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The Carbon-13 NMR Spectra and *e*-Values of Vinyl Compounds

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The $Q-e$ scheme has been proposed by Alfrey and Price[1] for systematizing large amounts of copolymerization data. In this scheme the Q value is associated with the resonance stabilization, and e is correlated with the polarity of the double bond or of free redical. Although these values have been determined for a wide variety of monomers and they agree fairly well with general chemical knowledge concerning the effect of substituents on resonance stabilization and on polarity,[2,3] direct evidence for their significance have not yet been obtained. In this paper we have correlated the e values of various monomers with the ^{13}C chemical shifts of their vinyl groups and have obtained additional support for the interpretation of the e values as a measure of polarity.

The ^{13}C chemical shifts of the vinyl group have been reported for several vinyl compounds (H_2C_β=$C_\alpha H$–X).[4–9] By plotting the ^{13}C chemical shifts of the β-carbon of the vinyl monomers, $\delta_{C\beta}$, against their e values, a fairly good straight line was ob-

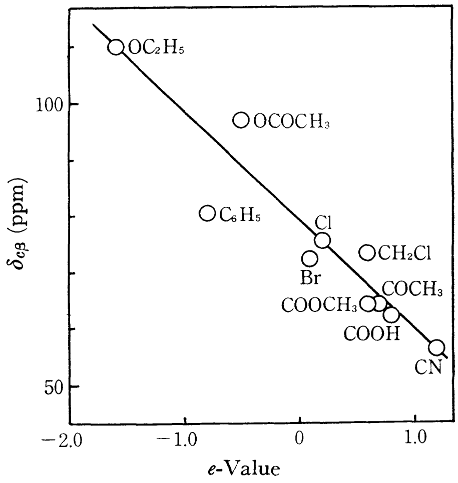

Fig. 1. $\delta_{c\beta}$ *vs.* e value.
δ is referred to CS_2, the high field shift being shown as the positive value.

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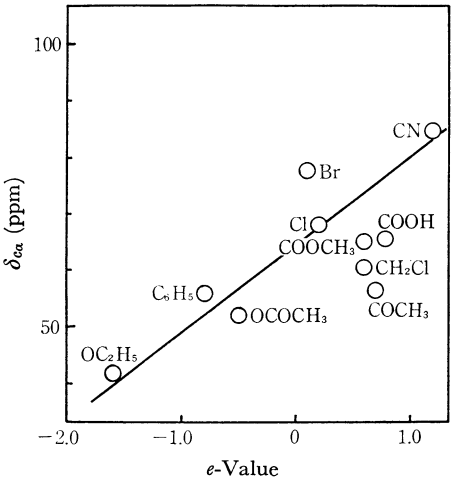

Fig. 2. $\delta_{C\alpha}$ *vs. e* value.

tained, as is shown in Fig. 1. The $\delta_{C\beta}$ value shifts to a lower field when the *e* value of the monomer becomes larger. A linear relationship was also obtained between the ^{13}C chemical shifts of α-carbon, $\delta_{C\alpha}$, and the *e* value, although the slope of the straight line was the reverse of that in Fig. 1 (Fig. 2). The ^{13}C chemical shift of the vinyl group has been reported to be mainly controlled by the π-electron density,[5,7,10] although it may also depend, to some extent, on some other factor such as the bond order or the average excitation energy. Therefore, it will show an upfield shift when the π-electron density on the carbon atom increases. Therefore, the results in Figs. 1 and 2 show that as the *e* value of the monomer increases, the π-electron density of the β-carbon decreases, and that of the α-carbon increases.

The vinyl compound with a positive *e* value generally has an electron-withdrawing substituent, and the π-electron in the double bond is drawn toward the substituent, so that the β-carbon is more electropositive. The reverse is the case with the monomer having a negative *e* value, and the β-carbon of the monomer of this type is more electronegative. The *e* value has been proposed as the measure of this polarity in the double bond. Therefore, the results mentioned above may be considered to be a convincing proof for the validity of the *e* value as a measure of the polarity.

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