Charge-Transfer Complexing in Polymer Mixtures. II. Donor Polymers from Aryliminodiethanols[1a]

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ABSTRACT: A series of electron donor polymers was prepared from aryliminodiethanols [$ArN(CH_2CH_2OH)_2$], where Ar is (a) phenyl, (b) *m*-tolyl, (c) *p*-anisyl, (d) 2,5-dimethoxyphenyl, (e) 3,4,5-trimethoxyphenyl and (f) 2-fluorenyl. In addition, the diethanol derivative of tetrahydroquinoxaline was prepared. Those polymers prepared at high molecular weight were tough, soluble, linear materials of well-defined structure. As a means of determining their donor abilities, charge-transfer complexes with chloranil and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone were studied and compared with model compounds.

Polymer chain-to-chain interactions are receiving increased research attention by polymer chemists. While hydrogen and ionic bonding have long been recognized as important contributors to polymer properties, interactions due to molecular complexing have only recently been studied. Some aspects of charge-transfer bonding in polymeric systems were recently reviewed.[1b–d]

Molecular complexes, which have been known for many years, were first reviewed in 1927.[2] It wasn't until 1952, however, that their theoretical aspects were explained and the term "charge-transfer" introduced by Mulliken.[3] Since then, the charge-transfer phenomenon has been studied from many viewpoints including spectra,[4] reactivity[5] and conductivity.[6] It is in the last area that most of the charge-transfer research in polymers was directed. The preparation of polymeric semiconductors, that have useful mechanical properties, was a goal of many workers. However, most of the materials prepared were dark, insoluble, brittle and, in some cases, ill-defined solids.

The purpose of our study was to prepare well-defined polymers which not only would undergo charge-transfer complexing with each other but would also possess usable mechanical properties, *e.g.*, toughness. In this paper we describe the synthesis and properties of the donor polymers. In subsequent papers in this series the acceptor polymers and the charge-transfer polymer mixtures will be reported.

The donor polymers which were previously described are almost exclusively of the addition type, *e.g.*, polystyrene,[7] polyacenaphthylene,[8] poly(vinylanthracene),[9] poly(2- and 4-vinylpyridine),[10] poly(N-vinylcarbazole)[11] and poly(phenylene).[12] Since these materials are generally quite brittle, we prepared condensation polymers for donors containing functional groups known to impart toughness.

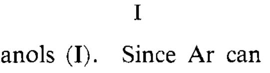
TABLE I

ELECTRIC MOMENTS OF BENZENE DERIVATIVES (C_6H_5A) SUBSTITUTED WITH ELECTRON-DONATING GROUPS[a]

A	Electric moment,[b] D
$N(CH_3)_2$	1.6
OH	1.6
NH_2	1.5
SH	1.3
OCH_3	1.2
CH_3	0.3
H	0

[a] C. R. Noller, "Chemistry of Organic Compounds," W. B. Saunders Co., Philadelphia, Pa., 1957, p 451. [b] The direction of the electric moment is toward the aromatic ring.

In order to obtain maximum intermolecular donor properties from a given aromatic ring, it should contain only electron donating groups. To determine which substituent would contribute the greatest amount of electron density to an aromatic ring, the electric moments of benzene derivatives are compared in Table I. The N,N-dimethylamino group is the best of the non-acidic substituents. A class of difunctional monomers that incorporates the dialkylamino group is the



$$HOCH_2CH_2\underset{\displaystyle Ar}{N}CH_2CH_2OH$$

I

aryliminodiethanols (I). Since Ar can be any substituted or unsubstituted aromatic ring, a wide range of donor capabilities is available.

No homopolyesters or carbonates of I were previously described but a few reports of its incorporation into copolymers were noted. Lincoln and coworkers used phenyliminodiethanol (PI diol) as a comonomer in polyethylene terephthalate preparations (up to 1%

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(1) (a) Paper I: T. Sulzberg and R. J. Cotter, *Macromolecules*, **1**, 554 (1968); (b) M. M. Labes, *J. Polym. Sci., Part C*, 95 (1967); (c) F. Gutman and L. E. Lyons, "Organic Semiconductors," John Wiley & Sons, Inc., New York, N. Y., 1967; (d) D. A. Seanor, *Advan. Polym. Sci.*, **4**, 317 (1965).

(2) P. Pfeiffer, "Organische Molekulverbindungen," 2nd ed, Ferdinand Enke, Stuttgart, Germany, 1927.

