Communications to the Editor

Determination of Vinyl Monomers Reactivity by Carbon-13 Nuclear Magnetic Resonance Spectroscopy

In radical copolymerization of two or more vinyl monomers, the resulting composition (controlling the properties of the final product) depends on the reactivity ratios (r_1,r_2), mainly determined by the electrostatic factor e as defined in the Alfrey-Price Q–e scheme.[1] Consequently, any direct and easy method for the determination of r_1, r_2 and e represents a most useful tool for the prediction of these composition and properties of the copolymers obtained.

After several attempts using UV[2] and IR[3] spectroscopy, a few papers have been published establishing correlations between reactivity parameters (r_1, r_2, and e) and ^{1}H as well as ^{13}C NMR spectroscopic data.[4–9]

Reconsidering these results, we have found that interestingly, a plot of the β-carbon chemical shifts ($\delta(C_\beta)$) vs. the corresponding e values (Figure 1) puts clearly in evidence a

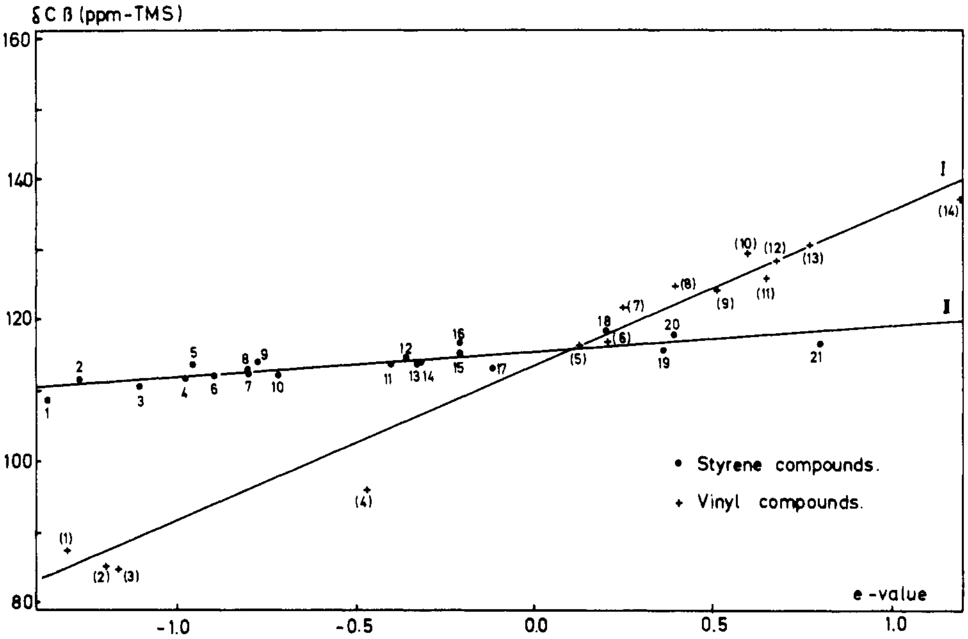

Figure 1. $\delta(C_\beta)$, ±0.1 ppm vs. Me_4Si, vs. Alfrey-Price e values. (I) Vinyl compounds: (1) $CH_2{=}CHOCH(CH_3)_2$; (2) $CH_2{=}CHO\text{-}n\text{-}Bu$; (3) $CH_2{=}CHOCH_2CH_3$; (4) $CH_2{=}CHOCOCH_3$; (5) $CH_2{=}CHCH_2Cl$; (6) $CH_2{=}CHCl$; (7) $CH_2{=}CHBr$; (8) $CH_2{=}C(CH_3)COOCH_3$; (9) $CH_2{=}CHCOO\text{-}n\text{-}Bu$; (10) $CH_2{=}CHCOOCH_3$; (11) $CH_2{=}C(CH_3)COOH$; (12) $CH_2{=}CHCOCH_3$; (13) $CH_2{=}CHCOOH$; (14) $CH_2{=}CHCN$. (II) Styrene compounds: 1, p-$N(CH_3)_2$; 2, α-CH_3; 3, p-OCH_3; 4, p-CH_3; 5, 2,5$(CH_3)_2$; 6, p-$C(CH_3)_3$; 7, stryene; 8, p-$Si(CH_3)_3$; 9, o-CH_3; 10, m-CH_3; 11, p-I; 12, m-Cl; 13, p-Cl; 14, p-Br; 15, m-Br; 16, p-CN; 17, p-vinylpyridine; 18, p-F; 19, o-Cl; 20, p-NO_2; 21, m-NO_2.

