## SHORT COMMUNICATIONS

# ESR Observation of Propagating Radicals of Vinyl Acetate in Stationary State

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ESR spectroscopy has been known to be potentially the best method for a clear understanding of the nature of propagating radicals in the radical polymerization of vinyl compounds and for the determination of the rate constants, because it is possible in principle to measure directly the structure, the electronic state, and the concentration of the radical. Unfortunately, the concentration of the propagating radical was too low to be detected by commercial ESR spectrometers. Thus, ESR studies on the propagating radical were performed under special conditions such as the frozen state<sup>1-3</sup> and the crystalline state,<sup>4,5</sup> or by the use of such a special technique as the flow technique.<sup>6-10</sup> Since these conditions for the measurement are far from the usual conditions of radical polymerization, these cannot be used for the quantitative estimation of the kinetic rate constants for the radical polymerization.

Recently, we succeeded in the detection of ESR spectra of the propagating radicals of methacrylates in solution polymerization at room temperature by using a new cavity designed specifically for photoreaction.<sup>11,12</sup> Although Bresler *et al.*<sup>13,14</sup> detected the propagating radicals in a bulk polymerization

system of vinyl compounds by using a special ESR spectrometer, they have not yet reported the ESR spectra of the propagating radicals in solution polymerization. We have observed more highly resoluted ESR spectra than Bresler's of the propagating radical of vinyl acetate (VAc) in solution polymerization by using the new cavity. We will report here the ESR observation of the propagating radicals of VAc in bulk and solution at room temperature, and the results of estimation of propagation rate constants  $(k_p)$  in the polymerization.

The purification of VAc, solvents, and benzoyl peroxide (BPO) was described previously.<sup>15</sup> A solution of BPO (0.010 g) in 1 ml of a mixture of VAc and benzene (volume 1 : 1) was charged under nitrogen into a flat quartz cell ( $3.5 \text{ cm} \times 3.0 \text{ cm}$ , 1.0 mm thickness). In bulk polymerization the initiator (0.003 g) was dissolved in 1 ml of VAc. The polymerization was carried out at  $32.5^{\circ}$ C in a cavity of the ESR spectrometer by being irradiated through the slotted opening of the cavity with a 500 w high pressure mercury lamp (USHIO 500).

The extent of polymerization was determined by the precipitation method in which the formed polymer was precipitated with hexane, reprecipitated from benzene and hexane, freeze-dried from the benzene solution, and weighed. The extent of polymerization after 15 minutes was used for the estimation of polymerization rate  $(R_p)$  for VAc.

The ESR spectrum of VAc shown in Figure 1 has four lines (1:3:3:1) with an equal spacing of about 19G, indicating that the interaction of  $\beta$ -protons with the unpaired electron of the propagating radical is equivalent and that the hyperfine splitting constant of  $\beta$ -protons is equal to that of  $\alpha$ -proton. Since it has been found that the propagating radical of methyl methacrylate rotates around the  $C_{\alpha}$ - $C_{\beta}$  bond at room temperature,<sup>11</sup> the chain end of VAc is also considered to rotate freely around the  $C_{\alpha}$ - $C_{\beta}$  bond at room temperature.

The radical rise and decay was followed by the change of the peak height of a resonance line (3364 Gauss) of the ESR spectrum with reaction time. The result in bulk polymeri-



Figure 1. ESR spectrum of poly(VAc) radical in benzene solution at room temperature: [VAc]=5.4 mol dm<sup>-3</sup>; [BPO]=4.1 × 10<sup>-2</sup> mol dm<sup>-3</sup>.

zation is shown in Figure 2. The radical concentration became constant after 20 second irradiation, and kept stationary for several minutes until stopping the irradiation. The radical rapidly decayed after stopping the irradiation. The result is, as far as we know, the first example which visually proved the assumption of the steady-state in radical polymerization.

The free radical concentration was measured by the area under the integrated ESR spectrum of VAc by using the relation between the area and the radical concentration which was calibrated by the spectra of 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (Tempol) of known concentrations dissolved in VAc or mixtures of VAc and solvents. From the radical concentration, the value of  $k_p$  was determined by using the following equation for the steady state polymerization:

$$R_{\rm p} = k_{\rm p} [{\rm M} \cdot ][{\rm M}]$$

where  $[M \cdot]$  and [M] are the concentration of radical and monomer, respectively. Results are shown in Table I along with data by the rotating sector method.<sup>12</sup> The values of  $k_p$  for



Figure 2. Rise and decay curve of the propagating radical in radical polymerization of VAc: [VAc]=5.4 mol dm<sup>-3</sup>;  $[BPO]=4.1 \times 10^{-2}$  mol dm<sup>-3</sup>.

Table I.	Propagation	rate constants	for vinyl	acetate at	32.5°C
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[VAc]	[BPO] mM	Solvent	$R_{\rm p} \times 10^{-5}$	$[\mathbf{M} \cdot] \times 10^7$	$k_{p} \times 10^{-2}$	
M			$M s^{-1}$	М	$M^{-1}s^{-1}$	
5.4	41.3	Benzene	99.6	3.1	5.9	
5.4	12.1	Ethyl acetate	168	1.8	17	
10.9	12.3		480	3.2	14	

VAc estimated in the ESR method were about three times as large as the value obtained by the rotating sector method.<sup>12</sup> We cannot at this time unambiguously mention the reason of the difference in the  $k_p$  values.

The  $k_p$  values in bulk and in ethyl acetate solution are about four times as large as that in benzene, which is consistent in trend with the result obtained by rotating sector method.<sup>12</sup>

Additional works on the solvent effect on the nature of the propagating radical and on the determination of the rate constants are now under way.

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