

## Copolymerization of Vinylferrocene and N-Vinylcarbazole. Conductivity Studies of the Trinitrofluorenone and Mixed-Valence [Fe(II), Fe(III)] Complexes of These Copolymers

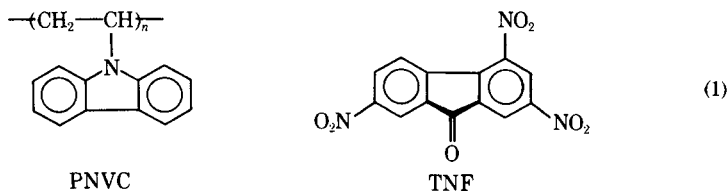
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### Synopsis

Vinylferrocene ( $M_1$ ) has been copolymerized with N-vinylcarbazole ( $M_2$ ) using azobisisobutyronitrile as the initiator. In benzene at 70°C, the reactivity ratios  $r_1 = 0.47$  and  $r_2 = 0.20$  were obtained. Using an  $e$  value of  $-1.34$  for N-vinylcarbazole, the calculated value  $e$  for vinylferrocene is about  $-2.8$ , in general agreement with the large negative  $e$  values vinylferrocene exhibits with other monomers which are electron rich. These copolymers were treated with trinitrofluorenone to give copolymers with carbazole-trinitrofluorenone charge-transfer complex sites (type B). The copolymers were oxidized with dichlorodicyanoquinone to give a series of copolymers with both ferrocenium and ferrocene sites in them (type C). In addition, type C copolymers were further treated with trinitrofluorenone to give a class of polymers having ferrocene, ferrocenium, and carbazole-trinitrofluorenone charge-transfer sites (type D). Introducing ferrocene and ferrocenium sites into the poly(vinylcarbazole-trinitrofluorenone) polymers resulted in an increase in their conductivity, but the polymers were no longer photoconducting.

### INTRODUCTION

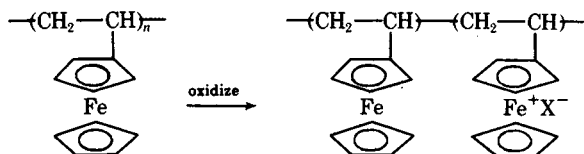
Poly(N-vinylcarbazole) (PNVC) and its 2,4,7-trinitro-9-fluorenone (TNF) charge-transfer complexes,



are among the most sensitive of the known organic photoconductors; but in the absence of light, PNVC is an excellent insulator with a low dielectric constant.<sup>1-3</sup> The 1:1 PNVC-TNF complex has a white-light sensitivity approximately equal to that of amorphous selenium when used for electro-

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static imaging.<sup>2</sup> Recently, we have shown that mixed-valence polymers of polyferrocenylene and poly(vinylferrocene) are semiconductors ( $\sigma = 10^{-7} - 10^{-11} \Omega^{-1} \text{cm}^{-1}$ ), while the unoxidized neutral polymers, eq. (1), were insulators.<sup>4</sup> Thus, we have undertaken the synthesis of vinylferrocene N-vinylcarbazole copolymers,



where  $X = \text{BF}_4^-$ , dichlorodicyanoquinone, or orthochloranil, in order (1) to study the photoconductivity of the PNVC-TNF system in the presence of the ferrocene units and (2) to see if introducing mixed-oxidation states of ferrocene into PNVC or PNVC-TNF polymers could induce these to become semiconductors.

