Cyclotrimerization *versus* non-aromatic polyene formation in catalysed cure of an arylpropargyl-ether-terminated monomer

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The arylpropargyl-ether-terminated monomer (1,4-HC≡$CCH_2OC_6H_4)_2CMe_2$ was polymerized to just before the gel point in the presence of various catalysts. Changes in the ^1H n.m.r. spectra show that (a) (η-Cp)$Co(CO)_2$ gives rise exclusively to acetylene cyclotrimerization, (b) (η-Cp)$_2$Ni and $(PPh_3)_2NiCl_2$ each result in both cyclotrimerization and non-aromatic polyene formation, and (c) $(PPh_3)_3RhCl$ gives branched eneyne dimers.

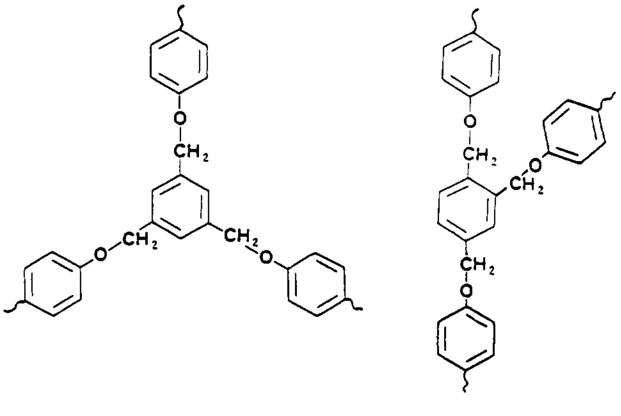
(Keywords: acetylene-terminated; arylpropargyl ether; catalysis; cyclotrimerization; polymerization; nickelocene)

High performance resins formed from acetylene-terminated monomers (ATMs) are currently being developed to replace, for example, epoxies when used under hot, wet conditions[1-3]. ATMs fall into two main categories, those terminated by arylacetylene and those by arylpropargyl-ether groups. In the case of the latter, we recently discovered that uncatalysed cure takes place via sigmatropic thermal rearrangement of the arylpropargyl-ether groups to 2*H*-1-benzopyran rings which then undergo polymerization[4]. We have previously found using differential scanning calorimetry (d.s.c.) that the catalysed cure of the arylpropargyl-ether-terminated monomer occurs at lower temperatures[5] thus suggesting that different crosslinking processes, via reactions such as cyclotrimerization or non-aromatic polyene formation, may be taking place depending on the nature of the catalyst. We report here that this is indeed so and that each of these two reactions can take place as evidenced by changes in the nuclear magnetic resonance (n.m.r.) spectra.

The arylpropargyl-ether-terminated monomer (1,4-HC≡$CCH_2OC_6H_4)_2CMe_2$ (**I**) was synthesized as previously described[4]. Polymerization of **I** was carried out to just before the gel point in the presence of (η-Cp)$Co(CO)_2$, (η-Cp)$_2$Ni, $(PPh_3)_2NiCl_2$, or $(PPh_3)_3RhCl$.

The ^1H n.m.r. spectrum of the (η-Cp)$Co(CO)_2$-catalysed resin (0.42 mol% ethynyl group at 140°C for 2 h under N_2; *Figure 1*) showed new resonances in the aromatic region and also around δ 5 ppm in the region for CH_2 groups bearing both a phenyl and a phenoxy substituent. This is consistent with the occurrence of cyclotrimerization of three HC≡$CCH_2OC_6H_4$– groups to form trisubstituted benzene moieties with the structures shown in *Scheme 1*. The catalyst (η-Cp)$Co(CO)_2$ is well known to give clean cyclotrimerization reactions with acetylenes[6].

