Preliminary communication

CATALYSIS OF CROSSLINKING OF AN ACETYLENE-TERMINATED MONOMER; HIGH ACTIVITY OF NICKELOCENE

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Summary

The crosslinking of the acetylene-terminated monomer $(1,4\text{-}HC{\equiv}CCH_2\text{-}OC_6H_4)_2CMe_2$ is catalyzed by $(\eta\text{-}Cp)_2Co$, $(\eta\text{-}Cp)Co(CO)_2$, $(Ph_3P)_2MCl_2$ (M = Ni, Pd), $(Ph_3P)_3RhCl$ and $(\eta\text{-}Cp)_2Ni$ (the last being highly active). Differential scanning calorimetry shows that the exotherm peak temperature is reduced.

Although crosslinked resins formed from acetylene-terminated monomers and prepolymers are of much current interest for use as heat stable matrices and adhesives in aerospatial applications [1—3], little has been published on catalysis of the cure reactions. We report here that several transition metal complexes, in particular nickelocene, are active catalysts which possibly alter the chemical structure of the cured product.

Acetylene-terminated monomers and polymers are usually cured thermally and the free radical reaction results in a network whose crosslink sites are linear conjugated polyenes formed from 6—8 ethynyl groups [4]. Cyclotrimerization of acetylene end-groups has also been observed to occur to a minor extent [5]. Curing in air inhibits the free radical reaction and results in a resin of greatly improved properties [1], possibly because of the formation of a product of different molecular structure.

It has been found that $(Ph_3P)_2NiCl_2$ lowers the cure temperature sufficiently ($<177°C$) for the resins to be used as adhesives for Al alloys [6, 7]. The physical properties indicated that the structures of the materials were altered by the catalyst. Soviet workers have used various Co, Ni and Ziegler catalysts in the preparation of crosslinkable polyphenylenes from diacetylenes [8, 9]; they found that the substitution pattern of the benzene residues formed by polycyclotrimerization depended to a great extent on the metal and ligands.

By using transition metal catalysts we hope to be able to encourage the cyclo-trimerization pathway. Many acetylene-terminated monomers contain transition metal residues and/or some oligomers as a result of the method of synthesis, but we have used a low-melting monomer, $(1,4\text{-}HC{\equiv}CCH_2OC_6H_4)_2CMe_2$ (I) for which this is not so. It was prepared as described [10] and recrystallized (m.p. 84°C) from propan-2-ol. The catalysts studied (II—VII) (Fig. 1), are all stable in air for at least short periods. They were brought into contact with I by grinding or by mixing in solution. Samples were heated under N_2 in glass tubes and it was found that in all cases the catalyst markedly lowered the curing temperature and gel time. In the case of nickelocene at a concentration of 0.15 mol% ethynyl
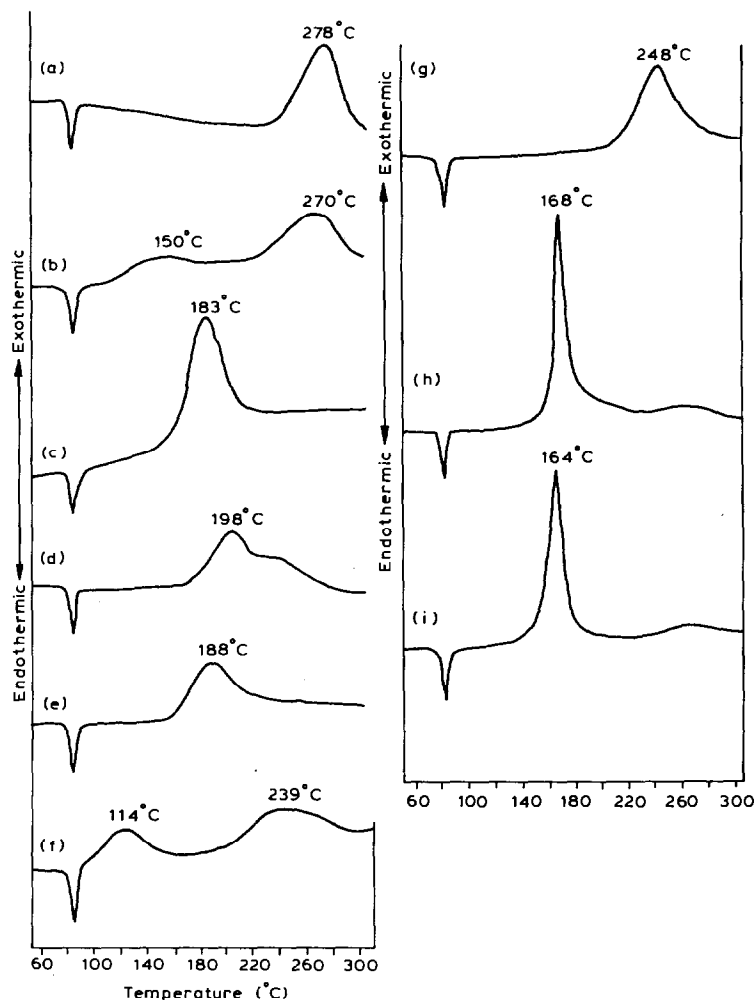

