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Preliminary Communication

Nickelocene-catalyzed polymerization of acetylenes

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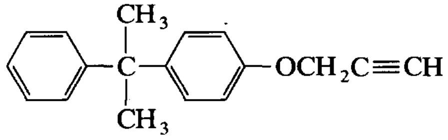
Abstract

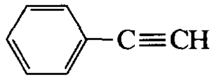
At 115°C in the absence of solvent, nickelocene catalyses the polymerization of phenylacetylene to give a mixture of cyclotrimers and linear alkene oligomers with 92% conversion after 6 h. In the case of 1-(1-methyl-1-phenylethyl)-4-(2-propynyloxy)benzene under similar conditions, nickelocene catalyses both cyclotrimerization and cyclotetramerization.

During a study into the effect of catalysts on the cure of acetylene-terminated monomers we found that nickelocene is an active catalyst for the polymerization of acetylenes [1]. To our knowledge, nickelocene alone has not previously been used as a catalyst in these reactions although when used with $F_3CC{\equiv}CCF_3$ it has been reported to give trace amounts of the cyclotrimer after 10 h at 358 K [2]. At 50°C in benzene for 25 h, 0.1–0.3 mol% $(\eta\text{-Cp})_2Ni \cdot 2AlBr_3$ catalyzes the conversion of acetylenes into a mixture of cyclotrimers and linear polymer [3]. However, under the same conditions no reaction was observed in the absence of $AlBr_3$ [3]. Although nickelocene has been claimed to be an active catalyst in the polymerization of acetylenes, an aromatic heterocyclic amine (*e.g.* pyridine) is a necessary component in this process [4].

We describe here the results of a study into the polymerization of monomers **I** and **II** catalysed by nickelocene in the absence of solvent. These two monomers were chosen as providing monofunctional models for the catalyzed cure of ethynylaryl and arylpropargyl ether terminated resins, respectively.



(I)



(II)

When heated above 110°C in the presence of nickelocene (0.08 mol% ethynyl group), **I** polymerized explosively. The process could be controlled by performing the reaction at 100°C for 3 h and then raising the temperature to 130°C for a further 7 h, after which monomer consumption had ceased. Initially, as the monomer melted the catalyst rapidly dissolved, forming a clear green solution which slowly turned dark brown. At the end of the reaction, HPLC showed the presence of three components, which were separated by column chromatography: (1) unchanged **I** (27%); (2) a colourless viscous oil (22%) identified by ^1H and ^{13}C NMR as being a mixture of the 1,2,4- and 1,3,5-cyclotrimers; and (3) a light yellow resinous material (49%) with a number average molecular weight (determined by VPO) of 1050, corresponding to a degree of polymerization of 4.

The ^1H NMR spectrum for this last fraction showed resonances in the δ 4.1–4.7 ppm CH_2 region and in the δ 5.8–6.1 ppm alkene region, indicating that the product had a nonaromatic polyalkene structure. The presence of a well-resolved HPLC peak suggested a single oligomer, this being either the linear tetramer with a terminal alkyne group shown in Scheme 1 or the corresponding cyclooctatetraene structure without any alkyne group. The absence of any alkyne carbon resonances in the ^{13}C NMR spectrum and of any $\nu(C{\equiv}C)$ stretch in the IR spectrum supported the latter structure. Additionally, in the ^{13}C NMR spectrum the only two CH_2 resonances observed were at δ 69.6 and 70.5 ppm. In particular, there was no CH_2 resonance in the δ 50–60 ppm region for the CH_2 carbon bearing both an alkyne substituent and an aryloxy group in the case of the linear structure shown in Scheme 1. The third

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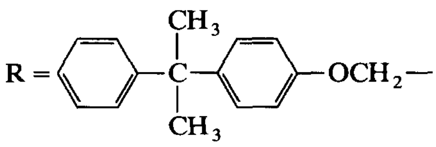
$RC{\equiv}C\!\left(CX{=}CY\right)_3H$

