width σ of 0.109 eV. The T_0 and σ values for the atactic polyacrylate are 949 K and 0.128 eV, respectively. The difference in the hole drift mobility for the isotactic and atactic polyacrylates may be due to the difference in both μ_0 and σ. The Gaussian width σ is determined by the fluctuation of polarization energy between a transient cation center and the neutral molecules surrounding the center. These two polymers have the same T_g (105 °C) and no excimer fluorescence originating from a specific dimeric conformation, which may act as a trapping center for holes in PVK. The small value observed for the isotactic polyacrylate is related to the high stereoregularity of the polymer main chain, which should induce the ordered arrangement of carbazole chromophores. The slightly higher value of μ_0 determined for the isotactic polyacrylate may also be consistent with the ordered alignment of the chromophores, since the wave-function decay constant γ is expected to be smaller in a crystalline or paracrystalline array of hopping site molecules than in the disordered state.

Pendant-type photoconductive polymers, which have high chromophore content and high μ_0 values, have generally also exhibited high σ values, so that the polymers have lower carrier mobilities than the corresponding molecularly doped systems. It was shown in eq 4 that the σ value is more effective on the carrier mobility than the μ_0 value. Therefore, it is concluded that since the highly stereoregular polyacrylate has particularly low σ and high μ_0 values it exhibited a high hole drift mobility.

In conclusion, it has been shown that stereoregular structures enhance the hole drift mobility of pendant-type photoconductive polymers. The present result provides a new insight into the field of photoconductive organic materials.

References and Notes

(1) Pearson, J. M.; Stolka, M. In *Poly(N-vinylcarbazole)*; Huglin, M. B., Ed.; Gordon and Breach: New York, 1981; p 159.
(2) Hughes, R. C. In *Photoconductivity in Polymers, An Interdisciplinary Approach*; Patsis, A. V., Seaner, D. A., Eds.; Technomic: Westport, CT, 1976; p 158.
(3) For example: Yokoyama, M. *Kobunshi* **1985**, *34*, 728-731.
(4) Itaya, A.; Okamoto, K.; Kusabayashi, S. *Polym. J. (Tokyo)* **1985**, *17*, 557-565.
(5) Stolka, M.; Pai, D. M.; Renfer, D. S.; Yanus, J. F. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 969-983.
(6) Yamazaki, M.; Tsutsumi, N.; Yamamoto, M.; Nishijima, Y. *Polym. Prepr., Jpn.* **1984**, *33*, 2535-2538.
(7) Gaidelis, V.; Krisščiūnas, V.; Montrimas, E. *Thin Solid Films* **1976**, *38*, 9-14.
(8) Oshima, R.; Uryu, T.; Senō, M. *Macromolecules* **1985**, *18*, 1045-1048.
(9) Günewald, M.; Pohlmann, B.; Movaghar, B.; Würtz, D. *Philos. Mag. B* **1984**, *49*, 341-356.
(10) Flowers, R. G.; Flowers, L. W. *J. Chem. Soc.* **1948**, *70*, 3019-3021.
(11) Kamogawa, H.; Koizumi, H.; Nanasawa, M. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *18*, 9-18.
(12) Uryu, T.; Ohaku, K.; Matsuzaki, K. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 1723-1734.
(13) Matsuzaki, K.; Uryu, T.; Ishida, A.; Takeuchi, M. *J. Polym. Sci., Polym. Chem. Ed.* **1967**, *5*, 2167-2177.
(14) Natta, G.; Longi, P.; Pellino, E. *Makromol. Chem.* **1964**, *71*, 212-214.
(15) Klöpffer, E. *J. Chem. Phys.* **1969**, *50*, 2337-2343.
(16) Mort, J.; Knight, J. *Nature (London)* **1981**, *290*, 659-663.
(17) Gill, W. D. *J. Appl. Phys.* **1972**, *43*, 5033-5040.
(18) Oshima, R.; Biswas, M.; Wada, T.; Uryu, T. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 151-154.
(19) Bässler, H. *Philos. Mag. B* **1984**, *50*, 347-362.
(20) (a) Fujino, M.; Mikawa, H.; Yokoyama, M. *Photogr. Sci. Eng.* 1982, 26, 84-8 (b) Lange, J.; Bässler, H. *Phys. Status Solidi B* **1982**, *114*, 561-569.

