New catalyst systems for the polymerization of acetylene

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The catalytic activities of WCl_6–Ph_4Sn, $MoCl_5$–Ph_4Sn and tetrabenzyltitanium were examined in the polymerization of acetylene. The structure, morphology and electrical conductivity of the doped and non doped polyacetylene were also studied.

Keywords Polymerization; catalyst; acetylene; doping; structure; morphology; electrical conduction

INTRODUCTION

Unlike vinyl polymers, acetylenic polymers are characterized by their colour, semiconductivity, paramagnetism, and geometric isomerism. Acetylenic monomers, however, do not form high polymers by conventional radical, cationic, or anionic polymerization[1]. Only a few transition metal catalysts are known to polymerize acetylenes to give high polymers: for example, $Ti(OC_4H_9)_4$–$4(C_2H_5)_3Al$ for acetylene[2]: Fe(III) acetylacetonate–3(iso–$C_4H_9)_3Al$ for alkylacetylenes[3], and WCl_6 and $MoCl_5$ for phenylacetylene and other substituted acetylenes[4–14]. However, it was reported recently that acetylene was polymerized in the presence of halides and oxohalides of molybdenum and tungsten[15,16]. In the present work, we examined the polymerization of acetylene by WCl_6–Ph_4Sn, $MoCl_5$-Ph_4Sn (which are effective catalysts for the polymerization of phenylacetylene) and the tetrabenzyl derivative of titanium (which is able to polymerize α-olefins[17]). The structure, morphology and electrical conductivity of the doped and non doped polyacetylene were also studied.

EXPERIMENTAL

Materials

Acetylene and toluene were purified as reported previously[18]. WCl_6, $MoCl_5$ and tetraphenyltin (Ph_4Sn) were commercially available (purity > 99%) and were used without further purification. Tetrabenzyltitanium was prepared by the usual method[17].

Polymerization

The preparation of the catalyst solutions and polymerization were carried out under high vacuum. The catalyst solutions were prepared as follows. The WCl_6–Ph_4Sn and $MoCl_5Ph_4Sn$ were obtained by mixing equimolar amounts of respectively WCl_6 and $MoCl_5$ and Ph_4Sn in toluene, and these were also aged at 30°C for 15 min before use. These catalysts were all soluble. The polymerizations were performed as described previously[18].

Measurements

The i.r. spectra of polymers were obtained using a spectrometer, Perkin–Elmer 577. Scanning electron microscopy was performed on a Jeol JSM 35.

The electron spin resonance spectra of polymers were observed as described in a previous paper[19].

RESULTS AND DISCUSSION

Polymerization of acetylene

Figure 1 shows the time–conversion curves for the polymerization of acetylene catalysed by WCl_6-Ph_4Sn, $MoCl_5$-Ph_4Sn, $Ti(CH_2$-$C_6H_5)_4$ and $Ti(OnBu)_4$–$AlEt_3(Al/Ti=4)$[18] in toluene. It is seen from *Figure 1*