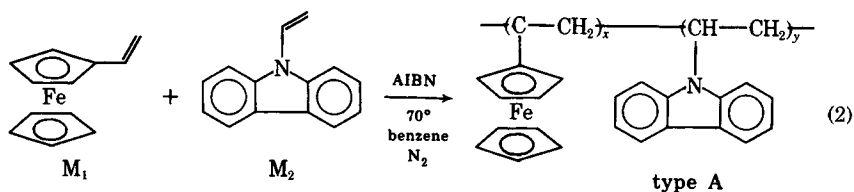
The copolymerization of N-vinylcarbazole with vinylferrocene in the presence of azo initiators, independently, is of particular interest. Recently, we have demonstrated that vinylferrocene is one of the most strongly electron-donating vinyl monomers known. Its  $e$  value<sup>5</sup> was determined to be  $-2.06$  from copolymerizations with styrene<sup>6</sup> and  $-2.07$  from copolymerizations with N-vinylpyrrolidone.<sup>7</sup> This may be compared to  $e = -1.96$  for 1,1-bis(*p*-anisyl)ethylene.<sup>8</sup> However, in copolymerizations with electron-withdrawing monomers such as acrylonitrile and methyl acrylate, the value of  $e$  for vinylferrocene varied ( $-0.73$  and  $-0.23$ , respectively).<sup>6</sup> This suggested that as the comonomer became strongly electron attracting, the polymerization was proceeding, in part, through a charge-transfer mechanism which was in competition with the terminal model. In relatively electron-rich monomers such as styrene ( $e = -0.80$ ) and N-vinylpyrrolidone ( $e = -0.84$ ), a charge-transfer contribution would not be expected. Since N-vinylcarbazole is a very electron-rich monomer ( $e = -1.34$ ), its use was ideal to extend the range of  $e$  values of comonomers used in vinylferrocene copolymerizations.

Since N-vinylcarbazole cationic polymerization is slow but homopolymerization proceeds conveniently at elevated temperatures<sup>9,10</sup> using conventional azo initiators, the choice of azobisisobutyronitrile (AIBN) as initiator was made. This was particularly convenient since all of the previous vinylferrocene reactivity ratio studies were done in this manner.<sup>6,7</sup>

## RESULTS AND DISCUSSION

### Copolymerization of Vinylferrocene with N-Vinylcarbazole

Vinylferrocene was copolymerized with N-vinylcarbazole under nitrogen in benzene solutions at  $70^\circ\text{C}$  using AIBN initiation, eq. (2):



Copolymer compositions were determined by elemental analysis (% Fe and % N). Mole ratios ( $M_1^0/M_2^0$ , where  $M_1 =$  vinylferrocene) of 70/30, 30/70, 73/27, 27/73, and 50/50 were used. From the composition-conversion data of preliminary runs, initial estimates of  $r_1$  and  $r_2$  were obtained by the method of Tidwell and Mortimer.<sup>11,12</sup> Using tables provided in reference 11, optimized  $M_1^0/M_2^0$  ratios were then selected and copolymerization reactions were performed at these ratios. Final values of  $r_1$  and  $r_2$  were calculated from all the data (Table I), and the confidence limits were obtained.<sup>11,12</sup> The best nonlinear least-squares fitted values are:  $r_1 = 0.47(+0.14, -0.11)$ ,  $r_2 = 0.20(+0.05, -0.06)$ . From these ratios, the value of  $e$  for vinylferrocene can be computed to be approximately in the range of  $-2.8$ . It should be noted that the Tidwell-Mortimer method<sup>11,12</sup> of calculating  $r_1$  and  $r_2$  makes the proper statistical use of all

TABLE I  
Copolymerization of Vinylferrocene ( $M_1$ ) with N-Vinylcarbazole at 70°C in Benzene<sup>a</sup>

Copolymer no.	Vinyl-ferrocene in feed, g	$M_1^0/M_2^0$ (mole ratio)	Reaction time, hr	Conversion, % yield	Mole-% $M_1$ in copolymer <sup>b</sup>
1	1.570	50/50	96	25.0	54.6
2	2.163	70/30	72	22.6	66.1
3	2.163	70/30	72	18.1	66.6
4	0.940	30/70	72	66.9	32.5
5	0.940	30/70	72	67.0	33.1
6	2.000	73/27	6	11.3	68.4
7	2.000	73/27	6	9.4	69.0
8	2.000	73/27	6	8.8	68.9
9	1.000	27/73	11	29.3	42.3
10	1.000	27/73	3	10.0	45.2
11	1.000	27/73	3	9.1	44.6
12	1.000	27/73	3	12.6	41.7
13	1.160	27/73	2.3	7.7	39.2
14	1.160	27/73	2.3	8.2	39.5
15	4.563	74.3/25.7	4	13.7	69.2
16	0.839	12.9/87.1	3	18.4	32.1
17	0.839	12.9/87.1	3	23.7	30.7
18	0.839	12.9/87.1	3	24.1	30.6
19	0.839	12.9/87.1	3	22.8	30.8
20	0.220	10/90	14 days	82.9	11.4
21	1.910	36/64	14 days	53.1	46.9

<sup>a</sup> AIBN, 0.5 wt-%, was used in each run.