The ^1H n.m.r. spectra of the $(PPh_3)_2NiCl_2$ (0.081 mol% ethynyl group at 130°C for 2 h under N_2) and (η-Cp)$_2$Ni catalysed (0.081 mol% ethynyl group at 100°C for 1 h under N_2) samples resemble each other, showing (a) new resonances of the type described above characteristic of cyclotrimerization, (b) several new OCH_2 resonances in the region δ 4.2–4.6 ppm, and (c) alkene resonances in the range δ 5.7–6.2 ppm. Thus, with these two catalysts, both cyclotrimerization and non-aromatic polyene (linear or cyclic) formation occurs. It has been previously found that $(PPh_3)_2NiCl_2$ gives rise to both cyclotrimerization and linear polyene oligomers, the proportion depending on the alkyne and reaction conditions[7]. To our knowledge, nickelocene alone has not previously been used as a catalyst in these reactions although with $F_3CC{\equiv}CCF_3$ it has been reported to give trace amounts of the cyclotrimer after 10 h at 358 K[8]. (η-Cp)$_2$Ni·$2AlBr_3$ catalyses the conversion of acetylenes into a mixture of cyclotrimers and linear polymers[9], but no reaction was observed in the absence of $AlBr_3$. Although nickelocene has been claimed to be an active catalyst in the polymerization of acetylenes, an aromatic heterocyclic amine (e.g. pyridine) was stated to be a necessary component in this process[10].



1,3,5-Trisubstituted 1,2,4-Trisubstituted

Scheme 1

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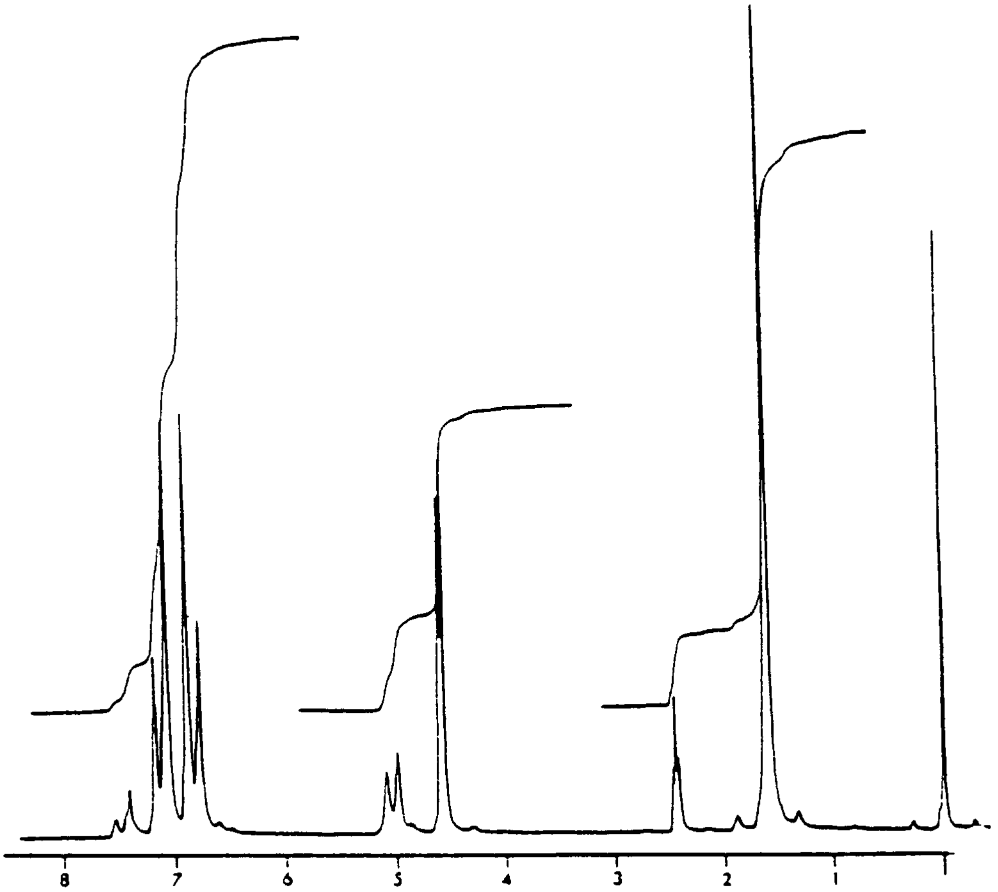
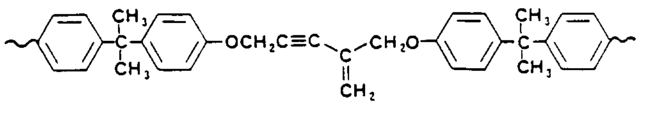