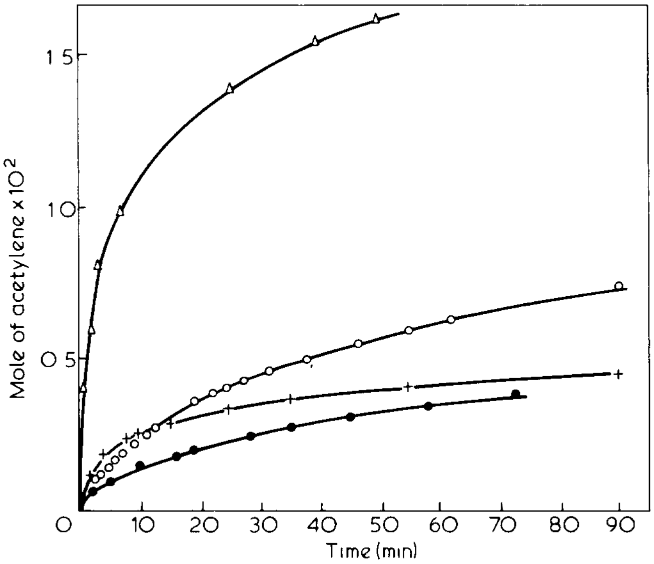

Figure 1 Time—conversion curves for the polymerization of acetylene initiated by new catalysts (1) $Ti(OBu)_4$—$Al(Et)_3$, △, Al/Ti = 4; (2) WCl_6—Ph_4Sn, ○, Sn/W = 1; (3) $MoCl_5$—Ph_4Sn, +, Sn/Mo = 1; (4) $Ti(BZ)_4$, ●. $[M_T]$ = 2 mole l^{-1}. Ageing time of catalyst (1) 60 min @ 20°C; (2) and (3) 15 min @ 30°C. $V_{toluene}$ = 10 ml $P_{acetylene}$ = 69 cm Hg; $T°$ = 20°C

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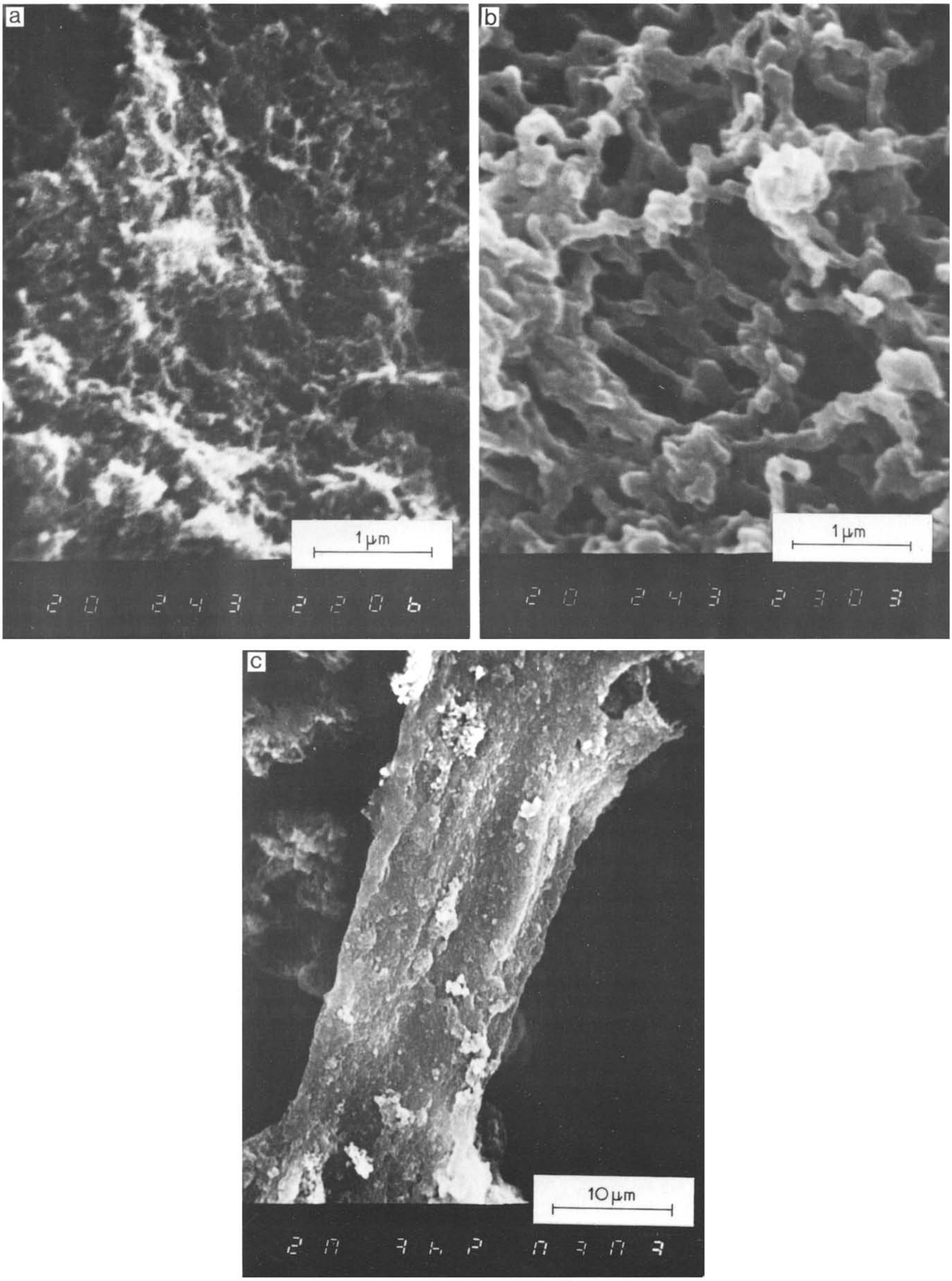