<sup>b</sup> Calculated from % Fe and % N determined by duplicate analyses (Galbraith Laboratories, Knoxville, Tenn.).

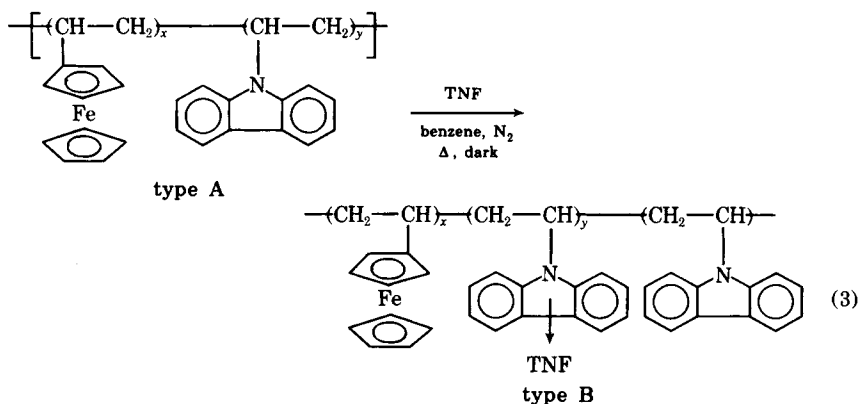
the individual copolymerizations, no matter what the percent conversion or starting  $M_1^0/M_2^0$  ratio is. Thus, all runs are not weighted equally. Rather, those with lower conversions and closer to the optimum  $M_1^0/M_2^0$  ratio are weighted more heavily.

The large confidence limits prevent a precise determination of  $e$ . However, it is clear that the large electron-donating character of vinylferrocene is maintained when  $M_2$  is N-vinylcarbazole. Those results strengthen the general conclusion that vinylferrocene exhibits values of  $e$  of at least  $-2.0$  with monomers which have  $e$  values from  $-0.4$  to  $-1.34$ . Vinylferrocene exhibits much smaller  $e$  values with comonomers having  $e = +0.4$  or greater.<sup>6,7,13</sup> This presumably is due to the fact that pure terminal-model copolymerization is no longer taking place when the comonomer is strongly electron withdrawing.

The polymers were characterized by IR, NMR, and gel permeation chromatography (GPC) in addition to elemental analysis. The molecular weights were low according to GPC studies ( $\bar{M}_n$  from 6000 to 2000). The low molecular weights probably play a role in the lack of precision in the  $r_1, r_2$  determinations. It was not possible to obtain high molecular weight copolymers in either benzene or ethyl acetate solutions, but the copolymerization studies in benzene were designed to allow the  $r_1, r_2, Q$ , and  $e$  determinations to be comparable to our previous studies.<sup>6,7</sup>

### Conversion of Vinylferrocene-N-Vinylcarbazole Copolymers to Charge-Transfer Complexes and Mixed-Oxidation States

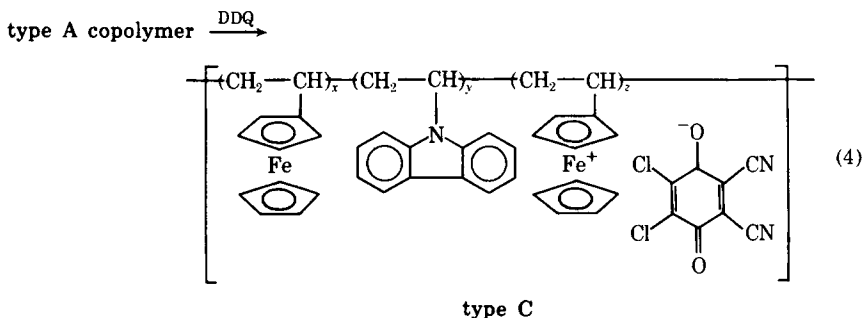
Vinylferrocene-N-vinylcarbazole copolymers (type A) were reacted with TNF in benzene solutions in the dark and under nitrogen. After refluxing for 8 hr, the benzene was evaporated to yield brittle, brown films of TNF-complexed polymers, type B, eq. (3):



