

## Mechanism of Charge-Transfer Polymerization: Formation of an Alternating Copolymer of *N*-Vinylcarbazole and Fumaronitrile

Yasuhiko SHIROTA, Akira MATSUMOTO,\* and Hiroshi MIKAWA

*Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadakami, Suita, Osaka 565, Japan.*

(Received February 3, 1972)

KEY WORDS Alternating Copolymer / *N*-Vinylcarbazole / Fumaronitrile / Charge-Transfer Complex /

Alternating copolymerization has currently been a subject of considerable interest both from synthetic and mechanistic viewpoints. Typically, systems such as styrene—maleic anhydride(MAn),<sup>1</sup> or *p*-dioxene—MAn<sup>2</sup> are known to undergo alternating radical copolymerization. Although the mechanism for alternation has long been the subject of controversy, recent extensive studies have made clear that the charge-transfer complex formed in many systems between the electron-donating and electron-accepting monomer pairs participates in the propagation step of the polymerization to regulate the alternation. The mechanism of self-propagation of the charge-transfer complex has been proposed by Iwatsuki and Yamashita.<sup>3</sup> Tsuchida and Tomono<sup>4</sup> have proposed participation of both the charge-transfer complex and the free monomer in certain systems such as styrene—MAn or 2-chloroethyl vinyl ether—MAn from the fact that in these systems the maximum point of the rate of copolymerization appears at a higher concentration of either monomer.

With regard to *N*-vinylcarbazole(VCZ) which has recently received much attention in the field of the polymerization initiated by an electron acceptor, no alternating copolymerization has been known to date, although several examples of radical copolymerization with other monomers have been reported.<sup>5</sup>

The authors wish to report the first example

of formation of an alternating copolymer containing VCZ as one component. When VCZ was copolymerized with fumaronitrile(FN) using azobisisobutyronitrile(AIBN) as a catalyst in benzene solution at 60°C, a copolymer formed preferentially together with a very small amount of VCZ homopolymer, these being separated by fractionation with benzene. In the absence of AIBN cationic polymerization of VCZ was initiated by FN.<sup>6</sup> The polymerization was conducted under dry nitrogen atmosphere after being degassed by several freeze-pump-thaw cycles.

The copolymer formed was entirely insoluble in benzene, easily soluble in tetrahydrofuran(THF), and partly soluble in acetone. It did not melt below 300°C. The molecular weight of the copolymer determined in dimethylformamide was about 10000. The IR spectrum of the copolymer is similar to that of VCZ homopolymer, but shows a weak C≡N absorption at 2250 cm<sup>-1</sup>. The facts that the characteristic peaks due to the vinyl group in VCZ and the *trans* out-of-plane =C—H deformation vibration at 965 cm<sup>-1</sup> in FN disappeared in the copolymer indicate that the polymerization proceeded at the olefinic double bonds of both monomers. Noticeably, the copolymer is characteristic in its absorption spectrum. The absorption maxima due to the carbazyl moiety observed at 344 and 330 nm in VCZ homopolymer shifted towards the violet region by about 10 nm, respectively, in the copolymer, appearing at 333 and 320 nm (in THF). The copolymer composition was found to be always constant from the UV absorption in THF

\* Present address: Sagoshi Factory, Unichika Co. Ltd., Sagoshi, Hyogo, Japan.

solution at 333 nm irrespective of widely varied monomer feed ratios and to be almost 1:1 (VCZ:FN) from both calculation using the molar extinction coefficient of VCZ homopolymer and from the nitrogen analysis (Table I, Figure 1). In calculation of the copolymer composition it was assumed that the molar extinction coefficient value of the carbazyl group does not change between VCZ homopolymer and the copolymer at their absorption maxima, 344 and 333 nm, respectively. Fumaronitrile itself does not polymerize alone under comparable reaction conditions. Thus the copolymer is assumed to be the alternating copolymer between VCZ and FN. When the initial copolymerization rate was plotted against monomer feed ratios, the maximum point was found at the molar ratio 7:3 (VCZ:FN) as shown in Figure 1.