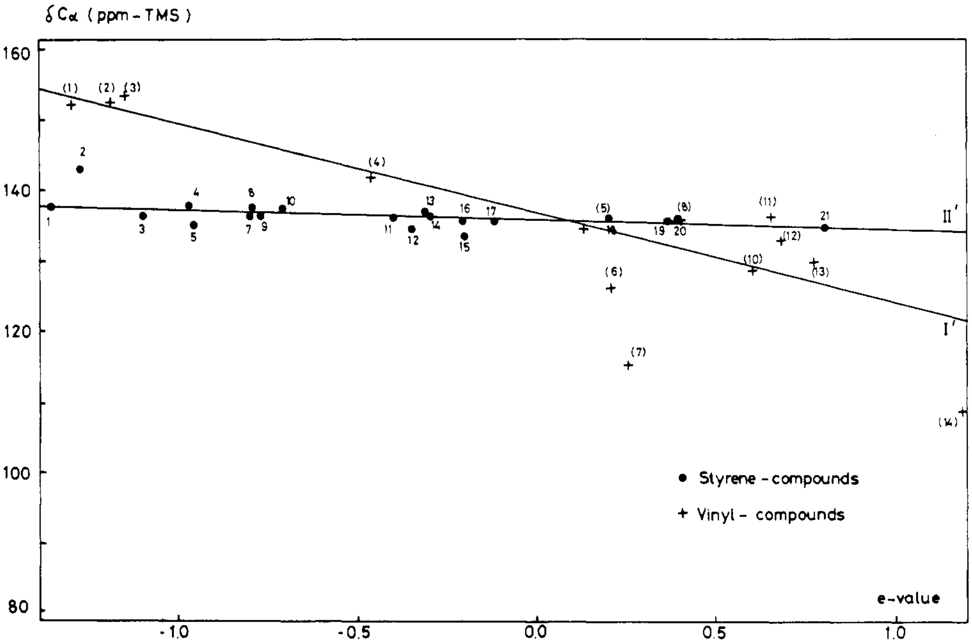

Figure 2. $\delta(C_\alpha)$, ± 0.1 ppm vs. Me_4Si, vs. Alfrey-Price e values. For I and II see the caption for Figure 1.

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linear and characteristic relationship for *each* family of compounds, although Hatada[8] reported only one general linear correlation between these parameters for a whole set of vinyl compounds including styrenes. In spite of the well known[13] poor sensitivity of the $\delta(C_\alpha)$ toward the influence of substituents, the plot of $\delta(C_\alpha)$ vs. e (Figure 2) also indicates a similar trend.

The e values are linearly correlated with Hammett's constants σ;[10] moreover, it is reported that the relationship between ^{13}C chemical shifts and σ values is also linear.[11] It is consequently expected that $\delta(C)$ and e values will be correlated by a linear relationship, as demonstrated by the empirical observations.

In our plot (Figure 1), line I correlates $\delta(C_\beta)$ and e values for aliphatic vinyl monomers (22 ppm per e-value unit, the same slope as in Hatada's relationship) and line II correlates $\delta(C_\beta)$ and e values for substituted styrenes (3.5 ppm per e value unit). In Figure 2, the slopes of lines I′ and II″ are respectively 12.5 and 1.25 ppm per e-value unit, confirming the lower sensitivity of $\delta(C_\alpha)$ toward the substituents effects. (In fact, the points corresponding to vinyl aliphatic compounds give a poorer linear fit.)

Apparently, the delocalization of inductive and mesomeric effects of the substituents, in the conjugated system formed by the aromatic ring, overshadows their influence on the vinyl group.

