Synthesis of Electron Acceptor Monomers and Their Copolymers with N-Vinylcarbazole

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ABSTRACT: The synthesis and characterization of eight new acrylate, methacrylate, and styryl monomers containing strongly electron accepting di- or tricyanovinyl groups are described. These monomers copolymerized radically with N-vinylcarbazole, and the properties of the copolymers are presented.

In the preceding paper[1a] the synthesis of monomers and polymers containing the electron-donating dithiole ring was described. Such compounds are of interest because of their possible electrical conductivity.[2] Recently, it has been shown that the incorporation of electron-accepting groups into an N-vinylcarbazole copolymer enhances photoconductivity to a greater extent than incorporation of small molecules alone.[1b] In this paper, the synthesis of monomers and polymers containing electron-accepting groups is described.

Results and Discussion

The new acrylate and methacrylate monomers were synthesized starting with o- and p-hydroxybenzaldehyde as shown below. Sharp melting crystalline solids were obtained and the monomer structures were completely in accord with analytical and spectroscopic data (see Experimental Section).


Ia, R = H,
    para compound
Ib, R = H,
    ortho compound
IIa, R = CH₃,
    para compound
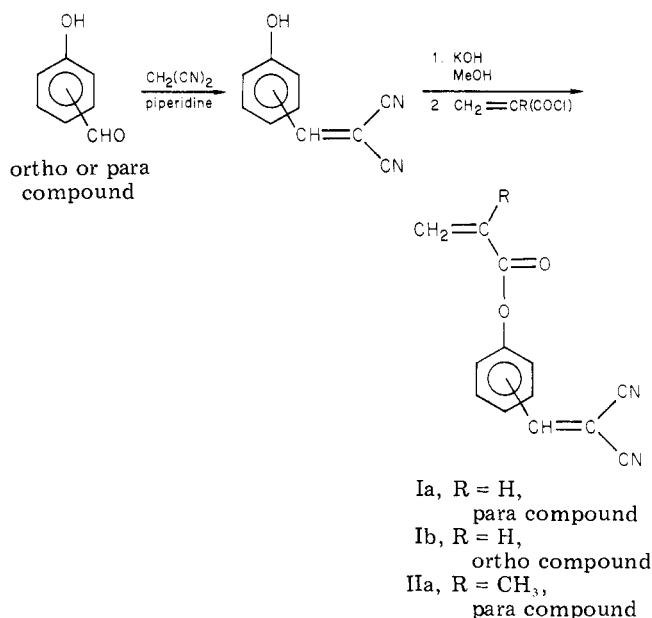
Compounds I and II are cyanostyrenes and such compounds are known to copolymerize.[3] In the case of I and II, such a reaction either in homo- or copolymerization would lead to cross-linking. In part to minimize this possibility, the compound containing a tetrasubstituted styryl double bond was synthesized in a manner analogous to that used for I and II.

In addition to the dicyanostyryl acrylates, it was of interest to prepare acrylate monomers with the more strongly electron-withdrawing tricyanostyryl unit. These compounds were synthesized starting with the previously prepared p-hydroxybenzylidenemalononitrile.

IIIa, R = H
   b, R = CH₃

IV
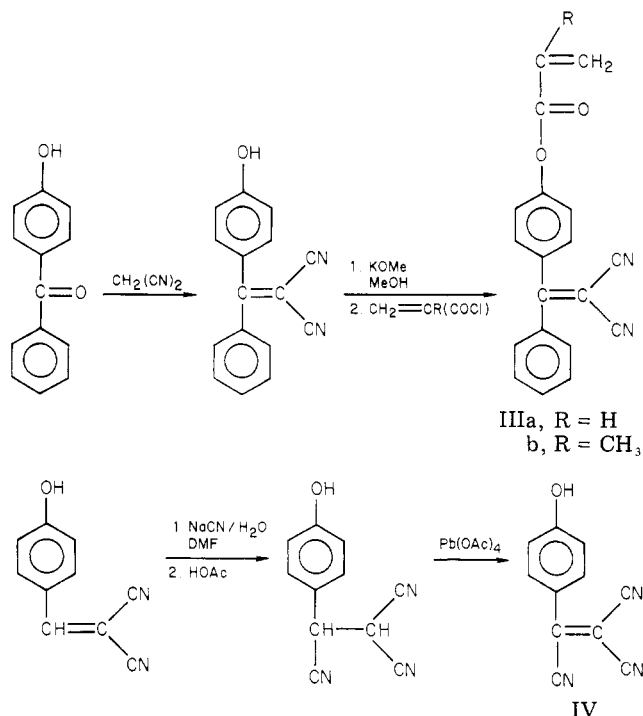
Oxidation of the HCN addition product using N-bromosuccinimide resulted in a mixture of compounds. However, oxidation with lead tetraacetate in acetic acid produced the α-cyano-p-hydroxybenzylidenemalononitrile (IV) in 70% yield. Attempted condensation of IV with acryloyl chloride and hydroxide or methoxide resulted only in the conjugate addition of the base to the tricyanovinyl group. However, using the nonnucleophilic base 2,2,6,6-tetramethylpiperidine (TMP) in tetrahydrofuran the acrylate V was obtained in 53% yield.

