

## ***Polymerization of N-Vinylcarbazole in the Presence of Magnetic Ferric Oxide Particles***

Polymerizations of vinyl monomers in the presence of magnetic metal oxide particles have been studied<sup>1-3</sup> for the purpose of the applications to recording media and absorption media of electromagnetic waves. Vinyl monomers do not polymerize directly by the metal oxide particles without pretreatment. An investigation was made of the polymerization of *N*-vinylcarbazole (*N*-VCZ) using magnetic metal oxide particles as an initiator.

Particles of Mn · Zn ferrite with an average size of 5000 and 10<sup>6</sup> Å, respectively, were used. These ferrites were obtained from Hitachi Metal Co., Ltd., and were dried at 60°C for 6 h *in vacuo* following Soxhlet extraction with methyl alcohol for 20 h before use. *N*-VCZ (mp 65°C) was obtained from Nakarai Chemicals Co., Ltd. and refined by recrystallization with *n*-hexane before use. The polymerization of *N*-VCZ in the presence of ferrite was carried out at a desired temperature under nitrogen atmosphere with stirring. The polymer–ferrite mixtures obtained were diluted with toluene and precipitated by excess methyl alcohol. The precipitated mixtures containing monomer were Soxhlet-extracted with methyl alcohol for 20 hrs, and became free from residual monomer. The conversion was calculated from the difference in the weight of the mixture after extraction and that of the ferrite initially added. Polymerization conditions for *N*-VCZ are shown in Table I. In the presence of ferrite, the polymerization proceeded, while, in its absence, no polymerization could be detected. At low temperature, the rate of polymerization, however, was relatively slow. The effect of ferrite on the polymerization process is shown clearly in Figure 1. The rate of polymerization initiated by the small size was larger than that by the large size ferrite (see Table I) and thus seems to depend on the surface area of the particles.

It should be noted that the ferrite particle–polymer mixture obtained by polymerization gave a stable colloidal dispersion in an appropriate solvent. But a large amount of homopolymer was found in the ferrite–polymer mixture. The mixture was then extracted with benzene so as to free it from the homopolymer. A small amount of small size ferrite along with the homopolymer was extracted through a filter (Toyo Filter Paper No. 89 from Toyo Roshi Co., Ltd.), but ferrite particles before polymerization did not pass through the filter. This suggests that ferrite particles are stable, capable of forming a colloidal dispersion in an appropriate solvent by reacting with *N*-VCZ. The surface of ferrite particles was observed with a scanning

TABLE I  
Polymerization of *N*-VCZ in the Presence of Magnetic Ferric Oxide

Sample	Ferric oxide	Polymerization conditions <sup>a</sup>				Conversion (%)
		Ferric oxide		<i>N</i> -VCZ (g)	Reaction temp. (°C)	
		(Å)	(g)			
Control	—	—	—	1.0	80	0
M <sub>1</sub>	Mn Zn ferrite	10 <sup>6</sup> <sup>b</sup>	0.5	1.0	80	21
M <sub>2</sub>	Mn Zn ferrite	10 <sup>6</sup> <sup>b</sup>	0.5	1.0	60	7
M <sub>3</sub>	Mn Zn ferrite	10 <sup>6</sup> <sup>b</sup>	0.5	1.0	40	1
M <sub>4</sub>	Mn Zn ferrite	10 <sup>6</sup> <sup>b</sup>	1.0	1.0	80	50
M <sub>5</sub>	Mn Zn ferrite	5 × 10 <sup>3</sup>	1.0	1.0	80	66
N <sub>1</sub>	γ-Fe <sub>2</sub> O <sub>3</sub> <sup>c</sup>	5 × 10 <sup>3</sup>	1.0	1.0	90	93

<sup>a</sup> Polymerizations were carried out in 6 mL of toluene for 6 h.

<sup>b</sup> Main particle size was ca. 10<sup>6</sup> Å, but many particles were smaller than 10<sup>5</sup> Å.

<sup>c</sup> Acicular ratio: 9/1.

