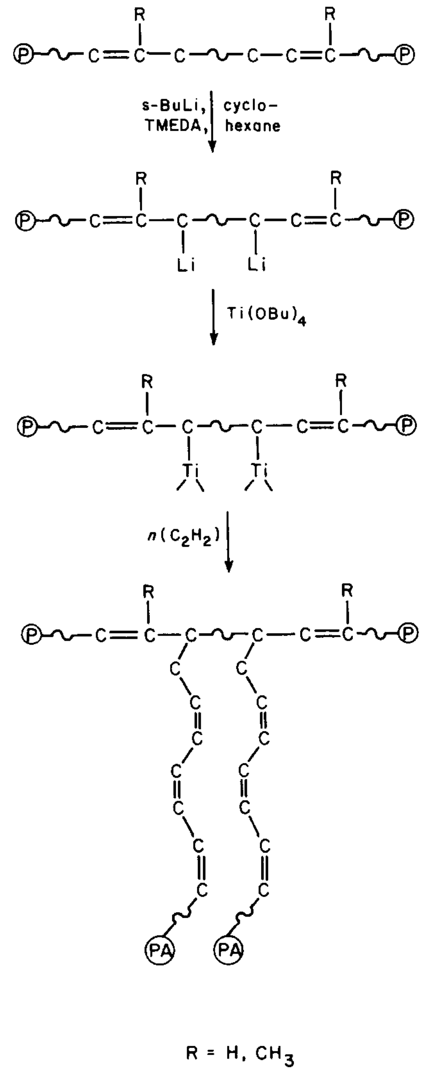

Figure 1 Scheme of the reactions

Table 1 Main synthetic results

Run	s-BuLi × 100(mmol) / C$_4$ units (mmol)	Lithiation time (h)	Titanation time (min)	Li/Ti	PA (wt%)
1	5	2	2880	2:2	–
2	5	2	5	1:1	5[a]
3	5	2	5	2:1	15
4	5	2	5	2:1	5

[a] The copolymer precipitates after 2 min of acetylene bubbling

resulting material is not soluble and precipitation of a gel occurs. In contrast with a ratio of Li/Ti equal to 2:1 the formation of the crosslinked material is strongly depressed and the polymerization of acetylene occurs without appreciable formation of gel. In this situation we obtain a PA amount by weight which is the same as or, in some cases, more than that obtained with the 1:1 ratio of Li/Ti. Probably these phenomena are related to the reduction of Ti(IV) to Ti(III) by Li-alkyl. The formation of Ti(III) active centres is due both to the alkylation of a titanium atom by a Li-polymeryl and to its reduction by another Li-polymeric species. One therefore can expect that an increased number of active centres is formed on varying the Li/Ti ratio from 1:1 to 2:1. This hypothesis should be substantiated by more experimental work on and more information about this complex system.

We obtained similar results in a series of polymerizations of acetylene on polyisoprene using the same synthetic route reported here[7]. From the recovered unreacted polyisoprene and from the amount of polyacetylene obtained in the copolymer, an increase of active centre number on the polymer backbone using a 2:1 Li/Ti ratio instead of a 1:1 one was suggested. I.r. spectra on the film cast from the blue solution reveal the presence of polybutadiene and *trans*-PA. The *cis*-isomer could not be detected. The u.v.–vis. spectra are very similar to those of the other PA copolymer reported by us[8]. However the absorption maxima are shifted towards lower wavelengths, thus implying shorter conjugation length. The maximum is centred at 580 nm (20 double bonds), while in previously prepared PA it was centred at 640 nm (40 double bonds). Also from the u.v.–vis. spectra no evidence of *cis*-isomer can be detected.

The n.m.r. spectra cannot give information on the PA protons, the lack of signal being attributed both to chain rigidity and to micellar aggregation in solution[9]. The X-ray as well as ED spectra of copolymer films cast from the reaction solution exhibit the usual patterns already described[10], namely the overlap of the spectra of the copolymer constituents. The halfwidth of the peak is relatively larger than that found in the copolymer synthesized according to the other route[9], indicating a smaller dimension of PA microdomains (about 50 Å) normal to the chain direction.

TEM examinations of copolymer thin films, as-cast and OsO$_4$ vapour-stained, are consistent with a nearly complete polydisperse morphology in which PA microdomains (less than 50 Å in size, nearly spherical in shape and slightly brighter in *Figure 2*) are embedded in an amorphous matrix of PB. Some wormlike aggregates are also apparent in the same figure; however, in view of several observations carried out under different conditions, we think that the polydisperse morphology is really representative for this comb-like copolymer, similar to that found in block PA copolymer reported by Baker[2]. The complete segregation found is confirmed both by WAXS and ED patterns. Moreover the PA microdomain dimensions are comparable with the conjugation length, as determined by u.v.–vis. spectra, and also with the coherence domain sizes, as derived from

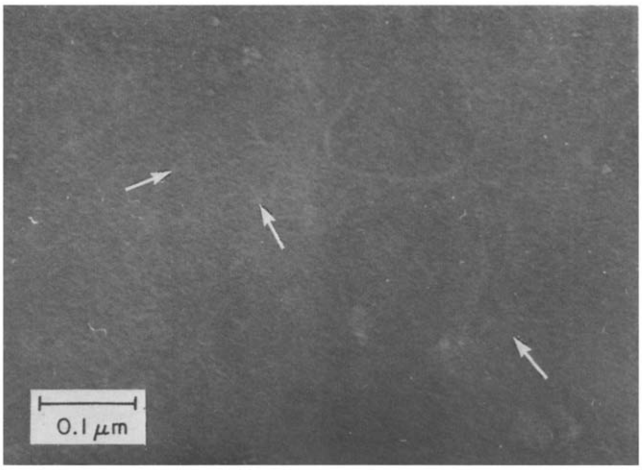

Figure 2 Typical micrographs of the copolymer thin film, lightly stained with OsO$_4$. PA microdomains appear slightly brighter and are indicated by arrows

X-ray line broadening (see above). Upon I_2 doping the copolymer film increases its conductivity till $1.4 \times 10^{-3}\,\Omega^{-1}\,\mathrm{cm}^{-1}$. There is a direct dependence of the conductivity values on amount of PA in the copolymer. However, the conductivity values attainable are not as high as in the previously prepared PB–PA copolymers[7].

We believe that a smaller amount of grafted PA, a shorter conjugation length and a reduced PA domain size readily account for our results.

In conclusion, the percolation model[11], namely conductive spheres (PA microdomains) embedded into a dielectric medium (PB areas), could be applied to this copolymer in order to explain the observed electrical properties as recently proposed for similar materials[3].

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