V
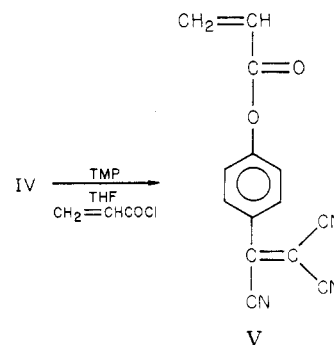
Our objective was to prepare monomers with strongly electron accepting functional groups. The acrylate monomers described here meet that criterion; the presence of an unshared pair of electrons on oxygen attached to the

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Table I
Ultraviolet Absorption Data for New Monomers[a]

| monomer	mp, °C	λ_{max}, nm	ϵ
Ia	89.5–90.50	234	12 500
		323	14 500
Ib	114–115	295	9 850
IIa	105.0–105.5	318	14 800
IIIa	122.5–123.5	231	9 300
		307	11 300
IIIb	101–102	230	9 200
		305	11 100
V	108–109	247	5 740
		350	10 200
VI	113–114	230	10 000
		338	32 500
VII	124–125	243	11 000
		350	9 000

</div>

[a] Compounds I–III in absolute ethanol. Compounds V–VII in THF.

benzene ring could certainly have an effect, perhaps deleterious, on the electron accepting capacity of the di- or tricyanovinyl group. It is known that the p-acetoxy group is inductively electron withdrawing (Hammett σ = +0.31),[4] but it is not obvious what the effect of a p-acryloyl group would be on the electron-accepting capacity of the p-cyanovinyl substituent. We, therefore, synthesized the cyanovinylstyrene derivatives VI and VII.

p-Vinylbenzaldehyde was synthesized from p-chlorostyrene, and the crude product was treated directly with malononitrile and piperidine in ethanol giving an overall yield of 35% of VI.

p-(Tricyanovinyl)styrene (VII) was prepared from VI by hydrocyanation followed by lead tetraacetate oxidation in an overall yield of 20%.

Attempted radical homopolymerizations of the acrylic monomers using AIBN in refluxing benzene were not successful. Although polymerization conditions were not exhaustively studied, it is possible that once radical addition to a di- or tricyanovinyl group occurs, the resulting radical is too inert to carry the chain, and consequently
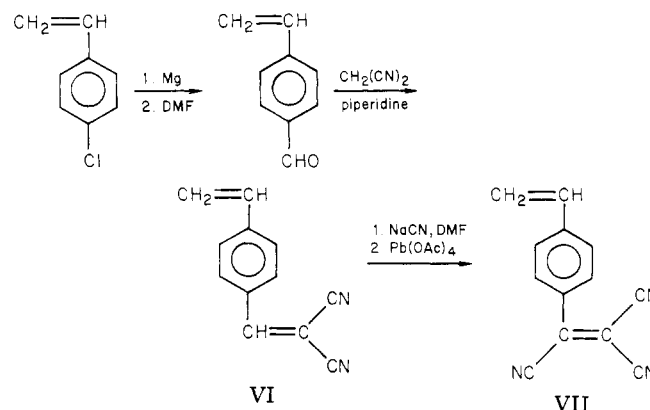
the monomer behaves as its own inhibitor.

The new monomers copolymerized with equimolar quantities of N-vinylcarbazole, using AIBN in refluxing THF. The copolymers contained 50–62% N-vinylcarbazole. Results are presented in Table I. Because N-vinylcarbazole is known to polymerize cationically in the presence of electron acceptors, it was necessary to determine if this process occurred with our monomers producing a mixture of homo poly(N-vinylcarbazole) and copolymer. The NMR spectrum of the products showed that they were copolymers. Poly(N-vinylcarbazole) has two exceptionally high field signals in the aromatic region of its NMR spectrum due to ring current interactions between adjacent carbazole units in the polymer.[5] This high field signal was absent in the copolymers synthesized here as was true in the case of n-butyl acrylate–N-vinylcarbazole copolymers.

The copolymers were all colored; the dicyano copolymers were dark-red or rust colored. Interaction between donor and acceptor units is indicated by the UV spectra in Table II.

