

### Synthesis of Polymers with Polar Side Groups. III. Tricyanovinylolation of Poly(*N*-vinylindole) and *N*-Vinylindole—Fumaronitrile Copolymer, and Dielectric Properties of these Polymers

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**ABSTRACT:** New polymers with polar side groups, such as the tricyanovinylated poly(*N*-vinylindole) and the tricyanovinylated *N*-vinylindole—fumaronitrile copolymer, were synthesized by the reaction of poly(*N*-vinylindole) or *N*-vinylindole—fumaronitrile copolymer with tetracyanoethylene. The degree of the tricyanovinylolation for poly(*N*-vinylindole) did not exceed *ca.* 45% under the various reaction conditions examined. The dielectric properties of these polymers, including poly(*N*-vinylindole) and the *N*-vinylindole—fumaronitrile copolymer, were examined.

**KEY WORDS** Polymer / Polar Side Groups / Tricyanovinylolation / Poly(*N*-vinylindole) / *N*-Vinylindole—Fumaronitrile Copolymer / Dielectric Properties /

The tricyanovinylolation of aromatic amines at either *N*-position or *para*-position,<sup>1</sup> or indole and *N*-methylindole at the 3-position<sup>2,3</sup> by a reaction with tetracyanoethylene has been well known. However, no application of this reaction to polymer molecules has been made to date. As one part of our continuing study of the synthesis and dielectric properties of the polymers with polar side groups,<sup>4,5</sup> the introduction of the polar tricyanovinyl group into the pendant indole moiety of poly(*N*-vinylindole) and *N*-vinylindole—fumaronitrile copolymer was attempted in the present study.

#### EXPERIMENTAL

##### *Materials*

Commercially available indole was purified by three recrystallizations from *n*-hexane. *N*-Vinylindole was prepared from indole,<sup>6</sup> dried over metallic sodium and then potassium, distilled twice *in vacuo* under a dry nitrogen stream, and redistilled immediately before use: bp, 70°C/0.3 mmHg. Fumaronitrile was commercially obtained and purified as described in a previous paper.<sup>7</sup> Commercially available tetracyanoethyl-

ene (TCNE) was purified by repeated sublimations *in vacuo*. Solvents were purified and dried as usual.

##### *Synthesis of Poly(*N*-vinylindole)*

*N*-Vinylindole was polymerized in a benzene solution by cationic (BF<sub>3</sub>OEt<sub>2</sub>) and radical (2,2'-azobisisobutyronitrile) catalysts. A benzene solution of *N*-vinylindole was introduced into a glass tube of 1.8-cm diameter, and a benzene solution of the catalyst was added under a dry nitrogen atmosphere. The reaction solution freshly prepared in this manner was evacuated at 10<sup>-2</sup> mmHg by several freeze-pump-thaw cycles and then sealed. The reaction system was allowed to stand in a thermostat maintained at 10±0.1°C or 80±0.1°C. The polymer was precipitated with a large excess of methanol, filtered, washed with methanol repeatedly, and dried *in vacuo* at room temperature. Poly(*N*-vinylindole) was obtained as a white powder with softening points between 195 and 215°C. Found: C, 84.11; H, 6.63; N, 10.54%. Calcd for C<sub>10</sub>H<sub>9</sub>N: C, 83.88; H, 6.34; N, 9.78%.

##### *Synthesis of the *N*-Vinylindole—Fumaronitrile Copolymer*

*N*-Vinylindole was copolymerized with fumaro-

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nitrile using 2,2'-azobisisobutyronitrile (AIBN) as an initiator in a benzene solution. The details of this copolymerization are described in a previous paper.<sup>7</sup> The *N*-vinylindole—fumaritrile copolymers with different compositions were obtained as white powders. They did not soften below 300°C.

