

## Electron Spin Resonance Study of Stereospecific Polymerization of Vinyl Esters in Fluoroalcohols

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We have recently reported that fluoroalcohols have a remarkable stereochemical effect on the radical polymerizations of vinyl esters<sup>1</sup> and methacrylates.<sup>2</sup> A high syndiotactic-specificity was observed in vinyl acetate (VAc) polymerization in (CF<sub>3</sub>)<sub>3</sub>COH (*rr* = 50%) and ethyl methacrylate (EMA) polymerization in (CF<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>)COH (*rr* = 87%), and a high heterotactic-specificity was achieved in vinyl pivalate (VPi) polymerization in (CF<sub>3</sub>)<sub>3</sub>COH (*mr* = 61%). These results are in contrast to the widely-believed fact that the stereochemistry of a free radical reaction is little affected by solvents. The stereochemical effects of the solvents were ascribed to the hydrogen-bonding interaction between the fluoroalcohols and the ester side groups of the monomer and propagating species, which makes the side groups apparently bulkier, thus causing a steric repulsion among them. In addition to the solvent effect, we also reported that the bulkiness of the vinyl ester monomers significantly alters the polymerization stereochemistry, where the structure of the monomers may affect the structure and reactivity of the growing species. Although the solvents and the monomer structure effects have been discussed in our series of publications, we have not yet obtained direct information on the structure of the propagating species in either case, which may give a more detailed picture of the stereochemical mechanisms.

Electron spin resonance (ESR) spectroscopy can provide useful information on both the structures and properties of paramagnetic species.<sup>3</sup> The dynamics and electron density of propagating radicals can be learned from ESR spectra using both the line width and hyperfine splitting constant (hfc). If a hydrogen bond is formed in a fluoroalcohol solvent, the hfc may be changed depending on the strength of the interaction between an ester side group and a fluoroalcohol. Many reports concerning the conformation of propagating radicals using the ESR technique have been published, especially for methacrylate radicals,<sup>4</sup> and it is known that temperature can

affect the hfc values or line width of the ESR spectra.<sup>4a),5</sup>

Hence, the ESR spectra of poly(vinyl ester) propagating radicals would provide information about their structures and shed light on the reaction mechanism. Therefore, in the present study, we investigated the effect of the fluoroalcohol and the bulkiness of the monomers on the conformation of the poly(vinyl ester) radicals. The ESR spectra of the propagating radicals of VAc were clearly observed in both solution polymerization in (CF<sub>3</sub>)<sub>3</sub>COH and bulk polymerization at various temperatures. The spectra were interpreted in conjugation with the stereostructure of the obtained polymers. ESR signals were also obtained for the propagating radicals of VPi and vinyl 2,2-bis(trifluoromethyl)propionate (VF6Pi).

Although the ESR studies of the propagating radical of VAc in bulk or using benzene as a solvent have been reported,<sup>6</sup> a system in a polar solvent has never been examined except for a system in water involving adduct radicals of vinyl esters with OH•.<sup>7</sup> The only study on the conformation of poly(vinyl ester) radicals in relation to a solvent or the bulkiness of a monomer has been done using isopropenyl acetate as the monomer.<sup>8</sup>

### EXPERIMENTAL

#### Materials

VAc and VPi were distilled before use. VF6Pi was synthesized and purified as previously reported.<sup>9</sup> (CF<sub>3</sub>)<sub>3</sub>COH (Aldrich; purity > 99%) and di-*tert*-butyl peroxide (*t*BPO) (Kishida; purity > 99%) were used as received. The other reagents were purified by the usual methods.

#### Measurements

The polymerization was carried out using *t*BPO in an ESR quartz cell under UV light irradiation with a 500 W ultrahigh-pressure mercury lamp (USHIO USH-500 D). The ESR spectra were recorded on a JEOL JES RE2X