(3) R. S. Mulliken, *J. Amer. Chem. Soc.*, **74**, 811 (1952).

(4) J. N. Murrell, *Quart. Rev.* (London), **15**, 191 (1961).

(5) E. M. Kosower in "Progress in Physical Organic Chemistry," Vol. 3, Interscience Publishers, New York, N. Y., 1965.

(6) Y. Okamato and W. Brenner, "Organic Conductors," Reinhold Publishing Corp., New York, N. Y., 1964.

(7) W. Slough, *Trans. Faraday Soc.*, **58**, 2360 (1962), and British Patent 1,009,361 (Nov 10, 1965).

(8) A. Inami, K. Morimoto, and Y. Kayashi, *Bull. Chem. Soc. Jap.*, **37**, 842 (1962).

(9) H. Inoue, K. Noda, T. Takiuchi, and E. Imoto, *Kogyo Kagaku Zasshi*, **65**, 1286 (1962); *Chem. Abstr.*, **58**, 1539*a* (1963).

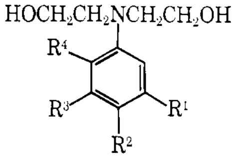
(10) S. B. Mainthia, P. L. Kronick, and M. M. Labes, *J. Chem Phys.*, **41**, 2206 (1964).

(11) A. M. Hermann and A. Rembaum, *J. Polym. Sci., Part C*, 107 (1967).

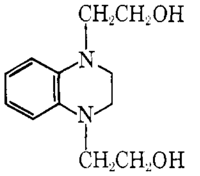
(12) S. B. Mainthia, P. L. Kronick, H. Ur, E. F. Chapman and M. M. Labes, *Polym. Preprints*, **4**, 208 (1963).

nitrogen) for increasing dye affinity.[13] Various ring-substituted phenyliminodiethanols were claimed to be useful in amounts up to 25 mol % for the same purpose.[14] Recently, brief mention was made of using PI diol in cross-linked polyester formulations.[15]

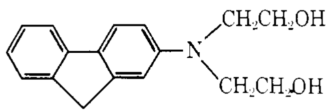
In this paper, the preparation and the properties of polymers from aryliminodiethanols II–VIII are discussed. Subsequent papers will detail work on preparing acceptor polymers and their interactions with the donor polymers.



II, $R_1 = R_2 = R_3 = R_4 = H$ (PI diol)
III, $R_1 = CH_3$; $R_2 = R_3 = R_4 = H$ (m-TI diol)
IV, $R_2 = OCH_3$; $R_1 = R_3 = R_4 = H$ (*p*-AI diol)
V, $R_1 = R_4 = OCH_3$; $R_2 = R_3 = H$ (2, 5-di-OMe PI diol)
VI, $R_1 = R_2 = R_3 = OCH_3$; $R_4 = H$ (3, 4, 5-tri-OMe PI diol)



VII (THQ diol)



VIII (2-FI diol)

Experimental Section

Monomers. Phenyliminodiethanol and *m*-tolyliminodiethanol are commercially available (Matheson Coleman and Bell) and were recrystallized several times from benzene–*n*-hexane. They melted at 58–59 and 70–71°, respectively (lit.[16] mp 55 and 72–73°).

p-Anisyliminodiethanol was prepared from *p*-anisidine and ethylene oxide (sealed tube, 100°) by the method of Ross,[16] mp 69–70° (lit.[16] mp 70–71°). 2-Fluorenyliminodiethanol was similarly prepared in a stainless steel bomb at 150°, mp 134–136° (lit.[17] mp 136–137°). Bisphenol A dichloroformate, mp 95–96°, was recrystallized from *n*-heptane. Isophthaloyl chloride, mp 44–45°, was recrystallized from *n*-hexane.

2,5-Dimethoxyphenyliminodiethanol. A mixture of 1 mol of 2,5-dimethoxyaniline and 2 mol of ethylene oxide was allowed to react in a sealed tube at 100° for 2 days. The resulting black liquid was flash distilled at 120–136° (0.02–0.04 mm). The distillate contained a solid (2,5-dimethoxyaniline) and a liquid. The latter, compound V, was redistilled at 125–128° (0.03 mm). Its structure is based on method of synthesis, infrared spectrum (hydroxyl and $-CH_2CH_2-$ bands present, but no aryl N–H bands) and polymerization with bisphenol A dichloroformate which gave a polymer, in quantitative yield, whose reduced viscosity was 0.29. The nmr spectrum in chloroform of this polymer showed 11 aromatic protons at 6.6–7.2 ppm, four $-OCH_2$ protons at 4.2–4.5 ppm, six $-OCH_3$ protons and four $-NCH_2-$ protons at 3.78 and 3.84 ppm, and six $-CH_3$ protons at 1.67 ppm.