### *Tricyanovinylations of Poly(N-vinylindole) and N-Vinylindole—Fumaritrile Copolymer*

Equimolar amounts (*e.g.*,  $8.0 \times 10^{-2}$  mol/l) of poly(*N*-vinylindole) and TCNE were mixed in a benzene solution, and a catalytic amount of pyridine was added. The reaction solution was then heated with stirring at 50°C for 20 hr. A deep violet color characteristic of the charge-transfer complex between poly(*N*-vinylindole) and TCNE developed initially. The solution turned gradually to deep red, and the reaction products precipitated from the reaction solution. When the reaction was carried out in a basic solvent such as tetrahydrofuran (THF) or *N,N*-dimethylformamide (DMF), the tricyanovinylation reaction proceeded homogeneously. In this case the pyridine catalyst was not added. The reaction mixture was first poured into a large excess of methanol, and the tricyanovinylated poly(*N*-vinylindole) which precipitated was collected by filtration with a glass filter, washed with methanol repeatedly, dried *in vacuo* at room temperature, and further reprecipitated from THF with *n*-hexane and dried *in vacuo* at room temperature. The tricyanovinylated poly(*N*-vinylindole) was obtained as a deep red powder; it did not soften below 280°C. Found: C, 77.66; H, 4.00; N, 17.80%. Calcd for the tricyanovinylated poly(*N*-vinylindole) (tricyanovinylation degree 44.6% determined from N%): C, 77.58; H, 4.62; N, 17.80%. IR spectrum (KBr):  $\nu_{\text{CN}}$  2220  $\text{cm}^{-1}$ . Electronic absorption

spectrum ( $\lambda_{\text{max}}$  in THF): 229, 258, and 465 nm.

The same procedure described above was followed for the tricyanovinylation of the *N*-vinylindole—fumaritrile copolymer, DMF being used as a solvent. The tricyanovinylated *N*-vinylindole—fumaritrile copolymer thus obtained was a red powder with no softening below 300°C. Found: C, 73.73; H, 3.94; N, 22.33%. Calcd for the tricyanovinylated *N*-vinylindole—fumaritrile copolymer (tricyanovinylation degree 6.5% determined from N%): C, 73.17; H, 4.38; N, 22.33%. IR spectrum (KBr):  $\nu_{\text{CN}}$  2240 and 2220  $\text{cm}^{-1}$ . Electronic absorption spectrum ( $\lambda_{\text{max}}$  in DMF): 280 and 440 nm.

### *Measurements*

The IR spectra were taken with a Hitachi EPI-G-2 infrared spectrophotometer. The electronic absorption spectra were taken with a Hitachi 124 spectrophotometer. The molecular weight of the polymer was determined with a Mechrolab VPO Model 302 at 65°C in DMF. Measurements of the dielectric constant and loss were carried out with a G. R. Capacitance Bridge Type 1615A at room temperature. Disk samples of 10 mm in diameter and 1.45-mm thickness were used for the measurements.

## RESULTS AND DISCUSSION

### *Preparation of Poly(N-vinylindole) and N-Vinylindole—Fumaritrile Copolymer*

*N*-Vinylindole has been shown to polymerize thermally and with cationic, free-radical, and Ziegler—Natta catalysts,<sup>8,9</sup> although detailed studies have not been made. In the present study poly(*N*-vinylindole) was prepared with boron trifluoride diethyletherate and AIBN catalysts in a benzene solution. The polymerization data are summarized in Table I. The

**Table I.** Polymerization of *N*-vinylindole in a benzene solution

Exptl no.	<i>N</i> -Vinylindole, mol/l	Initiator $\times 10^2$ , mol/l	Reaction temp, °C	Reaction time, hr	Conversion, %	Molecular weight <sup>a</sup>	Softening point, °C
1	0.30	BF <sub>3</sub> OEt <sub>2</sub> 0.3	10	24	37.3	1400	210—215
2	0.67	AIBN 0.3	80	24	14.6	—	194—203
3	0.67	" 0.6	80	24	17.3	2000	198—210
4	0.67	" 1.0	80	17	12.4	—	194—205

<sup>a</sup> Determined from VPO at 65°C in DMF solution.

**Table II.** Copolymerization of *N*-vinylindole(VI) with fumaronitrile(FN) in a benzene solution at 80°C

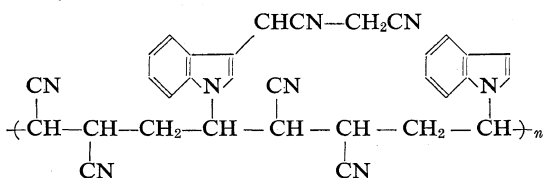
Exptl no.	VI, mol/l	FN, mol/l	AIBN × 10 <sup>-2</sup> , mol/l	Reaction time, min	Conversion, %	Molecular weight <sup>a</sup>	Nitrogen content, %	Mol fract of VI in copolymer <sup>b</sup>
1	0.51	0.49	1.0	60	53.4	4000	21.36	0.41
2	0.51	0.49	1.0	120	69.0	—	—	—
3	0.51	0.49	1.0	1440	80.8	4700	—	—
4	0.10	0.90	0.1	50	4.9	3400	21.98	0.38
5	0.50	0.50	0.1	50	10.1	—	22.12	0.38
6	0.90	0.10	0.1	50	2.4	3500	18.63	0.51

<sup>a</sup> Determined from VPO at 65°C in a DMF solution.

