

## Evidence for Alkylidenic Configuration of Polymethylene Chains on a Phillips Catalyst

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**Summary** I.r. measurements show that short polymethylene chains (about 20 CH<sub>2</sub> units) on a supported chromia catalyst are linked to surface Cr<sup>II</sup> ions *via* alkylidene groups, and suggest a novel mechanism of chain propagation.

ALTHOUGH no direct evidence has ever been advanced, it is generally accepted that the chain propagation mechanism in the Phillips process of ethylene polymerization is similar to that proposed several years ago by Cossee<sup>1</sup> for the Ziegler-Natta catalysts (insertion of  $\pi$ -bonded olefin into the alkyl chain). Recently Rooney, Green, and their co-workers<sup>2</sup> have proposed a different mechanism for the Ziegler-Natta process, comprising three basic steps: (a) elimination of  $\alpha$ -hydrogen in the alkyl chain leading to a hydrido-alkylidene compound; (b)  $\pi$ -bonding of olefin and interconversion of the complex into a hydrido-metal cyclobutane structure; (c) reversible elimination of hydrogen whereby the cyclo compound is transformed into the initial metal-alkyl linear complex.

We report here evidence that a similar mechanism is likely to be operative in the Phillips process. We have studied, by i.r. spectroscopy, a low-loading Phillips catalyst (0.5% Cr weight). Details of preparation and characterization of the samples have been given elsewhere.<sup>3</sup> We merely mention here that the catalyst is first treated in O<sub>2</sub> at 1023 K, then reduced by CO at 623 K. This procedure leads to a large concentration of Cr<sup>II</sup> at the surface.

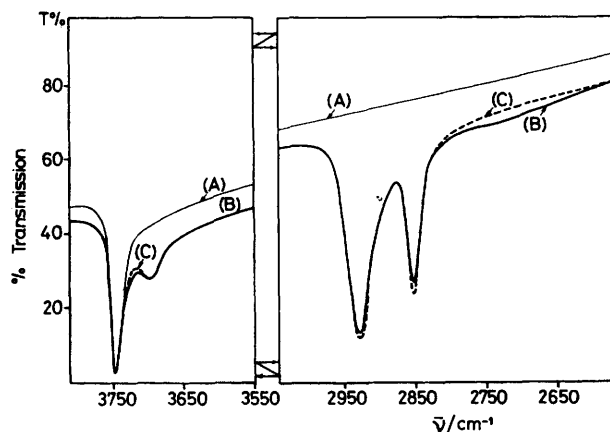


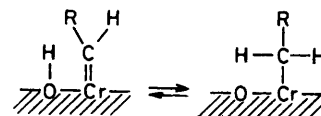
FIGURE. I.r. spectra of the Phillips catalyst showing the OH and CH stretching regions; (A) background; (B) after polymerization (C) with 10 kN m<sup>-2</sup> of CO.

From the amount of CO inhibiting the polymerization, we have evidence that some 10% of Cr ions are involved at the catalytic sites, in agreement with the literature.<sup>4,5</sup> The Figure shows the OH and CH stretching regions of the i.r. spectra [curve (A), untreated sample]. The 3750 cm<sup>-1</sup> band is due to free surface hydroxy-groups of silica. Surface polymerization of ethylene in the gas

phase was carried out at a pressure of  $800 \text{ N m}^{-2}$  only, for a short contact time (2 min) at 300 K; curve (B) shows the spectrum obtained after evacuation of ethylene. The new band at about  $3700 \text{ cm}^{-1}$  is due to silica hydroxy groups which are weakly interacting with the polymer chains. The bands at  $2855$  and  $2926 \text{ cm}^{-1}$  are the in phase and out of phase stretching modes of polymeric methylene groups. At this stage of polymerization, the polymer chains are 'living' ones, *i.e.* no chain termination has yet occurred.<sup>5,6</sup> In fact, mild heating at 453 K *in vacuo* causes the complete reversal of the polymerization process, *i.e.*, a gradual disappearance of the  $2855$  and  $2926 \text{ cm}^{-1}$  bands. On the basis of the values of extinction coefficients,<sup>7</sup> the measured absorbances of the two bands, and the estimated number of sites, we infer that the average length of the chains is only about 20  $\text{CH}_2$  units. The weak, broad band centred at  $2750 \text{ cm}^{-1}$  should be noted, as this feature has previously been overlooked.<sup>8</sup> Such an exceptionally low CH stretch is puzzling. We have evidence that this band is related to the  $\alpha$ -carbon atom, as it is irreversibly destroyed by oxygen to yield aldehydes.

Further information is obtained by interaction of CO at  $10 \text{ kN m}^{-2}$  pressure [curve (C)], which also causes the disappearance of the absorption at *ca.*  $2750 \text{ cm}^{-1}$ , together with an increase in the methylene stretching absorptions and the disappearance of an absorption at *ca.*  $3720 \text{ cm}^{-1}$ . The increase in the intensity of the  $\text{CH}_2$  modes roughly corresponds to one  $\text{CH}_2$  unit per chain. The effect of CO is completely reversible. This indicates that, upon CO adsorption, the species responsible for the  $2750 \text{ cm}^{-1}$

band are destroyed, together with some OH groups, to yield  $\text{CH}_2$  groups. We are thus led to suppose that the species causing the  $2750 \text{ cm}^{-1}$  absorption possess one H atom less than  $\text{CH}_2$ , *i.e.*, that they have an alkylidene structure. The few examples in the literature<sup>9</sup> on the CH stretching modes of alkylidene homogeneous complexes fully support our assignment.



SCHEME

Thus an equilibrium (Scheme) seems to exist for the polymeric chain (displaced to the right by carbon monoxide). The two basic features of the recently proposed mechanism,<sup>2</sup> namely the removal of an  $\alpha$ -hydrogen and the formation of an alkylidene compound are easily seen (Scheme). A noteworthy difference is that the  $\alpha$ -hydrogen does not form a hydride group but seems to be transferred to an adjacent surface oxygen. This point is however still under investigation, together with the overall mechanism of polymerization, the inhibiting effect of CO, and the detailed structure of the active centres.<sup>10</sup>

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