3,4,5-Trimethoxyphenyliminodiethanol (VI). A mixture of 1 mol of 3,4,5-trimethoxyaniline and 2 mol of ethylene oxide were allowed to react as above. The resulting dark, viscous oil was distilled at 170–194° (0.07 mm) to give 79% of 3,4,5-trimethoxyphenyliminodiethanol. Proof of structures is based on the method of synthesis, infrared spectrum (a broad –OH band at 2.90 μ, no sharp aromatic N–H doublet at 2.88 and 2.97 μ, a C–O stretching band at 9.55 μ and an –OH deformation band of 7.05 μ), and polymerization with bisphenol A dichloroformate which gave an 82% yield of a polycarbonate with a reduced viscosity of 0.21.

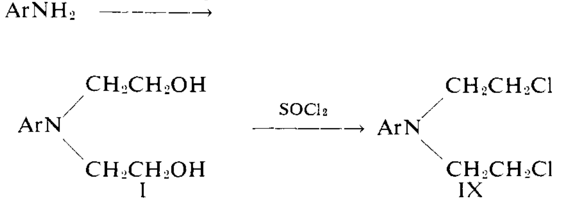
Tetrahydroquinoxalinediethanol (VII). A. Tetrahydroquinoxaline. Quinoxaline (10 g, 0.077 mol), lithium aluminum hydride (5 g, 0.13 mol), and 100 ml of dry ether were refluxed on a steam bath for 24 hr. A saturated solution of ammonium chloride was added slowly to the cooled reaction mixture to decompose the excess lithium aluminum hydride. The mixture was filtered, the solid washed with ether and the combined ether solutions were dried over magnesium sulfate. The ether was removed under vacuum and the residue recrystallized from 135 ml of a 1:1 benzene–*n*-hexane mixture. The tetrahydroquinoxaline (4.6 g, 45%) melted at 97–98° (lit.[18] mp 97.5°). Infrared spectrum had an N–H band at 3.08 μ.

B. Tetrahydroquinoxalinediethanol (VII). A mixture of tetrahydroquinoxaline (3.5 g, 0.037 mol) and ethylene oxide (3.3 g, 0.074 mol) was allowed to react in a stainless steel bomb (150°, 18 hr). The resulting viscous brown liquid was distilled at 210° (0.65 mm) to give 4.0 g of a brown (oxidizable!) liquid, yield 46%. Its infrared spectrum had an O–H band at 2.9 μ and no N–H band at 3.08 μ. Reaction with bisphenol A dichloroformate gave 77% yield of a polycarbonate with a reduced viscosity of 0.23.

Polymer Preparation. All of the polymers were best prepared *via* a low-temperature solution procedure as typified by the synthesis of poly(phenyliminodiethanol bisphenol A carbonate). A mixture of 1.81 g (0.01 mol) of phenyliminodiethanol, 3.53 g (0.01 mol) of bisphenol A dichloroformate and 40 ml of 1,2-dichloroethane (dried over molecular sieves, type 4A) was heated to 70° under a stream of argon. Pyridine (3 ml, 0.038 mol) was added all at once *via* a syringe. The solution, which reached reflux almost immediately, underwent several color changes (yellow to red to yellow to pale yellow) and a rapid buildup in viscosity (several minutes). After 1 hr, the reaction mixture was cooled, coagulated in 300 ml of methanol in a high-speed blender and the polymer collected. After washing twice with water in the blender, the colorless polymer was dried at 50° (20 mm). The polycarbonate, which was obtained in a yield of 93%, had a reduced viscosity of 0.52 (determined in chloroform at 25° using 0.2 g/100 ml).

Results and Discussion

Synthesis. Aryliminodiethanols (I), which are precursors to the N-phenylnitrogen mustards (IX), are readily prepared from an amine and ethylene oxide.



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[13] J. Lincoln, K. M. Hammond, and W. H. Groombridge, British Patent 734,416 (August 3, 1955).

[14] J. R. Caldwell and J. W. Wellman, U.S. Patent 2,899,408 (August 11, 1959).

