TABLE VI

VOLUME RESISTIVITIES OF DONOR POLYMER–2,3-DICHLORO-5,6-DICYANO-*p*-BENZOQUINONE (DDQ) COMPLEXES[a]

Polymer	Form	Volume resistivity,[c] ohm cm
Poly(*p*-AI diol bisphenol A carbonate)[b]	Film	1.3×10^{16}
Poly(*p*-AI diol bisphenol A carbonate)	Disk	1×10^{13}
Poly(2,5-dimethoxy PI diol bisphenol A carbonate)	Disk	1×10^{11}
Poly(3,4,5-trimethoxy PI diol bisphenol A carbonate)	Disk	2×10^{11}

[a] Equimolar amounts of DDQ used. [b] No DDQ used. [c] Volume resistivities determined by Dr. M. M. Labes and Dr. P. L. Kronick at the Franklin Institute, Philadelphia, Pa.

effect of adding 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) to several donor polymers. A thousandfold increase in conductivity occurs with the addition of DDQ to a *p*-anisyliminodiethanol polymer. A further 100-fold conductivity rise is noted when a second or third methoxyl group is present in the polymer. The effect of the third methoxyl group is negligible because the full power of its donating capability is masked by steric hindrance.

Conclusions

A series of polyesters and polycarbonates were prepared containing dialkyl substituted anilines as the predominant feature. These polymers are unique because they combine toughness and electron-donating ability. When mixed with various monomeric acceptor species, they underwent charge-transfer complexing to give highly colored materials.

Acknowledgment. We gratefully acknowledge the highly competent technical assistance of Mr. Peter J. Degen.

Charge-Transfer Complexing in Polymer Mixtures. III. Reaction of Aryliminodiethanol Polymers with Tetracyanoethylene

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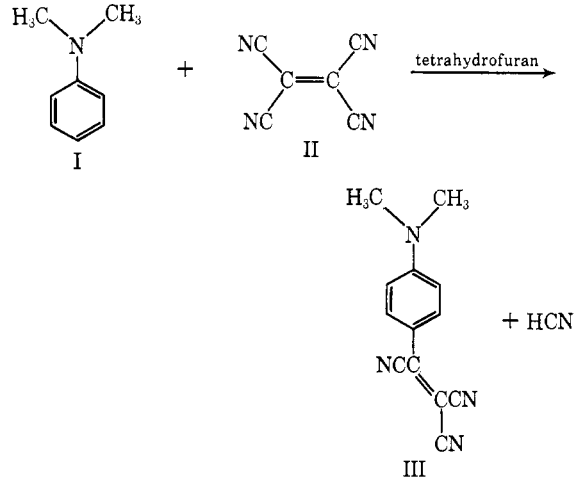
Received November 6, 1968

ABSTRACT: The reaction of tetracyanoethylene with the polyesters of several aryliminodiethanols was investigated. The products have the general formula

$$[ROCH_2CH_2N(Ar)CH_2CH_2O]_m—[ROCH_2CH_2N[ArC(CN)=C(CN)_2]CH_2CH_2O]_n$$

When R is $-COOC_6H_4C(<)C_6H_4OOC-$, Ar, the colors and visible absorption maxima are phenyl, red, 492 mμ; *m*-tolyl, red, 513 mμ; and 2,5-dimethoxyphenyl, purple, 535 and 395 mμ. The color of tricyanovinylated poly(tetrahydroquinoxaline-N,N′-diethanol bisphenol A carbonate) was green with absorption maxima of 590 and 435 mμ. Some insight into the mechanism of the reaction was made by studying the tricyanovinylation of polymers from *p*-anisyl- and 2-fluorenyliminodiethanols.