Experimental Section

Melting points were determined on a Fisher-Johns melting point or Mel-Temp apparatus and are uncorrected. Nuclear

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Table II
N-Vinylcarbazole Copolymers[a]

comonomer	η_{inh}	mol % of VCbz	% of conv	THF λ_{max}, nm	THF ϵ	DMF λ_{max}, nm	DMF ϵ
Ia	0.080	56	19	320	7 260	330	3 860
						454	3 000
IIa	0.092	57	14	328	9 050	328	7 100
						340 s	6 000
						435 s	3 300
						453	5 830
IIIa	0.061	50.4	11.3	324	10 000	324	16 500
						340	13 900
						466	1 620
IIIb	0.047	53	8.5	330	6 830	330	15 700
				343	7 010	342	16 200
						460	2 770
V	0.083	62	15.7	315	7 360	330	5 630
				365 s	1 980	344	5 460
				420 s	132	497	5 400
						526	6 150
Ib	0.032	58	3.1	330 s	3 460	320	6 200
VI	0.11	50	25	320	3 700	321	11 900
VII			5			830	20 400
						340 s	19 700
						588	400
homo(VCbz)	0.14	100	25	329	1 330		
				341	1 280		

</div>

[a] The comonomers (1.00 mmol each) were heated under reflux in 10 mL of freshly distilled THF containing 2.1 mg of AIBN under nitrogen for 24 h. Purification was affected by three precipitations from THF into hexane followed by removal of solvent under vacuum. ϵ values are calculated on the basis of the concentration of monomeric units without regard to complex formation. They should be used for comparison only.

magnetic resonance spectra were determined on a Varian Model T-60 (60 MHz) NMR spectrometer, using tetramethylsilane as an internal standard. Infrared spectra were determined using a Perkin-Elmer infracord or a Perkin-Elmer Model 337 grating infrared spectrometer and calibrated with a polystyrene film. Ultraviolet and visible absorption spectra were determined utilizing a Cary 14 recording spectrometer. Viscosities were determined using Ubbelohde type viscometers. Inherent viscosities (dL/g) were determined in 0.5% solution at 30.0 °C.

Elemental analyses were determined by Huffman Laboratories, Inc., Wheatridge, Colo.

Tetrahydrofuran (THF, J. T. Baker Co.) was distilled from lithium aluminum hydride under nitrogen, stored over 8A molecular sieves under nitrogen, and passed through an alumina column prior to use. Benzene and toluene (J. T. Baker Co.) were distilled from sodium under nitrogen and stored over 3A molecular sieves under nitrogen. Dimethylformamide (DMF, Matheson Coleman and Bell) was distilled from KOH and stored under nitrogen. Acetonitrile (Mallinckrodt Chemical Works) was distilled from calcium hydride under nitrogen and stored over 3A molecular sieves under nitrogen.

Azobis(isobutryronitrile) (AIBN, Matheson Coleman and Bell) was recrystallized from methanol.

4-(2′,2′-Dicyanovinyl)phenol and 2-(2′,2′-Dicyanovinyl)-phenol. These compounds were prepared in 75 and 80% yield according to the procedure of Schiemenz.[6]

Potassium 4-(2′,2′-Dicyanovinyl)phenoxide. To 1.68 g of potassium hydroxide (30 mmol) in 50 mL of methanol was added 5.10 g (30 mmol) of 4-(2′,2′-dicyanovinyl)phenol with stirring. The bright yellow solution was filtered, the solvent removed, and the resulting solid vacuum dried to yield 6.24 g (90%) of potassium 4-(2′,2′-dicyanovinyl)phenoxide.

Potassium 2-(2′,2′-Dicyanovinyl)phenoxide. To 1.68 g (30 mmol) of potassium hydroxide in 50 mL of methanol was added 5.10 g (30 mmol) of 2-(2′,2′-dicyanovinyl)phenol with stirring. The orange-yellow solution was filtered, the solvent removed, and the resulting solid vacuum dried to yield 5.90 g (85%) of potassium 2-(2′,2′-dicyanovinyl)phenoxide.

4-(2′,2′-Dicyanovinyl)phenyl Acrylate (Ia). To 2.08 g (10 mmol) of potassium 4-(2′,2′-dicyanovinyl)phenoxide in 20 mL of dry ethyl ether was added 1.35 g (15 mmol) of acryloyl chloride dropwise with stirring under nitrogen. The reaction mixture was stirred for 1 h and filtered. The pale yellow filtrate was cooled to 0 °C and the solvent removed yielding crude crystals of 4-(2′,2′-dicyanovinyl)phenyl acrylate. The solid was recrystallized from benzene/hexane two times yielding 1.86 g (83%) of product, mp 89.5–90.5 °C. The NMR spectrum (CDCl$_3$) showed peaks centered at τ 2.00 (doublet, J = 8 Hz, 2 H) and 2.60 (doublet, J = 8 Hz, 2 H) assigned to the aromatic protons, τ 2.23 (singlet, 1 H) assigned to the dicyanovinyl proton, and τ 3.67 (multiplet, 3 H) assigned to the acrylate vinyl protons. The IR (KBr) spectrum showed a conjugated CN stretch at 2190 cm^{-1} and a conjugated ester carbonyl stretch at 1750 cm^{-1}.

Anal. Calcd for C$_{13}$H$_8$N$_2$O$_2$: C, 69.62; H, 3.57; N, 12.50; mol wt 224. Found: C, 69.62; H, 3.77; N, 12.22; mol wt (mass spectrum) 224.