The ratio of carbazole to TNF units was varied from 1/1 to 1/0.1 by controlling the amount of TNF charged to the reaction. Control reactions of ferrocene or poly(vinylferrocene) with TNF, in both benzene and acetonitrile, showed that no oxidation of ferrocene units occurred when TNF

was present. This may be contrasted to the facile oxidation of ferrocene by dichlorodicyanquinone (DDQ) and *ortho*-chloranil.<sup>4,14</sup> While ferrocene and TNF may form weak charge-transfer complexes, there was no evidence of any color changes, expected if a complex were formed, on reacting the two. The poly(N-vinylcarbazole-TNF) complex, on the other hand, absorbs in the visible region from 1.6 to 2.8 eV<sup>1,2,15</sup> and is rather stable. Thus, in the type B polymers, it is assumed that only carbazole-TNF complexes and possibly some free, dissolved TNF<sup>15,16</sup> are present.

Type A copolymers were also reacted with DDQ in benzene. Very rapid electron transfer from iron to DDQ occurs to generate ferrocenium sites in the polymers, see eq. (4):

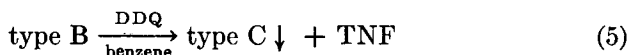


The type C polysalts then precipitated from solution. Control of the ferrocene/ferrocenium ratio in these copolymers is difficult to specifically design since variations in the  $M_1/M_2$  ratio in the type A polymers change the solubilities of the type C polymers and thus the amount of oxidation. However, by varying the DDQ charged into the reaction and the solvent (i.e., benzene, THF, or acetonitrile), it was possible to substantially vary the ferrocene/ferrocenium ratio.

It is now well known that unreduced DDQ is not found in a variety of ferrocene mixed-valence polymers.<sup>14</sup> This was confirmed in the type C polysalts by the absence of an  $1680\text{ cm}^{-1}$  IR band characteristic of the free DDQ carbonyl stretch. Thus, the Fe(II)/Fe(III) ratio was readily determined by elemental analyses (% Fe, % N, % Cl) as well as by Mössbauer spectroscopy.<sup>14</sup> The presence of both ferrocenium and ferrocene units is also indicated by IR. The C—H out-of-plane deformation bands at  $816\text{ cm}^{-1}$  (ferrocene rings) and  $845\text{ cm}^{-1}$  (ferrocenium rings) were observed.<sup>14,17</sup> Finally, control experiments demonstrated that poly(vinylcarbazole) (commercial sample) was not oxidized by DDQ, nor were carbazole-DDQ complexes detected under the conditions used to make the type C polysalts. Taken in total, these results confirm that the structure of type C polymers is that shown in eq. (4). Further structural confirmation is given in the experimental section.

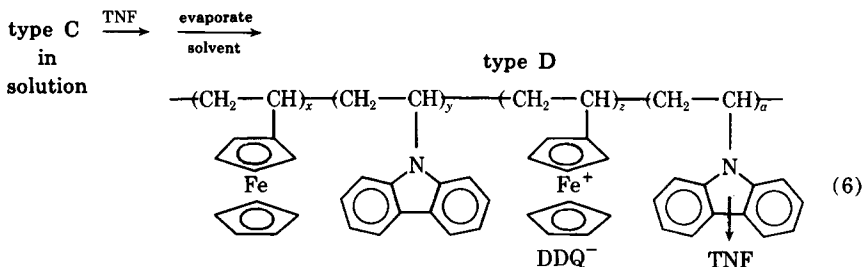
A final synthetic goal was to prepare copolymers with both carbazole-TNF complexes and the mixed [Fe(II)–Fe(III)] oxidation states. The reaction of type B copolymers, in benzene, with enough DDQ to oxidize

50% of the ferrocene moieties, instantaneously produced a blue-black precipitate. This precipitate exhibited the IR bands of the CH out-of-plane deformation for both ferrocene ( $816\text{ cm}^{-1}$ ) units<sup>17</sup> as well as the carbonyl band of the DDQ radical anion ( $1570\text{ cm}^{-1}$ ).<sup>14,18</sup> However, in these reactions, most of the TNF remained in solution, eq. (5):