In the preceding paper of this series, we described the synthesis of electron-rich donor polymers derived from substituted aryliminodiethanols.[1] With most acceptors, these polymers formed the expected charge-transfer complexes. The notable exception was tetracyanoethylene (TCNE). We found that some of these polymers underwent electrophilic attack to give tricyanovinylated polymers. The reaction of N,N-dimethylaniline with tetracyanoethylene was first reported by Heckert.[2] Product III was a blue crystalline solid. Other derivatives were further elaborated by McKusick and coworkers.[3] Recent detailed investiga-



(1) T. Sulzberg and R. J. Cotter, *Macromolecules*, **2**, 146 (1969).
(2) R. E. Heckert, U.S. Patent 2,762,810 (Sept 11, 1956), assigned to E. I. du Pont de Nemours and Co.
(3) B. C. McKusick, R. E. Heckert, T. L. Cairns, D. D. Coffman, and H. F. Mower, *J. Amer. Chem. Soc.*, **80**, 2806 (1957).

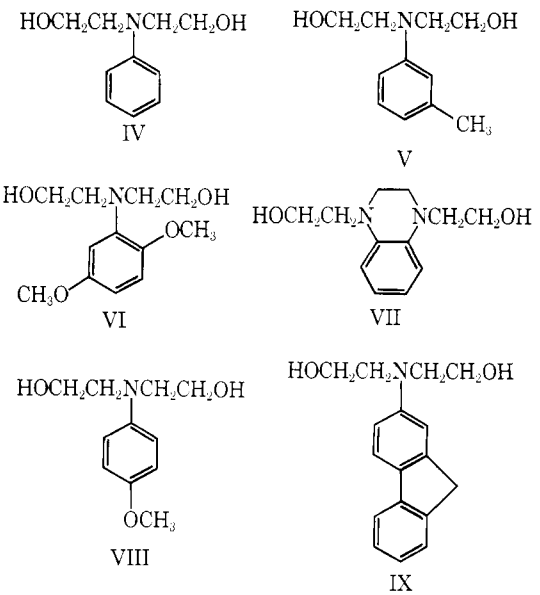
TABLE I

TRICYANOVINYLATION OF POLYARYLIMINODIETHANOL POLYMERS

No.	Polyaryliminodiethanol[a]	R.V.[b]	Molar ratio (TCNE/ polymer)	Solvent[c]	Reaction temp, °C	Product: Yield, %	Product: R.V.[b]	Product: Tricyanovinylation,[d] %
1	Poly(PI diol isophthalate)	0.23	1.0	DMF	60	42	0.19	33
2	Poly(PI diol isophthalate)	0.23	2.0	DMF	60	74	Insoluble	51
3	Poly(PI diol isophthalate)	0.23	1.0	Pyridine	55	76	0.22	
4	Poly(PI diol bisphenol A carbonate)	0.52	0.94	DMF	50	82	0.46	25
5	Poly(*m*-TI diol bisphenol A carbonate)	0.39	0.94	DMF	50	79	0.37	12
6	Poly(*m*-TI diol bisphenol A carbonate)	0.59	1.5	DMF	50	78	0.56	
7	Poly(2,5-diOMe PI diol bisphenol A carbonate)	0.29	1.0	DMF	50	67	0.26	15
8	Poly(THQ diol bisphenol A carbonate)	0.23	1.2	Pyridine	50	75	0.21	

[a] PI diol = phenyliminodiethanol; 2,5-diOMe PI diol = 2,5-dimethoxyphenyliminodiethanol; *m*-TI diol = *m*-tolyliminodiethanol; THQ diol = 1,2,3,4-tetrahydroquinoxaline-N,N′-diethanol. [b] Reduced viscosities in chloroform at 25° at 0.2 g/100 ml. [c] DMF = N,N-dimethylformamide. [d] The degree of tricyanovinylation was calculated from the per cent nitrogen that was present before and after reaction.

tions have shed light on the mechanism of the tricyanovinylation reaction.[4-7] In this paper, we describe the reaction of tetracyanoethylene with polyesters and polycarbonates of aryliminodiethanols IV–IX.