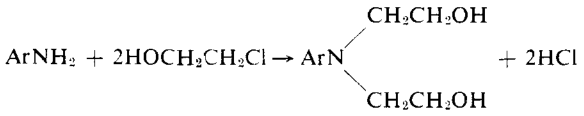
[15] A. D. Valgin, V. V. Korshak, and D. F. Kutepov, *Polym. Sci. USSR*, **8**, 204 (1966).

[16] W. C. J. Ross, *J. Chem. Soc.*, 183 (1949).

[17] J. L. Everett and W. C. J. Ross, *ibid.*, 1972 (1949).

[18] F. Bahlmann, *Ber.*, **85**, 390 (1952).

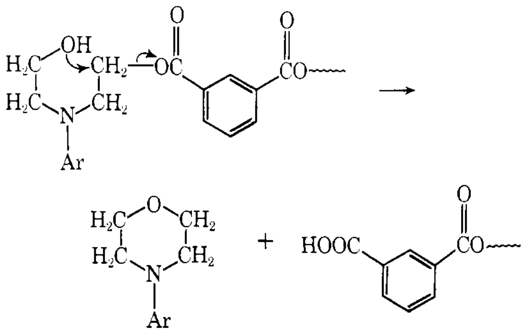
The reaction with ethylene oxide, which can be carried out in aqueous solution[19] or without solvent in a sealed tube,[16] gives high purity product. This is in contrast to the more difficult, alternate procedure which used ethylene chlorohydrin and an amine.[20]



$$ArNH_2 + 2HOCH_2CH_2Cl \rightarrow ArN(CH_2CH_2OH)_2 + 2HCl$$

These compounds (II–VI), especially those with additional electron-donating substituents and a free *para* position, were susceptible to air oxidation. After purification (distillation or recrystallization), they were stored under argon in sealed vessels. The polymers prepared from these aryliminodiethanols, however, were much less prone to oxidation.

The use of high-temperature, base-catalyzed melt procedures to prepare polyesters from the aryliminodiethanols led to low molecular weight, apparently decomposed polymers. In the reaction of phenyliminodiethanol with a diester of isophthalic acid, side reaction 1 probably interferes. Similarly, the uncatalyzed, high temperature (>200°) reaction of PI diol and isophthaloyl chloride gave much visible decomposition during reaction. A possible side reaction is the hydrogen chloride catalyzed Friedel–Crafts acylation of the highly nucleophilic aromatic ring by isophthaloyl chloride (reaction 2).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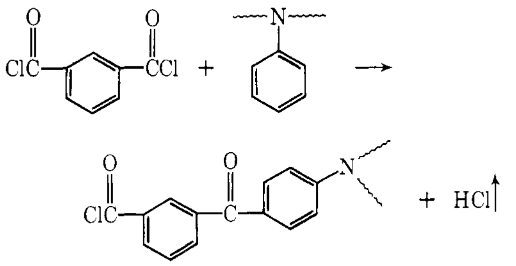
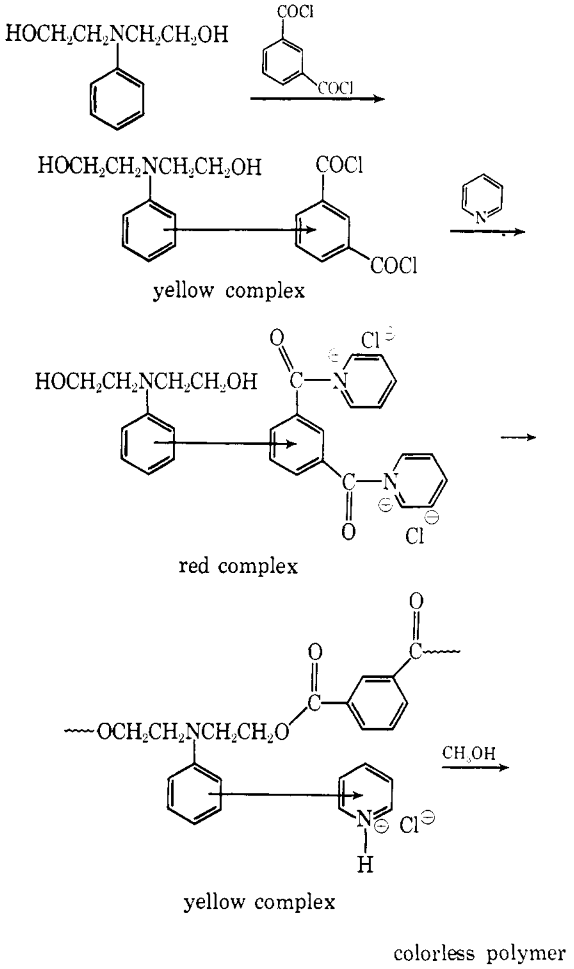