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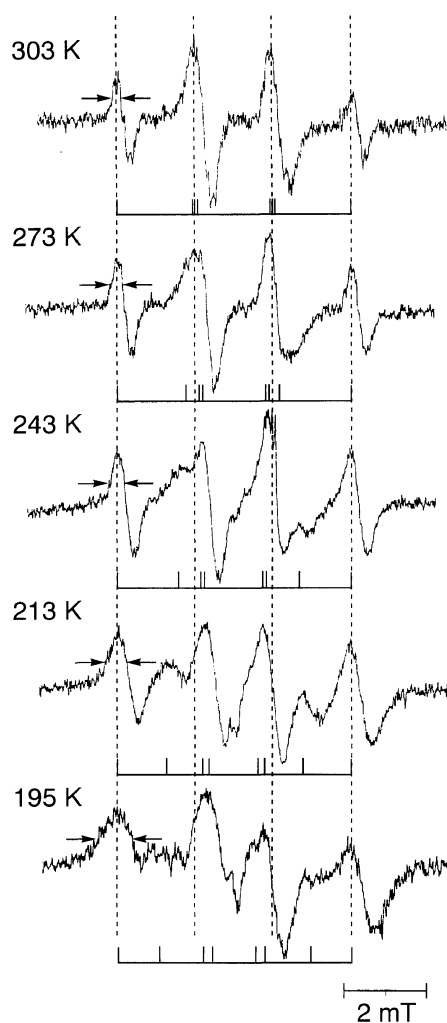
ESR spectrometer equipped with a TE<sub>011</sub> mode cavity (TE cavity) using a quartz cell with a diameter of 5 mm when benzene was used as the solvent, while a flat quartz cell (JES LC-11) with a width of 5 mm and thickness of 0.1 mm was employed for the measurements in (CF<sub>3</sub>)<sub>3</sub>COH. The operating conditions were as follows: modulation frequency, 100 kHz; sweep width,  $\pm 50$  G; modulation width, 2.0 G; time constant, 0.03 s; sweep time, 2–4 min.; microwave power 4 mW.

## RESULTS AND DISCUSSION

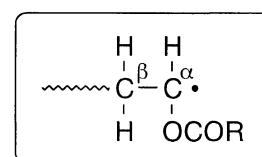
The radical polymerization of VAc in (CF<sub>3</sub>)<sub>3</sub>COH was investigated by ESR spectroscopy at various temperatures. As shown in Figure 1, clear ESR spectra were observed. Two kinds of important information were obtained from the spectra, *i. e.*, the hfc and line width of the peaks. The former is concerned with the electronic state and dynamics of the propagating radicals and the latter reflects the molecular motion and dynamics of the propagating radicals. The hfc and half-height width were determined as indicated for the top spectrum in Figure 1. Three hfc's were found for each spectrum. The three hfc's are most probably due to the coupling of the radical with

the  $\alpha$ -proton ( $H_\alpha$ ) and two  $\beta$ -protons ( $H_\beta$ ) although the detailed assignment of each hfc to the proton-radical coupling pair is not clear at this time (**Structure**). No clear assignment has also been reported for the ESR signals of a polystyrene radical.<sup>3e),10</sup> The proton and the radical may have a through-bond interaction. Hence, hfc may be affected by both the conformational relationship between the proton and the radical and by the electron density of the covalent bondings between the proton and the radical.<sup>3</sup>

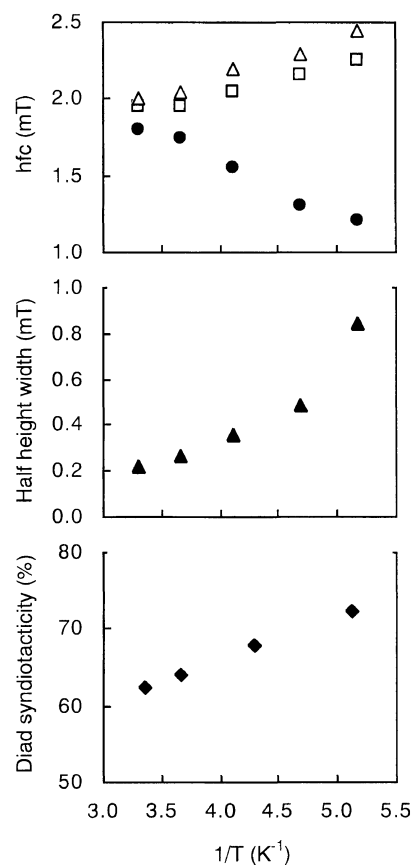
As shown in Figure 1, the spectral pattern changed with temperature. The temperature dependence of the hfc and half-line width is shown in Figure 2 along with that of the diad syndiotacticity of the polymers synthesized under the corresponding conditions in our previous study.<sup>1</sup> The three values of the hfc at 303 K were very close to each other (1.80, 1.95, and 2.00 mT). With a decrease in temperature, the hfc values changed gradually; one hfc value decreased from 1.8 to 1.2 mT and the other two values increased from 1.95 to 2.25 mT and from 2.00



**Figure 1.** ESR spectra of propagating radicals of VAc in (CF<sub>3</sub>)<sub>3</sub>COH at various temperatures. [VAc]<sub>0</sub> = 2.2 M, [tBPO]<sub>0</sub> = 0.5 M. Stick plots were based on the simulation for the ESR spectra.