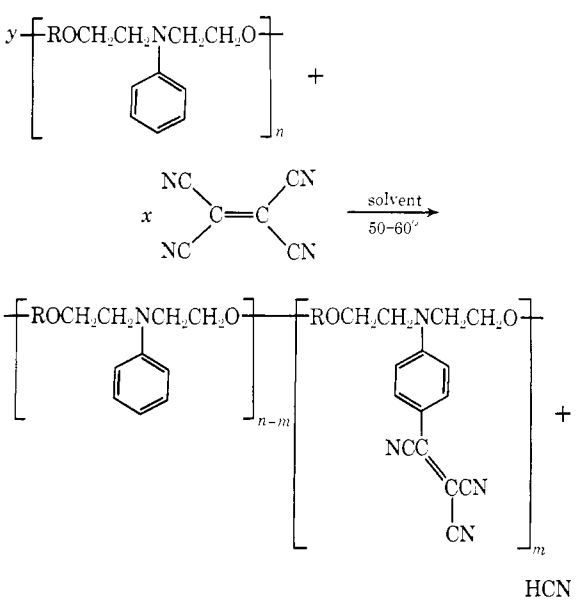
Experimental Section

The syntheses of the aryliminodiethanol monomers and polymers were described earlier.[1]

Tricyanovinylation. A solution of poly(*m*-tolyliminodiethanol bisphenol A carbonate) (1.92 g, 4×10^{-3} mol; reduced viscosity = 0.59 in chloroform) in 50 ml of pyridine was warmed to 50° with stirring under an atmosphere of nitrogen. Tetracyanoethylene (0.60 g, 4.7×10^{-3} mol) was added portionwise to the stirred polymer solution. It immediately turned a deep red. After 1 hr the solution was coagulated in methanol in a Waring Blendor. After washing twice with water and drying at 50°, 1.85 g (77%) of the red tricyanovinylated polymer (reduced viscosity = 0.56 in chloroform) was obtained. The infrared spectrum (film) had a strong cyano absorption band at 4.50 μ. The visible spectrum in chloroform had a strong absorption at 492 mμ (see Table IV for a comparison with previous work).

Discussion

A. Synthesis. The preparation of the highly colored, tricyanovinylated polyaryliminodiethanol esters and carbonates, which was readily accomplished in either N,N-dimethylformamide or pyridine, is depicted by the general equation



where R is the divalent radical from a diacid halide, and *m* is a function of *x*/*y* and the specific substituents present on the aromatic ring. The synthetic data, which are given in Table I, show that changing *x*/*y* from 1.0 to 2.0 (no. 1 and no. 2) increases the per cent of aromatic substitution from 33 to 51. The reaction appears to be susceptible to steric hindrance since the two *meta* substituted polymers (no. 5 and no. 7) give about one-half the degree of tricyanovinylation that

(4) Z. Rappaport, *J. Chem. Soc.*, 4498 (1963).
(5) N. S. Isaacs, *ibid.*, *B*, 1053 (1966).
(6) P. G. Farrell, J. Newton, and R. F. M. White, *ibid.*, *B*, 637 (1967).
(7) E. M. Kosower, *Progr. Phys. Org. Chem.*, **3**, 81 (1965).

the unsubstituted material (no. 4) does. The effect is even more pronounced since the less reactive polymers contain stronger electron donor groups and should be more nucleophilic.

It is interesting to note the mild conditions necessary to effect this reaction. This is dramatically illustrated by the negligible decrease in molecular weight of the polymer that occurs after reaction with tetracyanoethylene.

B. Physical Properties. i. Mechanical Properties. The mechanical properties of poly(*m*-tolyliminodiethanolbisphenol A carbonate) and two tricyanovinylated derivatives are given in Table II. Only small changes in their properties occurred. In fact, all three polymers were relatively tough, flexible materials.