This was not unexpected, since the polymeric carbazole-TNF charge-transfer complexes are known to be in equilibrium with free TNF and polymeric carbazole units in solution.<sup>15,16</sup> For example, Weiser demonstrated that when PNVC-TNF films are formed by solvent evaporation, the degree of complexing increases as the solvent evaporates.<sup>16</sup>

An alternate approach was successful. The vinylferrocene-N-vinylcarbazole copolymer (type A) was first converted to its type C mixed valence polysalt. Then this polysalt was dissolved into large volumes of benzene, acetone, or acetonitrile mixtures, and TNF was added, eq. (6):



The solvent was then progressively removed, and the carbazole-TNF complexes were formed. Evidence that TNF was complexed to carbazole rings was again apparent from the absorption in the 1.6 to 2.8 eV range.<sup>15,16</sup> This absorption is partially obscured by absorption from the ferrocenium ion at 2.01, 2.19, and 3.26 eV.<sup>19,20</sup> In type D polymers, the electroabsorption spectra over the 1.6 to 2.8 eV region would consist of a superposition of field-induced changes of the absorption of the charge-transfer complex, the beginning of the TNF absorption, and the ferrocene-ferrocenium absorption. Due to these complexities, attempts to further assign these spectra were not made. Previously, the electroabsorption spectrum of 1:1 PNVC-TNF was shown to exhibit two distinct peaks at 1.88 eV and 2.4 eV, and these had been attributed to the onset of two transitions within the charge-transfer band.<sup>15,16</sup>

That some TNF may be dissolved into (but not complexed to) the type D polymers cannot be ruled out.<sup>16</sup> However, separate crystals of TNF were not present in the type D polymers studied here. Of course, the exact structure of any PNVC-TNF polymer system must be cautiously assigned. Weiser,<sup>16</sup> for example, showed that the degree of TNF complexing in PNVC TNF films increases until a ratio of 1:0.6 (carbazole:TNF) is reacted. When the ratio was 1:1, only about 40% of the TNF molecules were actu-

ally complexed to carbazole units, while 72% of the TNF was complexed at a carbazole:TNF ratio of 1:0.1.<sup>16</sup> A quantitative estimate of the per cent TNF which is truly charge-transfer complexed in the polymers reported in this paper cannot yet be made.

### CONDUCTIVITY STUDIES

Direct current conductivity and photoconductivity measurements on the type A, B, C, and D polymers were performed using compressed pellets (0.3- to 0.5-g samples) and standard techniques described elsewhere.<sup>20</sup> Conductivities of selected example polymers with widely varying compositions are listed in Table II. The values reported are the average of five repeated measurements made on each of two separate samples. Measurements of different sample pellets of the same polymer agreed within 15% in all cases.

Overall, the following conclusions were reached:

1. Introduction of vinylferrocene into N-vinylcarbazole polymer chains reduces the photoconductivity response of the PNVC system. For example, even with only 5 to 10 mole-% of vinylferrocene in the type A polymers, only a small increase (by a factor of 1 or less) in conductivity is noted on irradiation with a 200-W white light at 200 volts.

2. The dark conductivity of PNVC is increased as the percentage of vinylferrocene incorporated in type A polymers is raised. However, type

TABLE II  
Representative Conductivity Studies of Type A, B, C, and D  
Vinylferrocene-N-Vinylcarbazole Copolymers

Polymer type and number <sup>a</sup>	M <sub>1</sub> /M <sub>2</sub> polymer	Fe(III), %	TNF-carbazole mole ratio	Conductivity $\sigma$ , <sup>b</sup> $\Omega^{-1} \text{ cm}^{-1}$	$E_{\text{act}}$ , eV
Type A (20)	11.4/88.6	0	0	$\sigma_{200\text{V}} = 3 \times 10^{-16}$ (insulator)	0.88
Type A (9)	42.3/57.7	0	0	$\sigma_{100\text{V}} = 5.98 \times 10^{-13}$ <sup>c</sup>	—
Type B (20)	11.4/88.6	0	0.50	$\sigma_{200\text{V}} = 1.86 \times 10^{-15}$	1.05
Type B (20)	11.4/88.6	0	1.00	$\sigma_{200\text{V}} = 2.92 \times 10^{-14}$	0.85
Type B (21)	46.9/53.1	0	0.05	$\sigma_{200\text{V}} = 4.8 \times 10^{-13}$	0.85
Type B (21)	46.9/53.1	0	0.20	$\sigma_{200\text{V}} = 7.0 \times 10^{-14}$	1.31
Type C (21)	46.9/53.1	50	0	$\sigma_{200\text{V}} = 5.8 \times 10^{-10}$	0.41
Type C (2)	66.1/23.9	54	0	$\sigma_{200\text{V}} = 1.4 \times 10^{-9}$	—
Type D (21)	46.9/53.1	50	0.20	$\sigma_{200\text{V}} = 1.04 \times 10^{-11}$	0.153 <sup>d</sup>
Type D (21)	46.9/53.1	50	0.60	$\sigma_{200\text{V}} = 3 \times 10^{-10}$	0.12