(2)

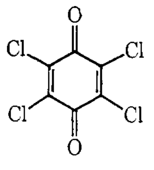
Since the high temperature, long reaction time methods are unsuitable, a very rapid, low temperature technique was developed. The monomers were dissolved in 1,2-dichloroethane (at a concentration that will give a solution containing 1 g of polymer/10 ml of solvent) and heated to 70° under an inert atmosphere. A 50% molar excess of pyridine was added and the reaction quickly exothermed to reflux (84°). This was accompanied by a series of color changes. Some postulated species that could cause these colors are depicted in Scheme I. Even though the reaction solutions change in color from yellow to red to yellow, the final products were colorless. The reaction rate is extremely high since viscous solutions are noted in a matter of minutes.

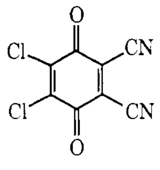
SCHEME I

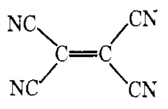


Mechanical Properties. The mechanical properties of the high molecular weight aryliminodiethanol polymers and poly(bisphenol A carbonate) are given in Table II. A complete list of the polymers prepared is given in Table III.

Donor–Polymer Complexing with Monomeric π Acceptors. To determine the relative donor abilities of the aryliminodiethanol polymers, a study of their complexes with chloranil (X), 2,3-dicyano-5, 6-dichloro-*p*-benzoquinone (XI) and tetracyanoethylene (XII) was undertaken. We found, however, that the last acceptor


X


XI


XII

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(19) M. H. Benn, L. N. Owen, and A. M. Creighton, *J. Chem. Soc.*, 2800 (1958).

(20) R. M. Anker, A. H. Cook, and I. M. Heilbron, *ibid.*, 917 (1945).

TABLE II

HIGH MOLECULAR WEIGHT ARYLIMINODIETHANOL POLYMER PROPERTIES[a]

Polymer	R.V.[b]	T_g[c]	T_m[d]	Tensile modulus, psi	Tensile strength, psi	Elongation, %	Impact, ft lbs/cu in.
Poly(PI diol bisphenol A carbonate)	0.52	70					
Poly(PI diol isophthalate)	0.35	60	120	275,000	5,000	2.3	4
Poly(*p*-AI diol bisphenol A carbonate)	0.80	60		335,000	5,000	5	6–9
Poly(PI diol bisphenol A carbonate) (1:19)	0.90	110		250,000	7,900	140	110
Poly(2-FI diol bisphenol A carbonate)	0.82	90		310,000	6,000	12	10
Poly(bisphenol A carbonate)	0.80	150		320,000	9,000	100	400

[a] Determined on films cast from chloroform. [b] Reduced viscosity in chloroform at 25° at 0.2 g/100 ml of solvent. [c] The glass transition temperature was measured by determining recovery characteristics as a function of temperature [see A. Brown, *Textile Res. J.*, **25,** 891 (1955)] in °C. [d] Crystalline melting point (°C).

TABLE III

ARYLIMINODIETHANOL POLYMERS

No.	Polymer	R.V.[a]
1	Poly(PI diol isophthalate)	0.35
2	Poly(PI diol bisphenol A carbonate) (50:50)	0.52
3	Poly(*m*-TI diol isophthalate)	0.32
4	Poly(*m*-TI diol bisphenol A carbonate) (50:50)	0.59
5	Poly(*p*-AI diol isophthalate)	0.22
6	Poly(*p*-AI diol bisphenol A carbonate) (50:50)	0.80
7	Poly(*p*-AI diol bisphenol A carbonate) (5:95)	0.90
8	Poly(*p*-AI diol bisphenol A carbonate) (25:75)	0.46
9	Poly(2,5-dimethoxy PI diol isophthalate)	0.24
10	Poly(2,5-dimethoxy PI diol bisphenol A carbonate) (50:50)	0.29
11	Poly(3,4,5-trimethoxy PI diol isophthalate)	0.14
12	Poly(3,4,5-trimethoxy PI diol bisphenol A carbonate) (50:50)	0.21
13	Poly(THQ diol isophthalate)	0.08
14	Poly(THQ diol bisphenol A carbonate) (50:50)	0.23
15	Poly(2-FI diol isophthalate)	0.17
16	Poly(2-FI diol bisphenol A carbonate) (50:50)	0.82

[a] Reduced viscosity in chloroform at 25° at 0.2 g/100 ml of solvent.