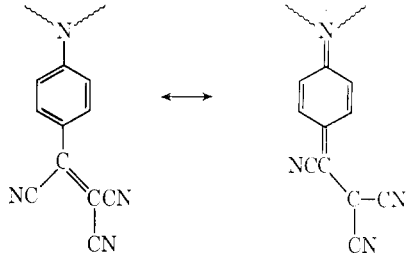
TABLE II

MECHANICAL PROPERTIES OF POLY(*m*-TOLYLIMINODIETHANOL BISPHENOL A CARBONATE) AND ITS TRICYANOVINYLATED DERIVATIVES

Solvent		DMF	DMF
TCNE/polymer ratio		1	1.5
Reduced viscosity	0.59	0.57	0.56
T_g,[a] °C	50	60	Room temp
Tensile modulus, psi	280,000	245,000	225,000
Tensile strength, psi	5,800	5,800	6,000
Elongation, %	15	18	5
Pendulum impact, ft lbs/cu in.	15	15	2-3

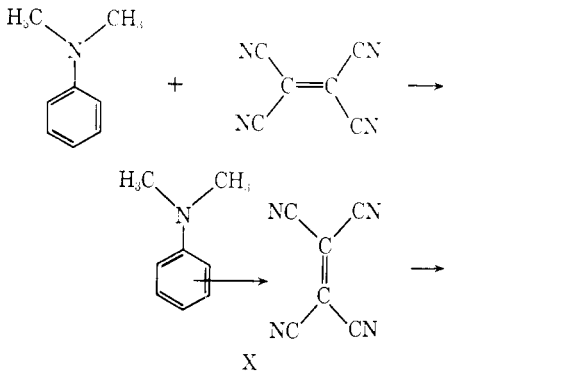
[a] The glass transition temperature was measured by determining recovery characteristics as a function of temperature [see A. Brown, *Textile Res. J.*, **25**, 891 (1955)].

ii. Visible Spectra. The brilliant colors exhibited by the tricyanovinylated polymers are due to the interaction of the strong electron-donating with the strong electron-accepting groups on the same aromatic ring. This interaction leads to the low energy resonance structures



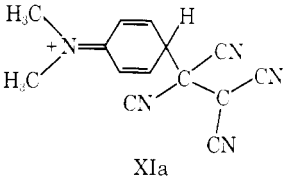
The colors of the polymers, which were found to vary with the aryliminodiethanol used, are listed in Table III. As anticipated, electron-donating groups caused the absorption maxima to shift to longer wavelengths. Changing the groups on the amine nitrogen of the tricyanovinylated species was shown to affect the position of the maximum absorption (see Table IV).

C. Mechanism. The mechanism of N,N-dimethylaniline tricyanovinylation was postulated by Rappoport to be a three-step reaction:[4] (i) rapid formation of a 1:1 π complex (X), (ii) formation of a σ complex that is first order in dimethylaniline and in the π complex, and (iii) slow formation of N,N-dimethyl-4-tricyanovinylaniline that is first order in σ complex



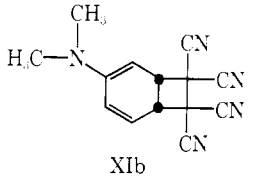
σ complex $\xrightarrow{-HCN}$ III

and in dimethylaniline. The σ complex, which was observed spectrophotometrically, was thought to be XIa. However, Kosower[7] favored the bicyclo[4.2.0]-



XIa

octa-2,4-diene structure XIb. As a means of distinguish-

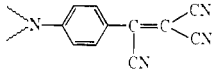
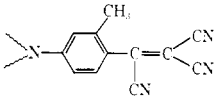
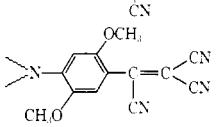
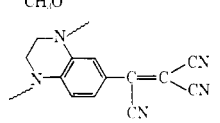


XIb

ing between structures XIa and XIb for the σ complex, we studied the reaction of poly(bisphenol A *p*-anisyliminodiethanol carbonate) (XII) with tetracyano-