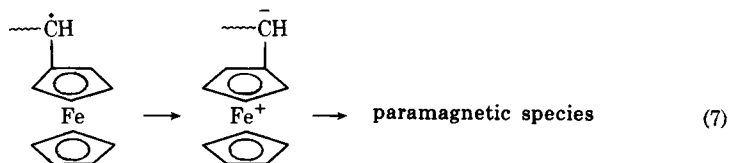
<sup>a</sup> Copolymer number from Table I.

<sup>b</sup> Compressed pellets were used, and Ohm's law was followed unless otherwise noted.

<sup>c</sup> Measurements were performed on sedimentation layers (0.23 mm), and Ohm's law was not followed.

<sup>d</sup> At 400 V, the value of  $E_{\text{act}}$  increased to 0.205 eV.

A polymers are still essentially insulators. The small increases observed are probably due to the presence of small amounts of a paramagnetic species, presumably Fe(III).<sup>21,22</sup> The presence of less than 0.5% ferrocenium units in poly(vinylferrocene) is known to cause an increase in conductivity from  $10^{-14}$  to about  $5 \times 10^{-12}$ .<sup>4,21</sup> Apparently, a step in the termination of polymer chains involves a sequence in which an electron is transferred from Fe to the chain:



This suggestion has been made previously and is supported by the observation of large ESR signals,<sup>21,22</sup> NMR line broadening,<sup>14,22</sup> and the fact that vinylferrocene polymerization is first order in initiator.<sup>22</sup>

3. Type A copolymers become semiconducting when mixed-valence states, Fe(II), Fe(III), are introduced by DDQ oxidation. Thus, type C polymers are semiconductors but they are not photoconductors.

4. Type D polymers, containing both mixed-valence states of iron and carbazole-TNF charge-transfer complexes, are semiconductors. However, they show poor photoconductivity response even with as high as 55% of the carbazole units complexed to TNF.

In summary, it appears that PNVC can be made mildly semiconducting by introducing ferrocene mixed-valence states, but the presence of ferrocene largely quenches the photoconductivity of the PNVC-TNF system. Attempts to successfully explain the above results depend, in part, on an understanding of the "pure" PNVC-TNF system. Gill has shown that no satisfactory explanation is yet available for the field dependence of the hole and electron drift mobilities in this system.<sup>23</sup> In "pure" PNVC-TNF films, the electron mobility rapidly decreased as the TNF concentration increased. This suggested that charge carriers are highly localized and that transport is taking place by a thermally assisted intermolecular hopping process.<sup>23</sup> Furthermore, both complexed and uncomplexed TNF units were held important in electron transport. Since the PNVC-TNF system, itself, is not yet understood, conjecture as to the role played by ferrocene and ferrocenium sites in the type A-D polymers would be premature.

## EXPERIMENTAL

Vinylferrocene was prepared and purified as previously described.<sup>14</sup> N-Vinylcarbazole was obtained commercially (Polysciences Corporation, Warrington, Pa.) and used without further purification, as was 2,4,7-trinitro-9-fluorenone. Polymerization solvents were rigorously dried before



use. The UV visible spectral measurements have been thoroughly described before.