2-(2′,2′-Dicyanovinyl)phenyl Acrylate (Ib). To 2.08 g (10 mmol) of potassium 2-(2′,2′-dicyanovinyl)phenoxide in 20 mL of dry ethyl ether was added 1.35 g (15 mmol) of acryloyl chloride dropwise with stirring under nitrogen. The reaction mixture was stirred for 1 h and filtered. The pale yellow filtrate was cooled to 0 °C and the solvent removed yielding crude crystals of 2-(2′,2′-dicyanovinyl)phenyl acrylate. The solid was recrystallized from benzene/hexane yielding 0.20 g (10%) of the product, mp 114–115 °C. The NMR spectrum (CDCl$_3$) showed peaks centered at τ 1.80 (multiplet, 1 H) and 2.60 (multiplet, 3 H) assigned to the aromatic protons, τ 2.10 (singlet, 1 H) assigned to the dicyanovinyl proton, and τ 3.70 (multiplet, 3 H) assigned to the acrylate vinyl protons. The ultraviolet spectrum (100% ethanol) had a λ_{max} at 295 nm (ϵ = 9850). The IR (KBr) spectrum showed a conjugated CN stretch at 2200 cm^{-1} and a conjugated ester carbonyl stretch at 1740 cm^{-1}.

Anal. Calcd for C$_{13}$H$_8$N$_2$O$_2$: C, 69.62; H, 3.57; N, 12.50; mol wt 224. Found: C, 69.48; H, 3.65; N, 12.64; mol wt (mass spectrum) 224.

4-(1′,2′,2′-Tricyanovinyl)phenol (IV). To 5.10 g (30 mmol) of 4-(2′,2′-dicyanovinyl)phenol in 20 mL of dimethylformamide was added 10 mL of aqueous 4 N sodium cyanide over a period of 2 min with stirring under nitrogen. The reaction mixture was stirred for 20 min and 30 mL of glacial acetic acid was added. Five minutes later 13.30 g (30 mmol) of lead tetraacetate was added in 2-g portions. The reaction mixture was stirred an additional hour and poured into 500 mL of ice water with stirring and the resulting precipitate collected and recrystallized from benzene/hexane three times, yielding 4.10 g (70%) of 4-(1′,2′,2′-tricyanovinyl)phenol (IV), mp 140–145 °C. The NMR spectrum (acetone-d_6) showed peaks centered at τ 2.00 (doublet, J = 9 Hz, 2 H) and 2.90 (doublet, J = 9 Hz, 2 H) assigned to the aromatic protons and τ 0.00 (broad singlet, 1 H) assigned to the hydroxyl proton. The IR (KBr) showed a broad OH stretch at 3000–2500 cm^{-1} and a conjugated CN at 2200 cm^{-1}.

Anal. Calcd for C$_{11}$H$_5$N$_3$O: C, 67.80; H, 2.57; N, 21.42; mol wt 195. Found: C, 67.97; H, 2.40; N, 21.47; mol wt (mass spectrum) 195.

4-(1′,2′,2′-Tricyanovinyl)phenyl Acrylate (V). To 1.95 g (10 mmol) of 4′-(1′,2′,2′-tricyanovinyl)phenol and 0.90 g of acryloyl chloride (10 mmol) in 20 mL of freshly distilled tetrahydrofuran was added 1.40 g (10 mmol) of 2,2,6,6-tetramethylpiperidine dropwise at 0 °C with stirring under nitrogen. The reaction mixture was filtered after 30 min and the solvent removed, leaving a pale yellow oil. The oil was recrystallized from hexane yielding 1.32 g (53%) of 4-(1′,2′,2′-tricyanovinyl)phenyl acrylate (V), mp 108–109 °C. The NMR (CDCl$_3$) showed peaks centered at τ 2.10 (doublet, J = 9 Hz, 2 H) and 2.70 (doublet, J = 9 Hz, 2 H) assigned to the aromatic protons and τ 3.80 (multiplet, 3 H) assigned to the vinyl protons. The IR (KBr) showed a conjugated CN stretch at 2190 cm^{-1} and a conjugated ester carbonyl stretch at 1740 cm^{-1}.

Anal. Calcd for C$_{14}$H$_7$N$_3$O$_2$: C, 67.50; H, 2.81; N, 16.84; mol wt 249. Found: C, 67.27; H, 2.95; N, 16.50; mol wt (mass spectrum) 249.

4-(2′,2′-Dicyanovinyl)phenyl Methacrylate (IIa). To 2.08 g (10 mmol) of potassium 4-(2′,2′-dicyanovinyl)phenoxide in 20 mL of dry ethyl ether was added 1.50 g (15 mmol) of methacryloyl chloride dropwise with stirring under nitrogen. The pale yellow filtrate was cooled to 0 °C and the solvent removed, yielding crude crystals of 4-(2′,2′-dicyanovinyl)phenyl methacrylate (IIa). The solid was recrystallized from ethanol/benzene, yielding 2.10 g (88%); mp 105–105.5 °C. The NMR spectrum (CDCl$_3$) showed peaks centered at τ 2.00 (doublet, J = 9 Hz, 2 H) and 2.70 (singlet, 1 H) assigned to the dicyanovinyl proton, τ 3.26 and 3.83 (multiplets, 2 H) assigned to the methacrylate vinyl protons, and τ 7.90 (singlet, 3 H) assigned to the allylic methyl protons. The IR (KBr) showed a conjugated CN stretch at 2190 cm^{-1} and a conjugated ester carbonyl stretch at 1735 cm^{-1}.