<sup>b</sup> All copolymers did not soften below 300°C.

poly(*N*-vinylindole) thus prepared were white powders, easily soluble in benzene, THF, dioxane, DMF, pyridine, and dimethylsulfoxide (DMSO), but insoluble in methanol, *n*-hexane, and carbon tetrachloride.

In an attempt to prepare a copolymer of *N*-vinylindole having a strong alternating tendency, *N*-vinylindole was copolymerized with an electron-accepting monomer, fumaronitrile, under initiation with a radical catalyst, since the successful synthesis of the 1:1 alternating copolymer of the analogous *N*-vinylcarbazole with fumaronitrile irrespective of the monomer-feed composition had recently been made in our laboratory.<sup>10</sup> The compositions of the copolymers obtained for the various monomer-feed compositions were all rich in fumaronitrile, despite the fact that fumaronitrile alone does not homopolymerize under the present radical-polymerization conditions. The copolymers were assigned as the 1:1 alternating copolymers in the main chain accompanied by the partial addition of fumaronitrile in the side indole group at its 3-position.<sup>7</sup> Thus, the copolymer between *N*-vinylindole and fumaronitrile turned out to be a polymer with polar side groups, *i.e.*, 3-(1,2-dicyanoethyl)-indole rings.



The results of the copolymerization of *N*-vinylindole with fumaronitrile are summarized in Table II, and these polymers were used for the tricyanovinylolation reaction and also for the

measurements of the dielectric properties.

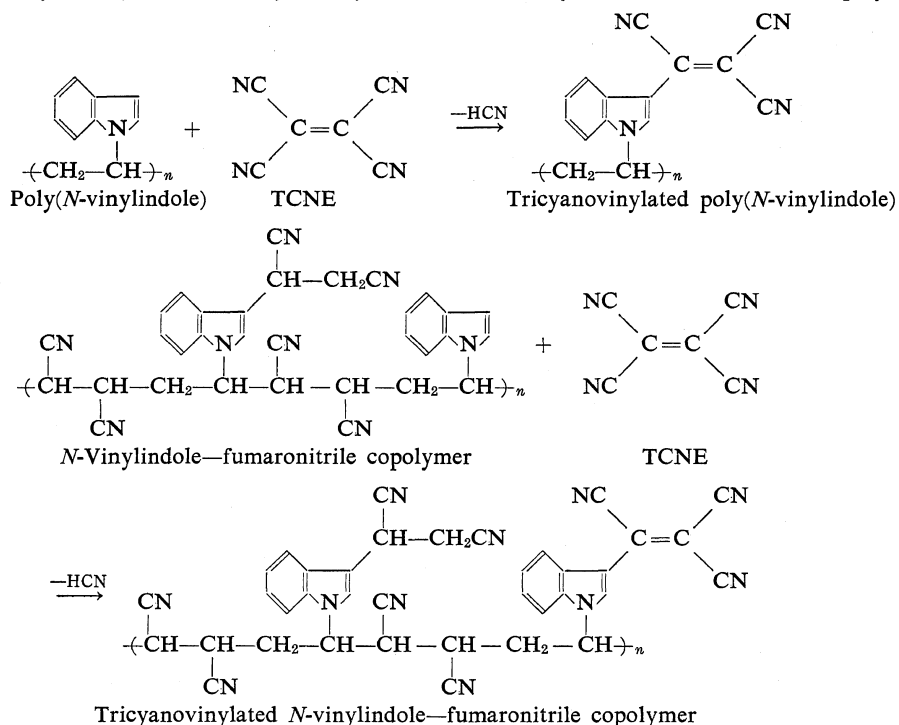
#### Tricyanovinylolation of Poly(*N*-vinylindole) and *N*-vinylindole—Fumaronitrile Copolymer

For the purpose of obtaining a polymer with polar side groups, the introduction of the tricyanovinyl group at the 3-position of the side indole groups of poly(*N*-vinylindole) and the *N*-vinylindole—fumaronitrile copolymer was undertaken by the reaction with tetracyanoethylene (TCNE) (Scheme 1).

