

SHORT COMMUNICATION

Reactivities and ^{13}C NMR Spectra of Alkyl Vinyl Ethers

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It is well known that the reactivity of alkyl vinyl ethers in cationic polymerization is greater as the alkyl group is more electron-repelling.¹⁻⁴ Although some attention has been paid to the reaction mechanism of alkyl vinyl ethers,^{3,5} a definite conclusion could not be reached. Recently Higashimura *et al.*^{6,7} studied the ^{13}C NMR spectra of β -substituted vinyl ethers and three alkyl vinyl ethers concerning the effect of the β -methyl group on the π -electron distribution in the olefinic double bond. They proposed a new model, in which a carbonium ion forms a complex with the ether oxygen and two olefinic carbon atoms, for the transition state in the polymerization reaction.

In our preceding paper⁴ the ^1H NMR spectra of vinyl ethers and of vinyl ether-trialkylaluminum complexes were investigated and correlations were found between the spectral characteristics and the relative reactivity of vinyl ether. In this paper we investigated ^{13}C NMR spectra of various alkyl vinyl ethers ($\text{C}_\beta\text{H}_2 = \text{C}_\alpha\text{HOR}$) and observed the close correlations between the chemical shift of C_α or C_β and the relative reactivity of vinyl ether in the copolymerization.

Methyl vinyl ether was obtained commercially. Other vinyl ethers were prepared from methyl vinyl ether and alcohols by ether exchange reactions catalyzed by mercuric acetate in the presence of molecular sieves.⁸ The vinyl ethers were purified by refluxing over lithium aluminum hydride and subsequent distillation under nitrogen atmosphere.

The ^{13}C NMR spectrum was taken at 22.5°C on a JEOL C-60 HL spectrometer with a 15.09 MHz RF unit for ^{13}C work using the neat liquid in an 8 mm ϕ sealed sample tube. The signal to noise ratio of the spectrum was enhanced by the

$^{13}\text{C}\{-^1\text{H}\}$ noise decoupling⁹ or by the accumulation of the spectra over 16 scans using a JEOL JRA-1 accumulator. Chemical shift measurements were made by the nuclear resonance single side band technique¹⁰ and their accuracies were within ± 0.2 ppm. Carbon disulfide was used as an external standard.

In Figures 1 and 2 the α - and β -carbon resonances are plotted against the relative reactivities of vinyl ethers. The reactivities are represented by $1/r_1$ which was determined in the copolymerization of the vinyl ether referred to M_2 with *n*-butyl vinyl ether (M_1) at -78°C in toluene with an EtAlCl_2 catalyst. As the reactivity increased, the α -carbon resonance shifted towards a higher field and the β -carbon resonance towards a lower field. It has been generally considered that the ^{13}C chemical shifts of the vinyl group are controlled mainly by the π -electron density in such a way that an upfield shift takes place when the π -electron density on the carbon atom increases.^{11,12} Therefore, the present results indicate

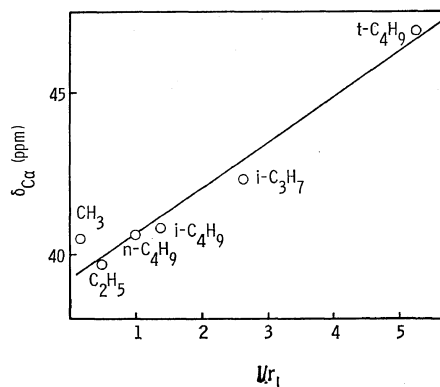


Figure 1. Plot of δ_{C_α} vs. $1/r_1$ for alkyl vinyl ether.

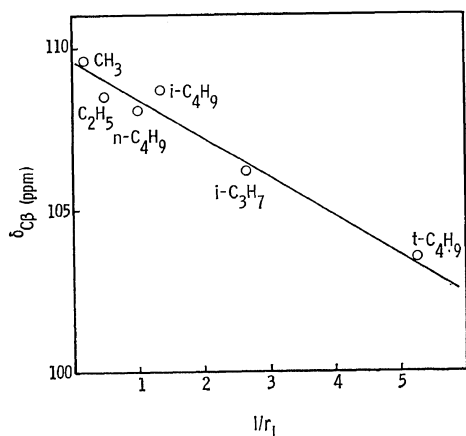
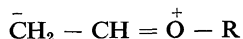


Figure 2. Plot of $\delta_{C\beta}$ vs. $1/r_1$ for alkyl vinyl ether.

that the higher the π -electron density on the α -carbon and the lower the density on the β -carbon, the higher the relative reactivity of the vinyl ether.

From the inspection of ^1H NMR spectrum of alkyl vinyl ether it has been suggested that the contribution of the following resonance form in the ether decreases in increasing order of its reactivity^{4,5} and the resonance stabilization may play an important role in determining the reactivity.⁴



The fact that the π -electron density on the β -carbon decreases as the relative reactivity of the ether increases, may be additional evidence for the above suggestion.

The above relationship between the β -carbon resonance and the reactivity clearly indicates that the attachment of the carbonium ion to the β -carbon cannot be the rate-determining step in

the cationic polymerization of alkyl vinyl ether. On the other hand, the relative reactivity of vinyl ether is parallel to the π -electron density on the α -carbon (Figure 1). From this result it is supposed that the π -electron density of α -carbon plays an important role in the rate-determining process of the cationic polymerization of alkyl vinyl ether.

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