Figure 2 Scanning electron micrograph of $(CH)_x$ synthesized: a, with $MoCl_5$—Ph_4Sn; b, with $Ti(CH_2$—$C_6H_5)_4$; c, with WCl_6—Ph_4Sn

Table 1 Structure of polyacetylene*

Catalyst	Structure *cis* %	 *trans* %
WCl$_6$–Ph$_4$Sn	10	90
MoCl$_5$–Ph$_4$Sn	10	90
Ti(CH$_2$–C$_6$H$_5$)$_4$	40	60
AlEt$_3$–Ti(OnBu)$_4$ (4–1)	60	40

* The conditions of the polymerization are given in *Figure 1*

that the reactivities lie in the following order: Ti(OnBu)$_4$-AlEt$_3$ $\gg$ WCl$_6$-Ph$_4$Sn > MoCl$_5$Ph$_4$Sn > Ti(CH$_2$-C$_6$H$_5$)$_4$. However, during the course of the polymerization, we have observed the formation of uniform films of polyacetylene on the quiescent surface of concentrated solutions of the soluble catalysts except for MoCl$_5$-Ph$_4$Sn for which we obtained a powder. On the basis of these results, further investigation is necessary in order to establish a mechanism of polymerization.

Structure of polyacetylene

The values of elemental analysis for the polymer formed agreed well with the theoretical values (e.g. H/C = 1.00 1.09).

The polymers were examined by i.r. and e.s.r. The results are shown in *Table 1*.

Scanning electron micrograph

Examination of the polyacetylene films and powder by electron microscopy showed that the morphology varies with the catalyst.

Figure 2 represents electron micrographs of specimens observed by scanning electron microscopy. They indicate that any surface shows a characteristic fibrillar morphology. The width of the fibril ranges from ~300 Å for polymer prepared with MoCl$_5$-Ph$_4$Sn to 2000 Å with Ti(CH$_2$-C$_6$H$_5$)$_4$ and to 120000 Å with WCl$_6$-Ph$_4$Sn.

Electrical conductivity of doped polyacetylene

The film obtained in the presence of Ti(CH$_2$-C$_6$H$_5$)$_4$ was doped with controlled amounts of electron-attracting species such as iodine, SbF$_5$ and CF$_3$SO$_3$H. Four platinum wires were attached to the films by means of gold paste and were connected to an apparatus for measuring theif d.c. conductivity by the four-probe method. The films were then treated with the vapour of the dopant at room temperature *in vacuo* for 10 h. Final compositions of the doped (CH)$_x$ were determined either by the elemental analysis of a piece of reference film or by the increase in weight of the reference film during doping. The results are given in *Table 2*.

Table 2 Conductivity of polyacetylene

Material	Conductivity $\sigma(\Omega^{-1}\ \mathrm{cm}^{-1})$ (20°C)
$[\mathrm{CH\,I_{0.24}}]_x$	20
$[\mathrm{CH(SbF_5)_{0.7}}]_x$	10
$[\mathrm{CH(CF_3SO_3H)_{0.18}}]_x$	10

Elsewhere WCl$_6$ and MoCl$_5$ appear as *p* type dopants which provide conductivity values comparable to those obtained with iodine or other well known dopants. A detailed study of (CH)$_x$ films, as doped, is under progress[19].

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