TABLE III

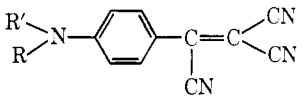
VISIBLE SPECTRA OF TRICYANOVINYLATED POLYARYLIMINODIETHANOL CARBONATES

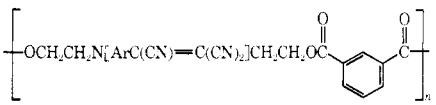
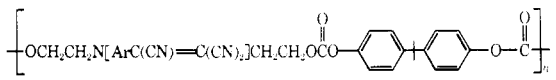
Tricyanovinylated[a] polymer species	λ_{max},[b] mμ	Color
	492	Red
	513	Red
	535 395	Purple
	590 435	Green

[a] The polymers are the 1:1 copolycarbonates of IV–VII and bisphenol A that were treated with tetracyanoethylene in DMF at 50°. [b] Spectra were determined in chloroform on the Cary 14 spectrophotometer.

TABLE IV

VISIBLE SPECTRA OF N,N-DISUBSTITUTED TRICYANOVINYLATED PHENYLIMINO COMPOUNDS

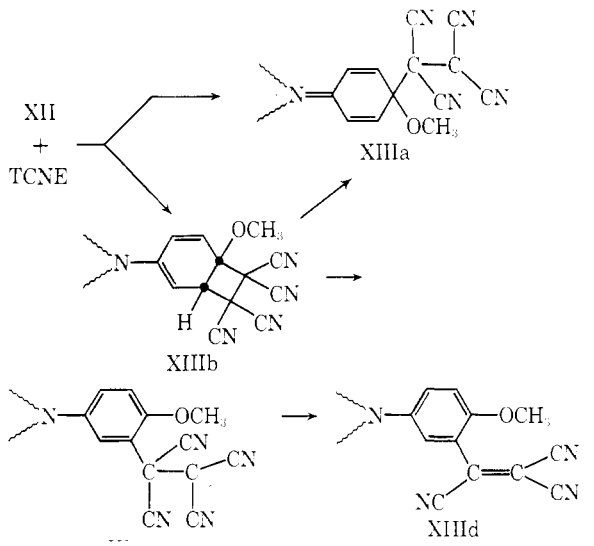


No.	Compound	λ_{max},[a] mμ
1	R = R′ = 	492
2	R = R′ = $PhCOOCH_2CH_2-$	505[b]
3	R = R′ = 	507
4	R = CH_3-; R′ = $PhCOOCH_2CH_2-$	510[b]
5	R = R′ = CH_3-	514[b]
6	R = R′ = CH_3-	515
7	R = R′ = CH_3CH_2-	521[b]

[a] Spectra were determined in chloroform on the Cary 14 spectrophotometer. [b] Reference 3.

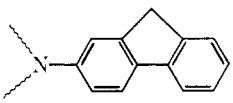
ethylene. The possible mechanisms are given in Scheme I. If XIIIb is the intermediate, then some

SCHEME I

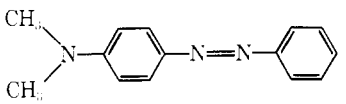


XIIId should be formed. In actual practice, no tricyanovinylation occurred in dimethylformamide at 60° for 2 hr. This evidence favors structure XIIIa, and therefore XIa, for the σ complex. Recently Farrell has claimed to have isolated the σ complex and assigned to it structure XIa.[6]

The specificity of the tricyanovinylation reaction was demonstrated by the reaction of a polymer of 2-fluorenyliminodiethanol (XIV) and *p*-dimethylaminoazobenzene (XV) with tetracyanoethylene. Since no reaction occurred in either case, we conclude that the *ortho* position is too sterically hindered and the *para* prime position too weakly nucleophilic to be tricyanovinylated under the present conditions.



XIV



XV

Conclusions

The reaction of tetracyanoethylene with the polyesters and polycarbonates of several aryliminodiethanols was studied. The resulting tricyanovinylated polymers were deeply colored materials possessing similar mechanical properties as the starting polymers. Evidence was presented favoring one of the proposed reaction pathways.

Acknowledgment. We gratefully acknowledge the highly competent technical assistance of Mr. Peter J. Degen.