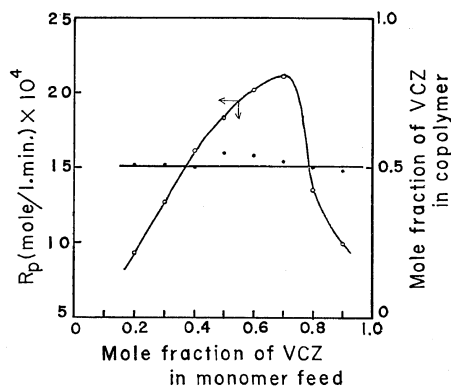
**Table I.** Compositions of VCZ-FN copolymers.

Mole fraction of VCZ in monomer feed	Concentration, mg/50 ml THF	Absorbance at 333 nm	Mole fraction of VCZ in copolymer
1.0 <sup>a</sup>	2.93	0.923 <sup>b</sup>	1.00
0.9	3.72	0.823	0.49
0.8	3.40	0.763	0.50 (0.57) <sup>c</sup>
0.7	3.10	0.710	0.52 (0.56) <sup>c</sup>
0.6	3.97	0.928	0.54 (0.53) <sup>c</sup>
0.5	3.27	0.775	0.55 (0.54) <sup>c</sup>
0.4	3.21	0.718	0.50 (0.55) <sup>c</sup>
0.3	3.97	0.905	0.51
0.2	4.05	0.920	0.51

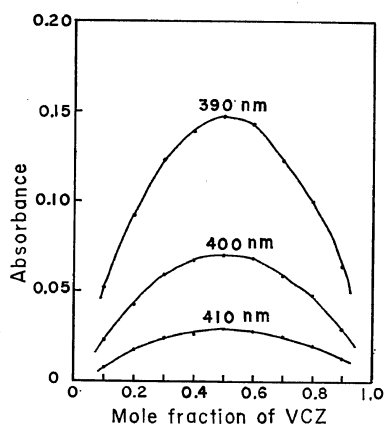
<sup>a</sup> VCZ homopolymer prepared with AIBN catalyst in benzene.

<sup>b</sup> Absorbance at 344 nm.

<sup>c</sup> Calculated from nitrogen analysis.



**Figure 1.** Initial copolymerization rates vs. monomer feed ratios, and copolymer compositions vs. monomer feed ratios:  $[VCZ] + [FN] = 0.8 \text{ mol/l}$ ;  $[AIBN] = 1 \times 10^{-3} \text{ mol/l}$ ; solvent, benzene; temp,  $60^\circ\text{C}$ ; polymerization time, 30 min.



**Figure 2.** Continuous variation method in the charge-transfer band of the system VCZ-FN:  $[VCZ] + [FN] = 0.1 \text{ mol/l}$ ; in benzene; at  $25^\circ\text{C}$ .

In the polymerization of VCZ initiated by an electron acceptor, the charge-transfer complex formed between VCZ and an electron acceptor generally participates in the initiation step of the polymerization. In the present polymerization it is suggested that the charge-transfer complex formed between VCZ and FN may participate in the propagation step of the polymerization. The formation of a 1:1 charge-transfer complex between VCZ and FN was confirmed by a continuous variation method in the charge-transfer absorption band as shown in Figure 2. Further studies are needed to clarify the mechanism and presently in progress.

## REFERENCES

- For example, F. R. Mayo, *Discuss. Faraday Soc.*, **2**, 304 (1947).
- S. Iwatsuki, Y. Tanaka, and Y. Yamashita, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **67**, 1467 (1964).
- S. Iwatsuki and Y. Yamashita, *ibid.*, **68**, 1138 (1965); S. Iwatsuki and Y. Yamashita, *J. Polym. Sci., Part A-1*, **5**, 1753 (1967).
- E. Tsuchida and T. Tomono, *Macromol. Chem.*, **141**, 265 (1971); E. Tsuchida, T. Tomono, and H. Sano, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **73**, 2031 (1970).
- R. Hart, *Macromol. Chem.*, **47**, 143 (1961).
- M. Nishimura, A. Matsumoto, Y. Shirota, S. Kusabayashi, and H. Mikawa, Reprint 19th Symposium on Macromolecular Chemistry, 21A05, 1970, p 117.