**Copolymerization of Vinylferrocene ( $M_1$ ) with N-Vinylcarbazole ( $M_2$ ) (molar ratio  $M_1/M_2 = 50/50$ )**

Copolymer 1 (Table I) was prepared as follows. Vinylferrocene (1.570 g, 0.0074 mole) and 1.43 g N-vinylcarbazole (0.0074 mole), 0.030 g AIBN and 10 ml dry, distilled benzene were placed in a Fisher-Porter tube. The solution was triply degassed by three freeze-thaw cycles ( $10^{-3}$ /torr pressure) followed by repressurization with purified nitrogen and a fourth degassing and repressurization to atmospheric pressure with nitrogen. The reaction tube was placed in a constant temperature water bath ( $70^\circ\text{C}$ ) for 96 hr. Upon cooling, the polymer solution was diluted with benzene and precipitated into 1600 ml methanol with vigorous stirring. The polymer was filtered and dissolved through the filter paper into a tared flask. After evaporation to dryness, 0.75 g (25%) of copolymer 1 was isolated. The polymer was purified by two additional reprecipitations: IR (KBr) 3090, 3050, 2900, 2930, 1600, 1485, 1450, 1365, 1225, 1160, 1125, 1108, 1025, 1000, 925, 815, 748, 722, 675, and  $602\text{ cm}^{-1}$ . For comparison, the IR spectra of the two monomers were taken: IR (vinylferrocene-KBr) 3090, 1630 (vinyl), 1410, 1385, 1240, 1050, 1030, 1000, 900, 815, and  $730\text{ cm}^{-1}$ ; IR (vinylcarbazole-KBr) 3050, 1645, 1615, 1595, 1580, 1485, 1450, 1415, 1370, 1335, 1300, 1225, 1160, 1125, 1105, 1025, 1000, 960, 925, 855, 748, and  $722\text{ cm}^{-1}$ ; NMR (copolymer 1,  $\text{CS}_2$ )  $\delta$  7.4 (*m*, carbazole ring protons),  $\delta$  4.1 (broad *m*, ferrocene ring protons),  $\delta$  1.5 (very broad *m*, chain protons); NMR (vinylcarbazole- $\text{CS}_2$ )  $\delta$  7.9 (*m*, 2H, ring protons 1 and 6),  $\delta$  7.5 (*m*, 7H, ring protons 2-7 and vinyl proton  $\alpha$  to N),  $\delta$  5.38 (*d*, 1H,  $J_{trans} = 16.2\text{ Hz}$ ,  $J_{vic}$  (not resolved),  $-\text{CH}=\text{CH}_2$ ),  $\delta$  4.99 (*d*, 1H,  $J_{cis} = 9.0\text{ Hz}$ ,  $-\text{CH}=\text{CH}_2$ ); GPC ( $30^\circ\text{-THF}$ )  $\bar{M}_n = 2362$ ,  $\bar{M}_w = 11,160$ ,  $\bar{M}_w/\bar{M}_n = 4.7$ ;  $|\eta|$  (THF,  $30^\circ$ ) 0.047 dl/g. Anal. 15.55% Fe, 3.24% N, which implies a molar ratio ( $M_1/M_2$ ) in the copolymer of 0.546/0.454. This preparation is representative of the others in Table I.

**Synthesis of Type B Polymers**

Copolymers of type A were dissolved into a large excess of benzene (10 ml benzene per 0.1 g polymer) under nitrogen. Then, a benzene solution of the appropriate amount of TNF was added in the dark at  $55\text{--}60^\circ\text{C}$ . The solution remained at this temperature overnight, after which time the benzene was slowly removed by evaporation. For example, 0.5 g copolymer 2 (Table I) and 0.02 g TNF in 25 ml (total) benzene were employed to give type B, no. 21, entry 5 in Table II. Brittle, brown films were formed except where large ratios of vinylferrocene were present. The IR (film) spectra of type B polymers contained the same bands as the type A polymers, in addition to very strong bands at  $1735\text{ cm}^{-1}$  (TNF carbonyl stretch),  $1530$  and  $1330\text{ cm}^{-1}$  (nitro groups). On microscopic examination, these materials were homogeneous.

### Type C and D Polymers

These were prepared as described in the text. The IR spectra of type C polymers exhibited bands at 3060, 2930, 2900, 2180 (CN stretch), 1580 (DDQ<sup>•</sup> carbonyl stretch), 1555, 1525, 1455, 1415, 1360, 1225, 1190, 1108, 1040, 1000, 880, 845, 816, 780, 750, 722, 710, and 675, while spectra of the type D polymers exhibited all the above bands in addition to bands at 1735 (TNF carbonyl stretch), 1530, and 1330 (*vs*, nitro groups).

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