Anal. Calcd for C$_{14}$H$_{10}$N$_2$O$_2$: C, 70.6; H, 4.20; N, 11.78; mol wt 238. Found: C, 70.32; H, 4.30; N, 11.65; mol wt (mass spectrum) 238.

4-(1′-Phenyl-2′,2′-dicyanovinyl)phenol (IV). This compound was prepared in 85% yield by modifying a procedure on McElvain and Clements.[7] The NMR spectrum (CDCl$_3$) showed peaks centered at τ 2.60, 3.10 (doublets, J = 9 Hz, 4 H), and 2.50 (multiplet, 5 H) assigned to the aromatic protons and τ 3.60 (broad singlet, 1 H) assigned to the hydroxyl proton. The IR (KBr) showed a broad OH stretch at 3100 cm^{-1} and a conjugated CN stretch at 2190 cm^{-1}.

Anal. Calcd for C$_{16}$H$_{10}$N$_2$O: C, 78.00; H, 4.06; N, 11.40; mol wt 246. Found: C, 77.83; H, 4.16; N, 11.35; mol wt (mass spectrum) 246.

Potassium 4-[1′-Phenyl-2′,2′-dicyanovinyl]phenoxide. To 25 mL of methanol was added 0.39 g (10 mmol) of potassium metal in small pieces under nitrogen at 0 °C. After the metal had completely reacted, 2.46 g (10 mmol) of 4-(1′-phenyl-2′,2′-dicyanovinyl)phenol was added. The solution was stirred for 5 min and filtered. The solvent was removed and the solid vacuum dried, yielding 2.50 g (87%) of potassium 4-(1′-phenyl-2′,2′-dicyanovinyl)phenoxide.

4-(1′-Phenyl-2′,2′-dicyanovinyl)phenyl Acrylate (IIIa). To 2.82 g (10 mmol) of potassium 4-(1′-phenyl-2′,2′-dicyanovinyl)-phenoxide in 25 mL of dry ethyl ether was added 1.35 g (15 mmol) of acryloyl chloride under nitrogen. The solution was stirred for 1 h and filtered. The pale yellow filtrate was cooled to 0 °C and

the solvent removed. The solid residue was recrystallized from benzene/hexane, yielding 2.34 g (78%) of 4-(1'-phenyl-2',2'-dicyanovinyl)phenyl acrylate (IIIa), mp 122.5–123.5 °C. The NMR spectrum (CDCl$_3$) showed peaks centered at τ 2.60 (multiplet, 9 H) assigned to the aromatic protons and τ 3.70 (multiplet, 3 H) assigned to the vinyl protons. The IR (KBr) showed a conjugated CN stretch at 2200 cm^{-1} and a conjugated ester carbonyl stretch at 1740 cm^{-1}.

Anal. Calcd for C$_{19}$H$_{12}$N$_2$O$_2$: C, 76.00; H, 4.00; N, 9.33; mol wt 300. Found: C, 75.77; H, 3.98; N, 9.26; mol wt (mass spectrum) 300.

4-(1'-Phenyl-2',2'-dicyanovinyl)phenyl Methacrylate (IIIb). To 2.82 g (10 mmol) of potassium 4-(1'-phenyl-2',2'-dicyanovinyl)phenoxide in 25 mL of dry ethyl ether was added 1.60 g (15 mmol) of methacryloyl chloride under nitrogen. The solution was stirred for 1 h and filtered. The pale yellow filtrate was cooled to 0 °C and the solvent removed. The solid residue was recrystallized from benzene/hexane, yielding 2.36 g (75%) of 4-(1'-phenyl-2',2'-dicyanovinyl)phenyl methacrylate (IIIb), mp 101–102 °C. The NMR spectrum (CDCl$_3$) showed peaks centered at τ 2.60 (multiplet, 9 H) assigned to the aromatic protons, τ 3.65 (multiplet, 1 H) and 4.20 (multiplet, J = 1 Hz, 3 H) assigned to the vinyl protons, and τ 7.95 (doublet, J = 1 Hz, 3 H) assigned to the allylic methyl protons. The IR (KBr) showed a conjugated CN stretch at 2190 cm^{-1} and a conjugated ester carbonyl stretch at 1730 cm^{-1}.

Anal. Calcd for C$_{20}$H$_{14}$N$_2$O$_2$: C, 76.45; H, 4.45; N, 10.20; mol wt 314. Found: C, 76.22; H, 4.30; N, 10.05; mol wt (mass spectrum) 314.