**Structure**

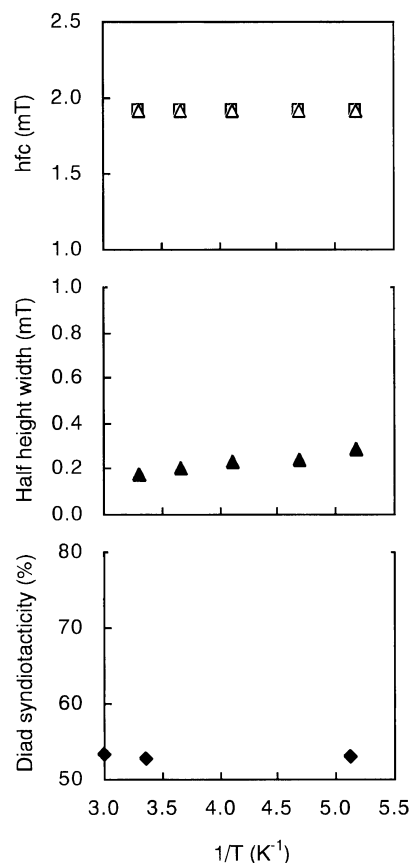


**Figure 2.** Temperature dependence of the hyperfine coupling constant (hfc) for poly(VAc) radical in (CF<sub>3</sub>)<sub>3</sub>COH, half-height width of a spectroscopic line at the lowest magnetic field, and diad syndiotacticity.

to 2.45 mT by lowering temperature from 303 K to 195 K. The absolute amount of the decrease (0.6 mT) for the first hfc was larger than those that increased for the other two hfc's (0.3 mT and 0.45 mT). The changes in the hfc values are considered to be due to some change in the conformation of the growing radical or the electron density of the covalent bondings around the propagating radical caused by the hydrogen bond between the ester side group of the radical and  $(\text{CF}_3)_3\text{COH}$ . This temperature effect seems to be consistent with the fact that the hydrogen-bonding interaction generally becomes stronger at lower temperatures. We might be able to tentatively assign the smallest hfc (1.2 mT at 195 K) to the coupling with the  $\text{H}_\alpha$  and the other two (2.25 and 2.45 mT at 195 K) to the coupling with the  $\text{H}_\beta$  because the electron density of the  $\text{C}_\alpha\text{-H}_\beta$  bonding should decrease to a larger extent compared with that of the  $\text{C}_\beta\text{-H}_\beta$  bonding due to the hydrogen bond formation. The decrease in electron density of covalent bonding is known to decrease the hfc.<sup>3</sup> The increase in the hfc's tentatively assigned to the  $\text{H}_\beta$ -radical coupling by lowering the temperature may be based on a conformational factor; reduced rotation around  $\text{C}_\alpha\text{-C}_\beta$  bond at low temperature may lead to a stable conformation that results in an increase in the  $\text{H}_\beta$ -radical coupling constant.<sup>3a),11</sup> In order to perform a more reliable assignment, the polymerization of a partially deuterated monomer is necessary. This aspect will be assessed in the future.

The line width of the spectra increased from 0.22 to 0.84 mT by lowering the temperature as shown in Figure 2. This indicates that the molecular motion of the propagating radical in the vicinity of the active center became slow at the lower temperatures. Because the increase in the line width was not very clear in the bulk polymerization as will be discussed later, this result implies that the hydrogen bond formation between  $(\text{CF}_3)_3\text{COH}$  and the ester groups of the growing species in the vicinity of the active center is responsible for the reduced molecular motion. In Figure 2, the change in the syndiotactic diad content of the obtained polymers seems to almost parallel the change in the hfc and line width. This suggests that  $(\text{CF}_3)_3\text{COH}$  may reduce the molecular motion of the growing radical to have a conformation suitable for syndiotactic monomer addition through the hydrogen-bond formation between the alcohol with the ester groups of the growing species in the vicinity of the active center and this effect of the alcohol becomes stronger as the temperature of the reaction decreases.

As control experiments, the radical bulk polymerization of VAc in the same temperature range was investigated by ESR spectroscopy. The ESR spectra of the propagating radicals were clearly observed as well as in the case of the solution system in  $(\text{CF}_3)_3\text{COH}$ . The temperature dependence of the hfc and line width values along with the results of diad syndiotacticity are shown in Figure 3. In the bulk polymerization systems of VAc, diad syndiotacticity (around 53%) was nearly independent of the temperature in the range from 333 to 195 K.<sup>1</sup> For the bulk systems, three distinctive hfc's were not identified. These values were close (*ca.* 1.9 mT) and did not show a clear change based on the temperature (from 303 K to 195 K). The line width slightly increased from 0.18 to 0.29 mT by lowering the temperature. This slight