The tricyanovinylolation was carried out by treating the polymer with an equimolar amount of TCNE at 50°C with stirring in a benzene, THF, or DMF solution. When the reaction was carried out in benzene, a small amount of pyridine was added in order to facilitate the elimination of hydrogen cyanide. The reaction proceeded homogeneously in THF or DMF, but in benzene the tricyanovinylated polymer precipitated from the reaction solution. The tricyanovinylolation of the *N*-vinylindole—fumaronitrile copolymer was carried out in a DMF or pyridine solution, since the copolymer was soluble only in DMF or pyridine. The tricyanovinylated poly(*N*-vinylindole) and the tricyanovinylated *N*-vinylindole—fumaronitrile copolymer were obtained as deep red and red powders, respectively. They were soluble in acetone, THF, DMF, DMSO, and pyridine, but insoluble in benzene, dioxane, methanol, and *n*-hexane. The tricyanovinylated polymers were identified by the infrared and electronic absorption spectra, and by elemental analyses. The infrared spectra of the tricyanovinylated polymers showed a strong absorption due to the stretching vibration of the conjugated nitrile group at 2220 cm<sup>-1</sup>. The electronic absorption spectra of the tricyano-

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**Scheme 1.** Tricyanovinylations of Poly(*N*-Vinylindole) and *N*-Vinylindole—Fumaronitrile Copolymer



vinylated polymers showed a new absorption band due to the conjugated 3-(1,2,2-tricyanovinyl)-indole chromophore with  $\lambda_{\text{max}}$  at 465 nm for the tricyanovinylated poly(*N*-vinylindole). In the case of the tricyanovinylated *N*-vinylindole—fumaronitrile copolymer the absorption maximum showed a blue shift, which appeared at 440 nm. The degree of the tricyanovinylation was determined from this absorption band using the molar extinction coefficient value ( $\lambda_{\text{max}}$  460 nm,  $\epsilon=13500$ ) for 3-(1,2,2-tricyanovinyl)-indole and from the nitrogen analyses; the values obtained by both methods were in close agreement with each other. The results of the tricyanovinyl-ation reaction are summarized in Table III.

It was found that the degree of tricyanovinyl-ation for poly(*N*-vinylindole) did not exceed *ca.* 45% under the different reaction conditions examined, which suggests that this value might be the maximum degree for the tricyanovinyl-ation reaction of poly(*N*-vinylindole). The steric hindrance resulting from the introduction of the bulky tricyanovinyl group may be largely responsible for this rather low value of the re-

action degree. It is known that a reaction of polymer substituents with a chemical reagents or an intramolecular reaction between polymer substituents does not generally go beyond a definite extent statistically even when the steric hindrance does not operate. For example, the maximum degree for the acetalization of poly-(vinyl alcohol) with formaldehyde, or the condensation reaction of poly(methyl vinyl ketone) has been shown by Flory to be 86.46%, based on a statistical calculation; this is in agreement with the experimental results.<sup>11</sup> Furthermore, when the effect of steric hindrance becomes appreciable, the maximum degree of the polymer reaction is markedly reduced. We have shown this by both experiments and statistical calculations for the acetalization reaction of poly(vinyl alcohol) with a bulky poly(acene aldehyde) such as 9-anthraldehyde, 9-acridinealdehyde, or 3-pyrenealdehyde.<sup>12</sup> Recently, E. A. Boucher has made a statistical calculation of the reaction degree for a hypothetical reaction in which the reactivity of a substituent depends on whether zero, one, or two of its neighbors have already

**Table III.** Tricyanovinylolation of poly(*N*-vinylindole)(poly-VI) and the *N*-vinylindole—fumaritrile copolymer(VI—FN copolymer) at 50°C

Exptl no.	Polymer, mol/l	TCNE, mol/l	Solvent	Reaction time, hr	TCV Degree, %			Softening point, °C
					1 <sup>a</sup>	2 <sup>b</sup>	Nitrogen, %	
Poly—VI <sup>c</sup>								
1	0.08	0.08	Benzene (catalytic pyridine)	20	43.5	—	—	Above 260°C
2	0.08	0.08	DMF	20	34.6	39.4	16.92	Above 260°C
3	0.14	0.14	THF	2.5	44.6	44.6	17.80	Above 280°C
VI—FN Copolymer <sup>d</sup>								
4	0.045	0.18	DMF	4	3.8	4.6	22.33	Above 300°C
5	0.045	0.18	DMF	24	6.5	—	—	Above 300°C
6	0.045	0.18	Pyridine	15	0.2	—	—	Above 300°C