4-(2',2'-Dicyanovinyl)styrene (VI). To 13.8 g (100 mmol) of *p*-chlorostyrene in 20 mL of THF in a 100-mL three-necked flask was added 2.40 g (100 mmol) of magnesium turnings and 0.20 g of ethylene bromide with stirring under nitrogen. The vigorous Grignard reaction was moderated with an external water bath until all of the magnesium was consumed. An ice bath was applied to the reaction vessel and 10 g (137 mmol) of dimethylformamide in 30 mL of THF was added slowly. The reaction mixture was stirred for two additional hours and worked up with saturated ammonium chloride solution. The ether layer was separated and the solvent removed under rotary evaporation, leaving a yellow oil. The yellow oil was diluted with 50 mL of ethanol (100%) and filtered to remove any polymeric precipitate. To the cooled solution of *p*-vinylbenzaldehyde was added 6.60 g of malononitrile and two drops of piperidine. The resulting precipitate was collected and dried, yielding 6.30 g (35%) of crude 4-(2',2'-dicyanovinyl)styrene (VI). Elution on neutral alumina with ethyl acetate yielded pure product, mp 113–114 °C. The NMR spectrum (CDCl$_3$) showed a peak centered at τ 1.67 (singlet, 1 H) assigned to the dicyanovinyl proton, τ 2.30 and 2.50 (doublets, J = 6 Hz, 4 H) assigned to the aromatic protons, and τ 4.00 (multiplet, 3 H) assigned to the vinyl protons. The IR (KBr) showed a conjugated CN stretch at 2190 cm^{-1}.

Anal. Calcd for C$_{12}$H$_8$N$_2$: C, 80.00; H, 4.45; N, 15.55; mol wt 180. Found: C, 79.92; H, 4.71; N, 15.30; mol wt (mass spectrum) 180.

4-(1',2',2'-Tricyanovinyl)styrene (VII). To 0.540 g (3 mmol) of 4-(2',2'-dicyanovinyl)styrene (VI) in 15 mL of dimethylformamide was added 1.5 mL of aqueous 4 N sodium cyanide solution (6 mmol) with stirring under nitrogen. The reaction mixture was stirred for 20 min and 10 mL of glacial acetic acid was added. After 10 min, 1.33 g (3 mmol) of lead tetraacetate was added at 0 °C and the solution stirred for 30 min. The reaction solution was then poured into 70 mL of ice water and the resulting precipitate collected. The solid residue was sublimed at 105 °C (0.10 mm Hg) to yield 0.124 g (20%) of 4-(1',2',2'-tricyanovinyl)styrene (VII), mp 124–125 °C. The NMR spectrum (CDCl$_3$) showed peaks centered at τ 1.90 and 2.35 (doublets, J = 8 Hz, 4 H) assigned to the aromatic protons and τ 3.80 (multiplet, 3 H) assigned to the vinyl protons. The IR (KBr) showed a conjugated CN stretch at 2190 cm^{-1}.

Anal. Calcd for C$_{13}$H$_7$N$_3$: C, 76.08; H, 3.42; N, 20.50; mol wt 205. Found: C, 76.00; H, 3.53; N, 20.27; mol wt (mass spectrum) 205.

Copolymerization of *N*-Vinylcarbazole and 4-(2',2'-Dicyanovinyl)phenyl Acrylate (Ia). To a solution of *N*-vinylcarbazole (0.192 g, 1 mmol) and 4-(2',2'-dicyanovinyl)phenyl

acrylate (0.224 g, 1 mmol) in 10.0 mL of freshly distilled THF was added 2.1 mg of AIBN (0.5% to monomers). The solution was heated to reflux for 24 h under nitrogen and precipitated into hexane three times for purification. The resulting material was dried in a drying pistol and yielded 0.08 g (19% conversion) of copolymer; softening temperature 131–170 °C. The IR (KBr) showed a conjugated CN stretch at 2200 cm^{-1} and an ester carbonyl stretch at 1740 cm^{-1}. Elemental analysis indicated that the copolymer was 44 mol % of the acrylate.

Copolymerization of *N*-Vinylcarbazole and 4-(2',2'-Dicyanovinyl)phenyl Methacrylate (IIa). To a solution of *N*-vinylcarbazole (0.193 g, 1 mmol) and 4-(2',2'-dicyanovinyl)phenyl methacrylate (0.238 g, 1 mmol) in 10.0 mL of freshly distilled THF was added 2.2 mg of AIBN (0.5% to monomers). The solution was heated to reflux for 24 h under nitrogen and precipitated three times into hexane for purification. The resulting material was dried in a drying pistol and yielded 0.07 g (15.7% conversion) of copolymer, softening temperature 145–165 °C. The IR (KBr) showed a conjugated CN stretch at 2190 cm^{-1} and an ester carbonyl stretch at 1740 cm^{-1}. Elemental analysis indicated that the copolymer was 38 mol % of the acrylate.