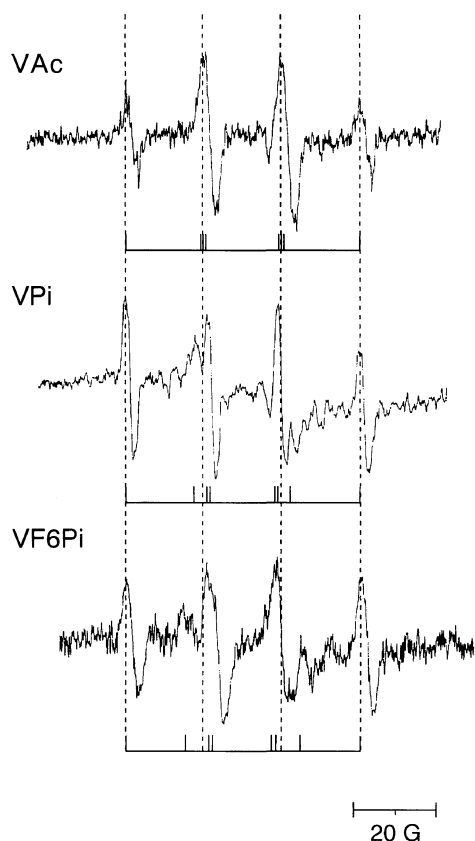


**Figure 3.** Temperature dependence of the hyperfine coupling constant (hfc) for poly(VAc) radical in bulk polymerizations, half-height width of a spectroscopic line at the lowest magnetic field, and diad syndiotacticity.

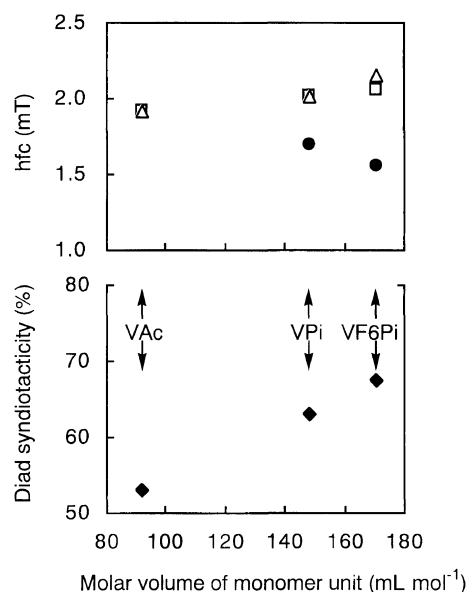
change may be simply based on a temperature effect. These observations are in contrast to the obvious and characteristic dependence of the hfc and line width on the temperature of the solution system in  $(\text{CF}_3)_3\text{COH}$ . This supports the above interpretation that  $(\text{CF}_3)_3\text{COH}$  affects the structure of the growing species and this is a reason for the stereoeffect of  $(\text{CF}_3)_3\text{COH}$  as well as the interaction between the monomer and  $(\text{CF}_3)_3\text{COH}$  which we found by the  $^1\text{H}$  NMR method in previous studies.<sup>1</sup>

We extended the ESR analysis to the polymerization systems of VPi and VF6Pi in a benzene solution at 273 K. The two bulky monomers are known to give polymers rich in *r* diad (for the bulk polymerization at 293 K:  $r = 62\%$  for VPi<sup>1b)</sup> and  $r = 66.6\%$  for VF6Pi<sup>9)</sup>). In these experiments, the bulky side groups in the vinyl esters in radical polymerizations may affect the ESR signals. The polymerization systems indicated well-defined ESR spectra (Figure 4). Three distinctive hfc's were found from the spectra. The hfc values were plotted *vs.* the molar volume (molecular weight/density) of each monomer unit in Figure 5. The set of the hfc values for the VAc, VPi, and VF6Pi systems are 1.90, 1.91, and 1.92 mT, 1.70, 2.02, and 2.02 mT, and 1.55, 2.05, and 2.25 mT, respectively. The hfc values appear to be influenced by the bulkiness of the monomer which can be quantified as molar volume.

The change in the hfc with the molar volumes of the monomers seems similar to the change in the hfc for the VAc system in  $(\text{CF}_3)_3\text{COH}$  with a decrease in tempera-



**Figure 4.** ESR spectra of propagating radicals of VAc, VPi, and VF6Pi in benzene at 273 K.  $[VAc]_0 = 2.2$  M,  $[VPi]_0 = 1.4$  M,  $[VF6Pi]_0 = 1.2$  M,  $[tBPO]_0 = 0.5$  M. Stick plots were based on the simulation for the ESR spectra.



**Figure 5.** Plot of the hyperfine coupling constant (hfc) at 273 K for propagating radicals of VAc, VPi, and VF6Pi and diad syndiotacticity against molar volume of the monomers.

ture. In addition, the change in  $r$  diad specificity with the molar volume of the monomers appeared to parallel the change in hfc.

On the basis of these results, we can conclude that the hydrogen bonding interaction between  $(CF_3)_3COH$  and the growing radical as well as that between  $(CF_3)_3COH$  and the monomer<sup>1</sup> leads to the altered stereochemistry of the monomer addition. Efforts are under way to obtain unequivocal assignment of the hfc values and to observe the ESR spectra of the propagating radicals from different classes of monomers such as the methacrylates in fluoroalcohols as solvents.

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