# Polycyclohexene: Homopolymerisation of Cyclohexene Under Mild Conditions

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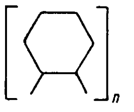
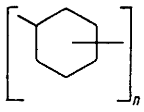
*Summary* The homogeneous catalyst system, $[Re(CO)_5Cl]$–$EtAlCl_2$ was found to promote the polymerization of cyclohexene to a molecular weight of *ca.* 2500; n.m.r. and i.r. spectroscopic evidence indicates that the polymer is completely saturated and the rings are retained.

We report the first example of homopolymerization of cyclohexene under relatively mild conditions; this was accomplished using the $[Re(CO)_5Cl]$–$EtAlCl_2$ system, which is also known to catalyse the metathesis of internal and terminal olefins.[1] The polymerization was carried out at 110 °C for 24 h in 20 ml of chlorobenzene, and the reaction solution contained 10 ml (0·098 mol) of cyclohexene, 1 mmol of $[Re(CO)_5Cl]$, and 2 mmol of $EtAlCl_2$. The final product, a white powder obtained in 53% yield, was purified by chromatography on silica gel and melted in the 95—100 °C range. Osmometric measurements revealed a number average molecular weight in the 900—1000 range, and gel permeation chromatography against low molecular weight polystyrene indicated the weight average molecular weight to be *ca.* 2500 (500—5000 range).

The 300 MHz $^1H$ n.m.r. spectrum shows a fairly broad envelope composed of three major bands in the 0·9—2 p.p.m. region [rel. to $(Me_3Si)_2O$ internal standard]. Notable is the absence of a signal in the olefinic region. The $^{13}C$ n.m.r. spectrum of polycyclohexene is very complex, and consists of around 30 signals in the 13·9—35·9 p.p.m. range, suggesting that the polymer is not stereo-regular.


(A)


(B)

The i.r. spectrum (KBr pellet) of polycyclohexene shows several structurally significant bands. Only aliphatic CH stretching bands are observed (2960—2800 cm$^{-1}$), and the band at 2650 cm$^{-1}$ indicates that the cyclic nature of the compound is intact.[2] The $CH_2$ scissoring vibration of cyclohexene is observed at 1440 cm$^{-1}$, also indicating that the 6-membered rings are retained in the polymer. Furthermore, absorptions at 890 and 850 cm$^{-1}$ provide further evidence for a polymerized ring system; these same bands have been observed in the spectra of polyvinylcyclohexane[3] and polycyclohexylacetylene,[4] as well as in the spectrum of cyclohexane itself. Finally, no bands in the 1600—1700 cm$^{-1}$ region, arising from C=C stretching modes, are observed.

As expected from the n.m.r. and i.r. studies, the polymer, dissolved in $CCl_4$, does not decolourize bromine. Therefore, the physical and chemical evidence at hand indicate the polymer to be made up of either repeating 1,2-cyclohexene units (**A**), or a combination of 1,2-, 1,3-, and/or 1,4-repeating units (**B**).

It should be noted that the polymerization of cyclohexene was reported in one other instance, and this was accomplished only under extremely harsh conditions (300 °C, 65000 atm).[5] Clearly, the procedures reported herein are much more convenient.

The catalyst system also promotes the polymerization of other cyclic olefins, and all appear to be totally saturated polymers.

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