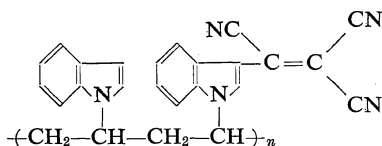
<sup>a</sup> The degree of tricyanovinylolation (TCV) was determined from the electronic absorption band at  $\lambda_{\max}$  465 nm for the tricyanovinylolated poly(*N*-vinylindole), and at  $\lambda_{\max}$  440 nm for the tricyanovinylolated VI—FN copolymer, using the molar extinction coefficient for 3-(1,2,2-tricyanovinyl)-indole ( $\lambda_{\max}$  460 nm,  $\epsilon=13500$ ).

<sup>b</sup> The TCV degree was determined from the nitrogen analysis.

<sup>c</sup> Poly-VI was obtained from Exptl no. 3 in Table I.

<sup>d</sup> The VI—FN copolymer was obtained from Exptl no. 1 in Table II.

reacted.<sup>13</sup> It is of interest to note that the present *ca.* 45-% value for the degree of tricyanovinylolation of poly(*N*-vinylindole) agrees with the value 43.2% calculated for the situation where no two adjacent substituents react. Thus, *ca.* 45-% tricyanovinylated poly(*N*-vinylindole) may possibly possess the alternating structure of the parent indole group and the 3-tricyanovinylated indole groups.



It then seemed to be of interest to examine the tricyanovinylolation for the 1:1 alternating copolymer of *N*-vinylindole with another comonomer, where the adjacent indole rings are separated from each other by the comonomer sequence. The *N*-vinylindole—fumaritrile copolymer was synthesized from this viewpoint. The copolymers obtained were 1:1 alternating copolymers in the main chain, but at the same time the 3-position of the indole ring was partially occupied by the 1,2-dicyanoethyl groups resulting from the addition of fumaritrile to the indole ring. The *N*-vinylindole—fumaritrile copolymer of the composition of 1:1.46

(*N*-vinylindole : fumaritrile) in which only *ca.* 54% of the indole rings in the copolymer can be available for the tricyanovinylolation reaction was allowed to react with TCNE. In this case also, the tricyanovinylolation reaction did occur, but it was found that the degree of the tricyanovinylolation of the copolymer was lower than that for the tricyanovinylolation of poly(*N*-vinylindole), as shown in Table III. It is suggested that the reactivity of the copolymer toward TCNE may be affected both by the linkage of the 1,2-dicyanoethylene group in the main chain and by the occupation of the 3-position of the indole ring by the 1,2-dicyanoethyl group.

#### Dielectric Properties of the Polymers

The results of the dielectric measurements at room temperature are summarized in Table IV.

The dielectric constant of the polymer was found to increase by introducing the polar side group into the polymer, as shown in Table IV. The higher value of the dielectric constant found for the *N*-vinylindole—fumaritrile copolymer compared with that for the tricyanovinylated poly(*N*-vinylindole) may be attributable to the fact that the 1,2-dicyanoethyl moiety in the *N*-vinylindole—fumaritrile copolymer is more flexible than the 1,2,2-tricyanovinyl moiety in the tricyanovinylated poly(*N*-vinylindole).

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Table IV. Dielectric properties of the polymers

Frequency	Poly-VI <sup>a</sup>		Tricyanovinylated <sup>c</sup> poly-VI		VI-FN Copolymer <sup>b</sup>		Tricyanovinylated <sup>d</sup> VI-FN copolymer	
	$\epsilon$	$\tan \delta, \%$	$\epsilon$	$\tan \delta, \%$	$\epsilon$	$\tan \delta, \%$	$\epsilon$	$\tan \delta, \%$
200 Hz	3.8	1.20	4.8	2.20	5.5	1.40	6.9	2.00
1 kHz	3.7	0.90	4.8	1.00	5.4	1.00	6.2	1.50
5 kHz	3.7	0.74	4.7	1.00	5.3	0.88	6.1	1.22
10 kHz	3.6	0.80	4.7	0.80	5.3	0.86	6.1	1.20

Abbreviations: <sup>a</sup> Poly(*N*-vinylindole); <sup>b</sup> *N*-Vinylindole—fumaronitrile copolymer. Tricyanovinylated degree, %: <sup>c</sup> 44.6; <sup>d</sup> 6.5.

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