Figure 1 ^{1}H n.m.r. spectrum (80 MHz) of I polymerized in the presence of (η-Cp)Co(CO)$_2$ (0.42 mol% ethynyl group) at 140°C for 2 h under N_2



Scheme 2

In contrast, the ^{1}H n.m.r. spectrum of the $(PPh_3)_3RhCl$-catalysed sample (0.081 mol% ethynyl group at 85°C for 3 h under N_2) shows no new resonances around δ 5 ppm and thus no cyclotrimerization has occurred. New OCH_2 resonances at δ 4.4 and 4.7 ppm, and alkene proton resonances at δ 5.55 and 5.6 ppm, are observed. These are consistent with the branched eneyne structure shown in *Scheme 2*, its formation being more favourable than that of the corresponding linear eneyne[11]. Branched eneynes readily polymerize to give linear polyenes[11,12]. In the present case, only dimerization is observed in the pre-gel stage of the reaction, this step accounting for conversion of >60% of the $HC{\equiv}CCH_2OC_6H_4$– groups. The second peak observed in the dynamic d.s.c. thermogram[5] thus presumably arises from the subsequent polymerization step.

In conclusion, we have shown that the catalysed cure of arylpropargyl-ether-terminated monomers takes place by quite different routes than that occurring in the absence of catalyst. The resulting resins are of very different chemical structure. In particular, by judicious choice of catalyst, resins with either non-aromatic polyene or benzene-type crosslink sites (or both) may be obtained. It is to be expected that these fundamental differences in chemical structure will affect the physical properties of the cured resins.

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References

1 Lee, C. Y.-C. in 'Developments in Reinforced Plastics' (Ed. G. Pritchard), Vol. 5, Elsevier, Barking, 1986, pp. 121–150
2 Hergenrother, P. M. in 'Encyclopaedia of Polymer Science and Engineering', (Eds H. F. Mark *et al.*), Vol. 1, 2nd Edn, Wiley, New York, 1985, pp. 61–86
3 Sergeev, V. A., Chernomordik, Yu. A. and Kurapov, A. S. *Uspekhi Khimii* 1984, **53**, 518 (*Russ. Chem. Rev.* 1984, **53**, 307)
4 Douglas, W. E. and Overend, A. S. *Eur. Polym. J.* 1991, **27**, 1279
5 Douglas, W. and Overend, A. *J. Organomet. Chem.* 1986, **308**, C14
6 Vollhardt, K. P. C. *Angew. Chem., Int. Engl. Edn* 1984, **23**, 539
7 Furlani, A., Bicev, P., Russo, M. V. and Fiorentino, M. *Gazz. Chim. Ital.* 1977, **107**, 373
8 Davidson, J. L. and Sharp, D. W. A. *J. Chem. Soc. Dalton* 1976, 1123
9 Reikhsfel'd, V. O., Lein, B. I. and Makovetskii, K. L. *Doklady Akad. Nauk SSSR* 1970, **190**, 125 (*Proc. Acad. Sci. USSR* 1970, **190**, 31)
10 Dubeck, M. and Filbey, A. H. US Patent 3 256 260 (*Chem. Abstr.* 1966, **65**, 7307a)
11 Carlton, L. and Read, G. *J. Chem. Soc. Perkin I* 1978, 1631
12 Kern, R. J. *J. Polym. Sci. A-1* 1969, **7**, 621