Fig. 1. DSC for catalyzed and uncatalyzed cure reactions (Heating rate 16°C min^{-1}; In and Sn calibrants). (a) uncatalyzed, $\Delta H - 155$; (b) (η-Cp)$_2$Co (II), c 0.076, $\Delta H - 180$; (c) (η-Cp)Co(CO)$_2$ (III), c 0.076, $\Delta H - 168$; (d) (Ph$_3$P)$_2$PdCl$_2$ (IV), c 0.076, $\Delta H - 181$; (e) (Ph$_3$P)$_2$NiCl$_2$ (V), c 0.076, $\Delta H - 158$; (f) (Ph$_3$P)$_3$-RhCl (VI), c 0.076, $\Delta H - 144$; (g) (η-Cp)$_2$Ni (VII), c 0.0076, $\Delta H - 153$; (h) (VII), c 0.076, $\Delta H - 179$; (i) (VII), c 3.8, $\Delta H - 179$. [c = concentration of catalyst in mol% ethynyl group; ΔH = enthalpy of polymerization in kJ per mole ethynyl group].

group the reaction occurred explosively almost as soon as the monomer had melted.

The results of differential scanning calorimetry (DSC) in sealed capsules (Fig. 1) show that all the catalysts greatly reduced the exotherm peak temperature and that for VII no further significant decrease occurred at concentrations greater than 0.076 mol% ethynyl group. In several cases two peaks occur. It is thought that the lower and higher temperature peaks result from catalyzed and uncatalyzed reactions respectively [7]. In most cases there is an increase in the enthalpy of polymerization (Fig. 1) over that for the uncatalyzed system, but this may not be significant. Cyclotrimerization would be expected to lead to a heat of polymerization of 188 ± 20 kJ per mole ethynyl group whereas reaction to give linear polyene structures would give 134 ± 20 kJ per mole ethynyl group [11]. The present results suggest that unlike the other catalysts, VI may lead to linear polyene structures. Whether cyclotrimerization or linear polyene formation occurs for a given catalyst depends to a large extent on the substituents on the ethynyl group [12]. However, the much studied cyclotrimerization catalyst III [13, 14] is known to lead to clean cyclotrimerization reactions [15]. The high activity of VII in catalyzing the crosslinking of acetylene-terminated monomers has not been reported previously, but various complexes formed by its reactions with acetylenes are known [16, 17]. Complex II reacts with $PhC{\equiv}CPh$ to give $(\eta\text{-Cp})(C_4Ph_4)Co$ [18], and $(\eta\text{-Cp})(C_5H_6)Co$ cyclotrimerizes $PhC{\equiv}CPh$ [12].

Work is proceeding on determination of the molecular structure of the crosslinked networks. Preliminary NMR studies indicate that cyclotrimerization may occur to a large extent.

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