Copolymerization of *N*-Vinylcarbazole and 4-(1'-Phenyl-2',2'-dicyanovinyl)phenyl Acrylate (IIIa). To a solution of *N*-vinylcarbazole (0.193 g, 1 mmol) and 4-(1'-phenyl-2',2'-dicyanovinyl)phenyl acrylate (0.300 g, 1 mmol) in 10.0 mL of freshly distilled THF was added 2.5 mg of AIBN (0.5% to monomers). The solution was heated to reflux for 24 h under nitrogen and precipitated three times into hexane for purification. The resulting material was dried in a drying pistol and yielded 0.056 g (11.3% conversion) of copolymer, softening temperature 132–161 °C. The IR (KBr) showed a conjugated CN stretch at 2185 cm^{-1} and an ester carbonyl stretch at 1750 cm^{-1}.

Copolymerization of *N*-Vinylcarbazole and 4-(1'-Phenyl-2',2'-dicyanovinyl)phenyl Methacrylate (IIIb). To a solution of *N*-vinylcarbazole (0.193 g, 1 mmol) and 4-(1'-phenyl-2',2'-dicyanovinyl)phenyl methacrylate (0.314 g, 1 mmol) in 10.0 mL of freshly distilled THF was added 2.5 mg of AIBN (0.5% to monomers). The solution was heated to reflux for 24 h under nitrogen and precipitated three times into hexane for purification. The resulting material was dried in a drying pistol and yielded 0.043 g (8.5% conversion) of copolymer, mp 140–152 °C. The IR (KBr) showed a conjugated CN stretch at 2200 cm^{-1} and an ester carbonyl stretch at 1730 cm^{-1}.

Copolymerization of *N*-Vinylcarbazole and 4-(2',2'-Dicyanovinyl)styrene (VI). To a solution of *N*-vinylcarbazole (0.193 g, 1 mmol) and 4-(2',2'-dicyanovinyl)styrene (0.180 g, 1 mmol) in 10.0 mL of freshly distilled THF was added 1.8 mg of AIBN (0.5% to monomers). The solution was heated to reflux for 24 h under nitrogen and precipitated three times into hexane for purification. The resulting material was dried in a drying pistol and yielded 0.093 g (25% conversion) of copolymer, softening temperature 158–176 °C. The IR (KBr) showed a conjugated CN stretch at 2190 cm^{-1}.

Copolymerization of *N*-Vinylcarbazole and 2-(2',2'-Dicyanovinyl)phenyl Acrylate (Ib). To a solution of *N*-vinylcarbazole (0.193 g, 1 mmol) and 2-(2',2'-dicyanovinyl)phenyl acrylate (0.224 g, 1 mmol) in 10.0 mL of freshly distilled THF was added 2.1 mg of AIBN (0.5% to monomers). The solution was heated to reflux for 24 h under nitrogen and precipitated three times into hexane for purification. The resulting material was dried in a drying pistol and yielded 0.013 g (3.1% conversion) of copolymer, softening temperature 118–137 °C. The IR (KBr) showed a weak conjugated CN stretch at 2180 cm^{-1} and an ester carbonyl stretch at 1730 cm^{-1}.

Copolymerization of *N*-Vinylcarbazole and 4-(1',2',2'-Tricyanovinyl)styrene (VII). To a solution of *N*-vinylcarbazole (0.0386 g, 0.20 mmol) and 4-(1',2',2'-tricyanovinyl)styrene (0.410 g, 0.20 mmol) in 4.0 mL of benzene was added 0.40 mg of AIBN (0.5% to monomers). The solution was heated to reflux for 20 h under nitrogen and precipitated into ligroin for purification. The resulting material was dried and yielded 0.0039 g (5% conversion) of copolymer, mp 165–225 °C. The IR showed a conjugated CN stretch at 2190 cm^{-1}. There was only enough material for a visible spectrum which is located in Table I. It indicates that the material is a copolymer. Crystals of a dark red complex, mp 86–88 °C, were also obtained from the reaction. In DMF, a

0.001 g/3 mL solution gave a λ_{max} of 390 nm (very broad) (ϵ = 8000) and a slight charge-transfer band at 600 nm (ϵ = 15).

References and Notes

(1) (a) J. E. Mulvaney and Daniel M. Chang, *Macromolecules*, preceding paper in this issue; (b) D. M. Chang, S. Gromelski, R. Rupp, and J. E. Mulvaney, *J. Polym. Sci., Polym. Chem. Ed.*, **15**, 571 (1977).

(2) For a discussion of this point with a thorough set of references, see C. U. Pittman, Jr., Y.-F. Liang, and M. Ueda, *Macromolecules*, **12**, 541 (1979).

(3) G. Noren and H. K. Hall, Jr., *J. Polym. Sci.*, **10**, 3183 (1972); H. K. Hall, Jr., and R. C. Daly, *Macromolecules*, **8**, 22 (1975).

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(5) D. J. Williams, *Macromolecules*, **3**, 602 (1970).

(6) G. P. Schiemenz, *Chem. Ber.*, **95**, 483 (1962).

