Application of Infrared Spectroscopy and Chemometrics to the analysis of structural composition of ethylene/butadiene copolymers.

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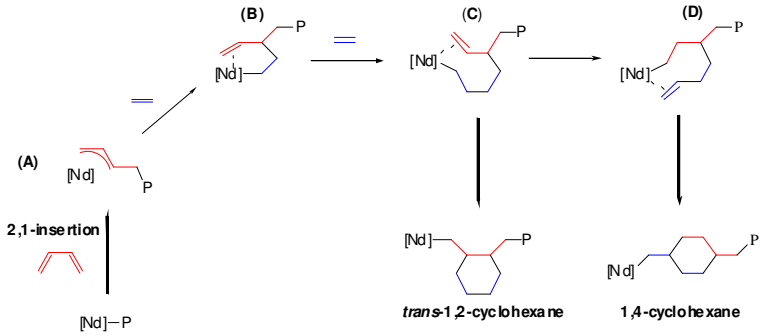
The introduction of unsaturations into the backbone of polyolefins is of interest for many applications, including the production of vulcanizable elastomers for the tyre industry. The copolymerization of conjugated dienes (butadiene, isoprene) with olefins, which are readily available monomers is a major challenge. Since the discovery of Ziegler-Natta catalysts, research efforts have focused on the copolymerization of these two classes of monomers. However as the two classes of monomers polymerize according to different mechanisms, only a very limited number of catalysts are liable to copolymerize them successfully. While the insertion of butadiene is often limited with most catalyst systems designed for olefin polymerization, we showed that neodymium metallocene catalysts insert butadiene with good efficiency.[1]

Interestingly a new class of polymers was obtained by copolymerization of ethylene with butadiene using catalyst systems based on the silylene-bridged bis(fluorenyl) complex {($Me_2Si(C_{13}H_8)_2$)Nd(□-BH_4)[(□-BH_4)Li(THF)]}$_2$. Actually, new elastomers containing *trans*-1,4 units, 1,2-units and unprecedented cyclohexane rings have been prepared.[2] These rings are formed by cyclocopolymerization of ethylene with butadiene (Scheme 1).



Scheme 1. Mechanism of intramolecular cyclisation

In the present paper, we report the preparation of a range of ethylene/butadiene rubber (EBR) with various microstructures (butadiene content, % of 1,4-*trans*, vinyl and ring units). These materials have been obtained by changing the structure of the precatalyst and the polymerization conditions.
The complex chemical composition of these new materials were determined by ^1H and ^{13}C NMR. However NMR analyses are tedious and time consuming . We have developped an efficient and rapid method for the determination of the EBR microstruture based on Infrared spectroscopy investigations. Indeed Fourier transform infrared spectroscopy with attenuated total reflectance (FTIR/ATR) requires no special sample preparation. Using a range of ethylene/butadiene of various chemical compositions, we perform a calibration by chemometric methods correlating the FTIR spectra with the microstructure of EBR determined by NMR.

This study has been used to generate calibration information allowing the quantification of the precise microstrucuture of unknown EBR samples by infrared spectroscopy.

References:

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