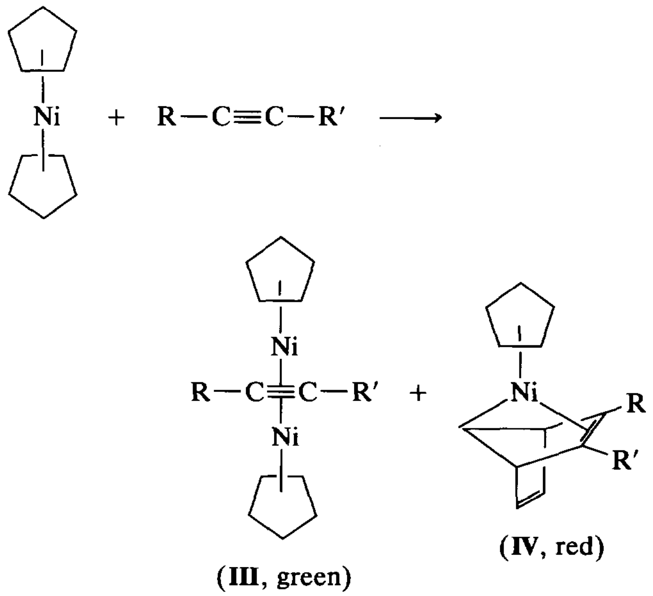


and X = R, Y = H
or X = H, Y = R

Scheme 1.

fraction was thus a mixture of the various cyclooctatetraene isomers (1,2,4,6-, 1,2,5,6-, 1,3,5,7-, and 1,2,4,7-). Hence nickelocene catalyzes both cyclotetramerization and cyclotrimerization of **I** with the former predominating.

The polymerization of **II** was carried out at 115°C under dinitrogen in the presence of nickelocene (0.081 mol% ethynyl group). After 6 h, consumption of monomer had ceased, with 92% conversion of monomer into polymer. Precipitation from dichloromethane/methanol gave rise to a methanol-insoluble orange polymer (39%) and a methanol-soluble fraction. The value of M_n for the methanol-insoluble polymer was 1600 (as determined by VPO), corresponding to a degree of polymerization of 15.7. The absence of a ν(C≡C) band in the IR spectrum and the presence of a broad resonance in the δ 6–8 ppm region in the ^{1}H NMR spectrum [5] suggested that the material was *trans-cisoidal* poly(phenylacetylene). Furthermore, the IR spectrum showed bands at 912, 970 and 1265 cm^{-1} characteristic of *trans* poly(phenylacetylene) [5], and there was also an absorbance at 885 cm^{-1} which is specific to *cis* poly(phenylacetylene) [5]. However, the other bands characteristic of *cis* poly(phenylacetylene) at 1380 and 740 cm^{-1} [5] were absent. The methanol-insoluble polymer was therefore *trans-cisoidal* poly(phenylacetylene). Microanalysis showed it to be analytically pure.



(III, green)

(IV, red)

Scheme 2.

The methanol-soluble material was separated into three fractions by column chromatography: (1) unchanged **II** (8%); (2) a white crystalline solid (24%), confirmed by ^{1}H NMR, IR and microanalysis as being a mixture of 1,2,4- and 1,3,5-triphenylbenzene; and (3) a yellow solid (21%). The value of M_n for the yellow solid was found by VPO to be 460, corresponding to a degree of polymerization of 4.5. The IR spectrum showed a ν(C≡C) stretch at 2250 cm^{-1} (but no ν(≡C–H) absorbance), as well as bands characteristic of both *cis* (885 and 740 cm^{-1}) and *trans* poly(phenylacetylene) (1625, 970 and 912 cm^{-1}) [5]. The ^{1}H NMR spectrum exhibited resonances in the δ 6.5–6.9 alkene region as well as aromatic proton signals, the integration ratio being 1 : 5. The yellow solid was therefore a mixture of low molecular weight linear oligomers of phenylacetylene.

Acetylenes react with nickelocene to form two types of air-stable compounds; green binuclear acetylene bridged **III** and red mononuclear **IV** (Scheme 2) [6]. Formation of the latter is favoured by the presence of electron-withdrawing substituents in the acetylene compound [6]. The complexes are prepared by reaction in THF for 20–30 h at room temperature [6], or in the case of the ethyne complex **III**, in THF at 12 atm and 80°C for 15 h [7]. The ethyne complex **III** as well as nickelocene itself have been claimed to be active catalysts in the solution polymerization of acetylenes at 70°C, both at atmospheric pressure and under high pressure [4]. The presence of an aromatic heterocyclic amine (*e.g.* pyridine), which forms the reactive complex with the nickel catalyst and can also act as solvent, is a necessary component in the process [4].

In conclusion, our results show that bulk polymerization of acetylenes takes place even in the absence of an aromatic amine. Under these conditions, monomer **I** gives *ca.* 50% cyclotetramerization, and **II** affords linear polyenes. Both monomers also give *ca.* 20% cyclotrimerization. We are currently investigating the reaction mechanism. The green colour observed initially may arise from formation of a **III**-type complex.

Acknowledgement

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