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Kinetics of Hydrolytic Aging of Polyester Urethane Elastomers

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ABSTRACT: The hydrolytic degradation of polyester urethane elastomers is due to the acid-catalyzed hydrolysis of the ester group. Acid content (A) and the reciprocal of the number average molecular weight (M^{-1}) increase by equivalent amounts indicating that each molecular chain scission produces one acid group. The time (t) dependence of A and M is given by $A = A_0 e^{kt}$ and $M^{-1} = M_0^{-1} + A_0(e^{kt} - 1)$, where the subscripts denote initial values. The fractional rate of increase in acidity, k, is a pseudo-first-order rate constant because the ester and water contents change only slightly with degradation. Values of k at 85 °C and 100% relative humidity are in the range 15–20% per day for polyurethanes, based on poly(caprolactone and tetramethylene adipate diols). At 100% relative humidity k obeys the Arrhenius equation between 35 and 85 °C with activation energies in the range 68–83 kJ/mol (16–20 kcal/mol). Values of k decrease with relative humidity, becoming zero in dry air.

Polyester-based urethane elastomers degrade in moist air, sometimes reverting to viscous liquids.[1,2] Lifetime prediction tests based on changes in physical properties can be misleading because of the reinforcing effect of crystals which form from degraded, lower molecular weight fragments.[3] More reliable tests based on specific molecular mechanisms are therefore desirable for critical uses of these materials. Schollenberger and Stewart showed that the degradation involved the acid-catalyzed hydrolysis of the ester linkage.[4] They suggested that the degradation should be autocatalytic, since an acid group is expected to form for each ester group hydrolyzed. If the logarithms of the acid numbers that they report are plotted vs. time, reasonably linear behavior is found, consistent with their suggestion. This paper develops the kinetics of the degradation mechanism and presents a method to predict the lifetime of the polymers.

Experimental Section

Polyester- and polyether-based thermoplastic elastomers were obtained from three manufacturers. Qualitative analysis[5] showed that the polyester urethanes contained 1,4-butanediol, p,p'-diphenylmethane diisocyanate, and either an adipate or a caprolactone polyester. Infrared spectra showed no bands attributable to carbodiimides, which have been used to stabilize polyester urethanes to moisture.[4] Weight fractions of diisocyanate were calculated from the nitrogen contents, which were determined in duplicate by a commercial laboratory. Poly(tetramethylene adipate and caprolactone diols) were obtained from commercial sources. Stabilized tetrahydrofuran was used as a solvent at 23–25 °C for gel permeation chromatography and at 25 °C for viscosity measurements on the commercial polyurethanes.

A hard segment polymer was made from diphenylmethane diisocyanate and butanediol (1:1 mol ratio) by the method of Lyman.[6] The polymer was insoluble in tetrahydrofuran but dissolved in dimethylformamide, in which the intrinsic viscosity, [η], was 0.81 dL/g at 25 °C.

A polyurethane potting compound which had reverted to a viscous liquid after 25 months of service in a military aircraft was made available to us for this study. The compound contained 20% inorganic filler which was separated by dissolving the organic component and filtering.

The acid content, A, was measured by dissolving polymer containing 10^{-5}–5×10^{-4} equiv of acid in 75 cm³ of dimethylformamide and titrating the solution with standard 0.02 N tetrabutylammonium hydroxide. This had been prepared from an ethanolic 1 M solution by dilution with methanol, isopropyl alcohol, and toluene (30:5:450 volume ratio); it was standardized against benzoic acid. A titration was run on the dimethylformamide solvent, and the titer was subtracted from that of the polymer solution. The titer of the blank was between 0.16 and 0.26 cm³ provided that the dimethylformamide had been stored over molecular sieve 4A, which had been heated previously under vacuum overnight at 170 °C. Solvent titers became much larger if this drying agent was not used, probably because of the formation of formic acid.[7] The solutions were protected from atmospheric carbon dioxide during the titrations by prepurging them with nitrogen and titrating them into narrow-mouthed bottles. Titrations were generally done in duplicate and were reproducible to 1–2 and 10–20% at acid contents of 50–80 $\times 10^{-5}$ equiv/g and 0.4–1.5 $\times 10^{-5}$ equiv/g, respectively. The chief difficulty in this method of determining A is that the yellow tint of the polymer solutions makes the end point imprecise when using a thymol blue indicator.

The number average molecular weights, M, were calculated from gel permeation chromatograms. A commercially available chromatograph with a septumless injector and a refractive index detector was used with a column set consisting of four microstyrogel-packed columns, one each of the nominal pore sizes 10^2, 10^3, 10^4, and 10^5 Å. The solvent flow rate was 1 cm³/min. A universal calibration ($M[\eta]$ as a function of retention volume[8]) was established by using polystyrene standards of narrow molecular weight distribution. Aged and unaged specimens of one of the polyurethanes were run through the chromatograph. A computer program and the universal calibration were used to calculate K in the Mark–Houwink equation ($[\eta] = KM^a$) by using each chromatogram and the separately measured intrinsic viscosity and assuming values of the exponent, a, equal to 0.5, 0.625, and 0.75. The arithmetic mean K for the set of polymers was calculated for each value of a, giving three Mark–Houwink equations