If the literature is unanimous[12] in stressing the interdependence of the Alfrey-Price's e parameter and the polarity of the vinyl bond (induced by the substituent), the weak slope of the $\delta(C_\alpha)$ or $\delta(C_\beta)$ vs. e relationship for substituted styrenes could even raise the question whether there is any correlation in this case. Further work to be published will confirm its existence.

In conclusion, the *linearity* of the different relationships obtained for these two families of vinyl monomers demonstrates the usefulness of ^{13}C NMR spectroscopy as a single and direct tool to estimate the relative reactivity of various vinyl compounds, by using the equations:

$$e(\text{vinyl X}) = \frac{\delta(C_\beta)(\text{ppm/Me}_4\text{Si}) - 113.5}{22}$$

$$e(\text{styrene X}) = \frac{\delta(C_\beta)(\text{ppm/Me}_4\text{Si}) - 115.5}{3.5}$$

where slopes (22 and 3.5) and intercepts (113.5 and 115.5) have been determined by a least-squares technique. Obviously, the method is more useful for aliphatic monomers, since the small slope of the styrene line precludes any precise graphical determination of e.

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References and Notes

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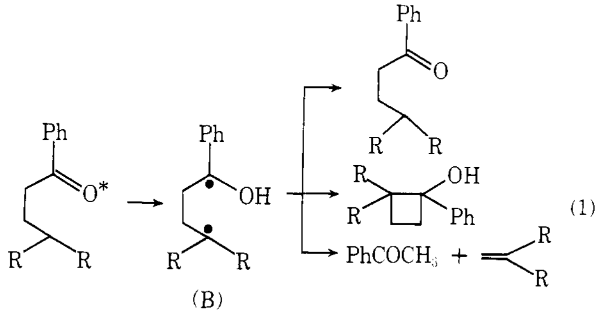
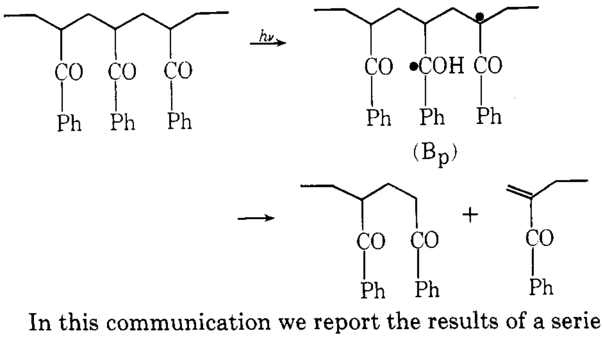
Importance of Intermolecular Biradical Reactions in Polymer Photochemistry. Poly(phenyl vinyl ketone)

The chemistry of the biradicals generated in the Norrish type II reaction has received considerable attention during the last few years.[1-8] Reaction 1 illustrates the mechanism in the case of phenyl alkyl ketones, where the reaction usually occurs solely from the triplet manifold.[9]

The first report on the trapping of B originated in Wagner's laboratory and recognized the possible relevance of the results in polymer chemistry.[1] Three years later, we were able to show that type II biradicals initiate the polymerization of methyl methacrylate quite efficiently.[6] More recently we have pointed out that intermolecular reactions of type II biradicals in polymers could be expected to be of importance.[5,10] While the intermediacy of biradicals in the photochemistry of polymers containing carbonyl groups is widely accepted,[7,11-15] the possibility of their undergoing intermolecular reactions has not been given serious consideration. Reaction 2 illustrates the mechanism of photodegradation of poly(phenyl vinyl ketone), PPVK. The quantum yields of reaction 2 are lower than one,[15] suggesting that a considerable fraction of biradicals (B_p) revert to the parent PPVK.



(1)



(2)

In this communication we report the results of a series of biradical trapping experiments. The details of the measurements, in particular those demonstrating that we are examining biradical processes, are similar to those reported in previous papers.[3,5,6,8] Each of the systems which we describe quite briefly here is interesting by itself and we are currently examining them in detail. However, our immediate aim is not in rigorously detailing the molecular interactions involved in each case, but rather, to demonstrate the necessity of re-

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