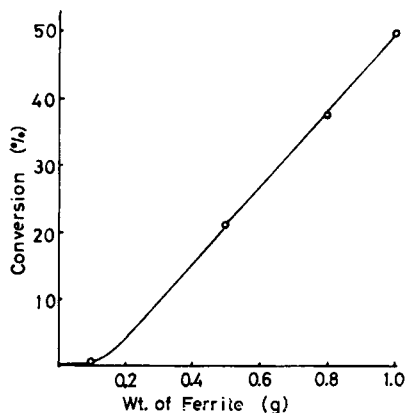
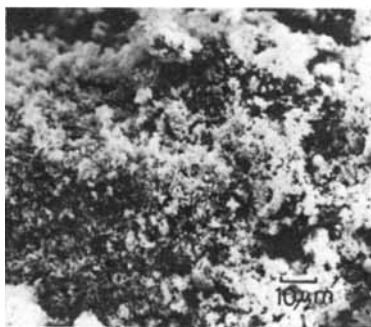


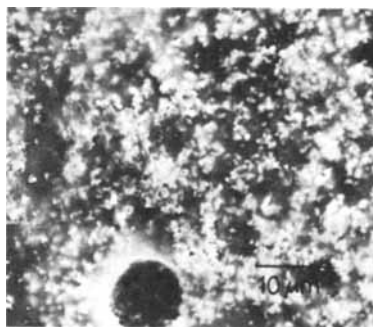
Fig. 1. Effect of ferrite on the polymerization of *N*-VCZ. Polymerizations were carried out in 6 mL of toluene at 80°C for 6 h. Weight of *N*-VCZ used was 1.0 g.

electron microscope (Nihon Denshi JXA 733) and the micrographs are shown in Figures 2(a)–(c). The surface of the ferrite particles was found to be covered with polymer after treatment with *N*-VCZ [Fig. 2(b)]. An observation was made of each particle remaining on the filler following treatment with benzene. The particle surface seemed even smoother than before [Fig. 2(c)]. Apparently, polymer is attached to ferrite even after extraction with benzene.

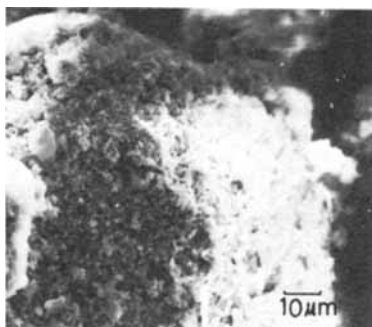
The polymerization of *N*-VCZ occurred rapidly on the surface of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (Hitachi Maxwell Co., Ltd.; length 5000 Å; an acicular ratio of 9/1). As shown in Table I, the conversion of N<sub>1</sub> was 93%. When the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>–polymer mixture was extracted with benzene using a filter (Toyo



(a)



(b)



(c)

Fig. 2. Micrographs of Mn·Zn ferrite surfaces: (a) without polymerization treatment; (b) after polymerization for 6 h at 80°C; polymerization conditions: *N*-VCZ, 1.0 g, ferrite, 1.0 g; (c) extracted with methyl alcohol for 24 h and then with benzene for 24 h.

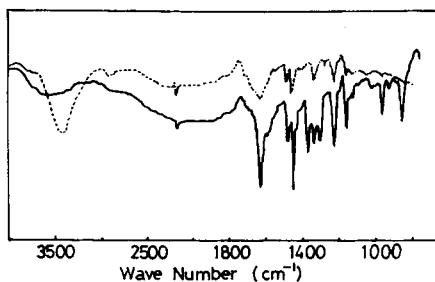


Fig. 3. A comparison of the IR spectra of *N*-VCZ with  $\gamma$ - $\text{Fe}_2\text{O}_3$  reacted with *N*-VCZ: (—) *N*-VCZ monomer; (---)  $\gamma$ - $\text{Fe}_2\text{O}_3$  reacted with *N*-VCZ and extracted with methyl alcohol and benzene.

Filter Paper No. 89) to which a small magnet had been attached, only the homopolymer passed through the filter. Consequently, polymer weight bound to  $\gamma$ - $\text{Fe}_2\text{O}_3$  was ca. 8%. The IR spectrum of the sample was measured with an infrared spectroscopy (Hitachi 200-10 type) compared with that of *N*-VCZ (monomer) as shown in Figure 3. Peaks corresponding to *N*-VCZ can be seen for  $\gamma$ - $\text{Fe}_2\text{O}_3$  treated with *N*-VCZ.

It is known that *N*-VCZ can be polymerized by free radical initiators and by inorganic and organic initiators.<sup>4</sup> Moreover, Ohkita et al.<sup>5</sup> found that *N*-VCZ polymerizes through a radical-cationic mechanism in the presence of carbon black. The mechanism of polymerization in the presence of ferric oxide is not clear, but may be similar to that of carbon black, since the polymerization is sensitive to both water and alcohol.

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