TABLE IV

VISIBLE SPECTRA OF ELECTRON DONORS WITH CHLORANIL

Compound	λ_{max}, mμ	χ_i[d]
Benzene	347[a]	1.000
Biphenyl	441[a]	0.704
Anisole	448[a]	0.827
Naphthalene	478[a]	0.618
1,4-Dimethoxybenzene	543[b]	0.692
Anthracene	625[a]	0.662
N,N-Dimethylaniline	654[c]	0.586
N,N-Dimethyl-*m*-anisidine	676[c]	0.576
N,N-Dimethyl-*p*-anisidine	730[c]	0.504

[a] G. Briegleb, "Elektronen-Donator-Acceptor Komplexe," Springer-Verlag, Berlin, 1961. [b] A. Zweig, J. E. Lehnsen, and M. A. Murray, *J. Amer. Chem. Soc.*, **85,** 3933 (1963). [c] A. Zweig, J. E. Lancaster, M. T. Neglia, and W. H. Jura, *ibid.*, **86,** 4130 (1964). [d] Huckel coefficients of the energies of the highest occupied molecular orbital (see footnote *c*).

TABLE V

VISIBLE SPECTRA OF DONOR POLYMERS AND SUBSTITUTED DIMETHYLANILINES WITH CHLORANIL

Polyisophthalate of	λ_{max}, mμ	Substituted dimethylaniline	λ_{max}, mμ[a]
II	635	H	654
III	660	*m*-OCH_3	676
IV	735	*p*-OCH_3	730

[a] See Table IV, footnote *c*.

(XII) reacted with some of the polymers. This reaction will be discussed in detail in a succeeding paper.[21] The spectra and conductivity of complexes of X and XI with donor polymers were determined.

A. Spectra. The classical method for determining the strength of charge-transfer complexes is *via* ultraviolet and visible spectrophotometry.[22] A linear relationship exists such that, with a given acceptor, a decrease in the ionization potential of the donor gives charge transfer absorption maxima at a higher wavelength. The relative strengths of the donor polymers are seen from the data in Tables IV and V. Table IV, which compares the absorption maxima of some donor–chloranil complexes with the calculated energy coefficients of the highest occupied molecular orbital of the donor,[23–25] confirms the high donor capability of substituted anilines. With only a simple substitution on the benzene ring, *i.e.*, the dimethylamino group, we obtained a powerful donor species. The applicability of this data to the aryliminodiethanol polymers is demonstrated in Table V.

B. Conductivity. Since the formation of donor–acceptor complexes can be visualized as an electronic interaction between polarized molecules, they should be better electrical conductors than the uncomplexed materials. The data in Table VI demonstrate the

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(21) T. Sulzberg and R. J. Cotter, to be published.

(22) L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964.

(23) C. A. Coulson and R. Daudel, "Dictionary of Values of Molecular Constants," 2nd ed, Centre de Chemie Théoriqué de France, Paris, France, 1959.

(24) (a) See Table IV, footnote *b*. (b) See Table IV, footnote *c*.

(25) See Table IV, footnote *a*.

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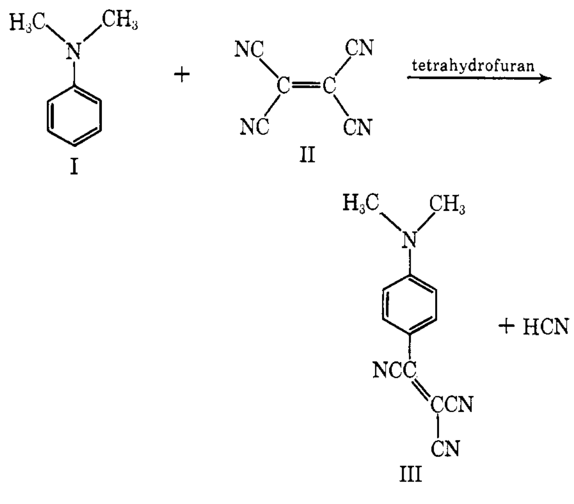
ABSTRACT: The reaction of tetracyanoethylene with the polyesters of several aryliminodiethanols was investigated. The products have the general formula

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

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-



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[2] R. E. Heckert, U.S. Patent 2,762,810 (Sept 11, 1956), assigned to E. I. du Pont de Nemours and Co.

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