Donor-Acceptor-Containing Quinodimethanes. Synthesis and Copolyesterification of Highly Dipolar Quinodimethanes

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ABSTRACT: Three novel quinodimethane monomers with an electron-acceptor moiety containing an ester group and an electron-donor moiety containing a hydroxyl group were synthesized. These 7,7-[(hydroxyalkanediyl)diamino]-8-carbomethoxy-8-cyanoquinodimethane derivatives are highly crystalline and show a high degree of electron delocalization from the donor moiety to the acceptor moiety. These highly dipolar units are copolymerized by polyesterification with more flexible α-hydroxy-ω-carbomethoxy compounds to yield polymers in which all the dipoles are pointing in the same direction. These copolymers are fusable and are soluble in polar organic solvents.

Introduction

We wished to prepare polyesters containing highly dipolar units, with all dipoles pointing in the same direction. The quinodimethane unit presented itself as the best choice for this purpose.

The polymerization of quinodimethane derivatives bearing only electron-withdrawing groups via a vinyl-type polymerization is well-known,[1,2] and the incorporation of such an acceptor quinodimethane unit itself in the polymer backbone has also been reported.[3] But there are no examples of polymers incorporating a donor-acceptor quinodimethane molecule into the polymer backbone.

We describe the syntheses of donor-acceptor-substituted quinodimethanes that have the appropriate functionalities needed to make condensation polymers. We selected quinodimethane derivatives with an acceptor moiety containing an ester group and with a diamine donor moiety containing a hydroxyl function.

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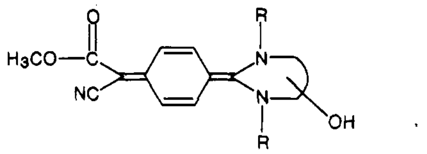
Table I
Spectral Properties of Donor-Acceptor Quinodimethanes

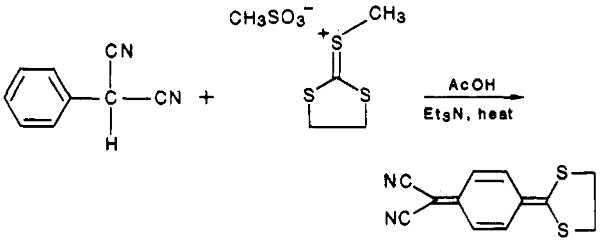
compd	IR[a] C=C	IR[a] C≡N	IR[a] C(=O)OR	UV[b]
DTQ	1596	2183	1683	480, 507, 543, 588
DAQ	1581	2177	1624	397[c]
DEQ	1585	2160	1628	394[c]
DIQ	1592	2162	1641, 1621	348

[a] KBr pellet, given in wavenumbers. [b] Acetonitrile solvent, given in nanometers. [c] DMF solvent.

Copolymerization of these monomers with other α-hydroxy-ω-carbomethoxy monomers will be described.



The synthesis of these monomers is based on a study by Gompper on the synthesis and reaction of 7,7-(ethylenedithio)-8,8-dicyanoquinodimethane.[4,5] Condensation of equimolar amounts of an arylmalononitrile with an *S*-methyl-1,3-dithiolane-2-thione salt leads to this donor–acceptor quinodimethane. Nucleophilic displacement of ethanedithiol by diamines forms 7,7-diamino-8,8-dicyanoquinodimethane.



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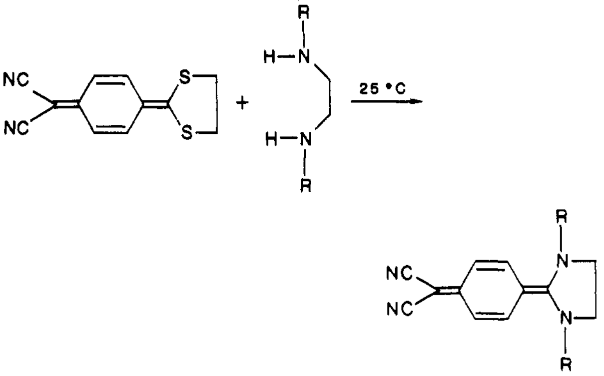

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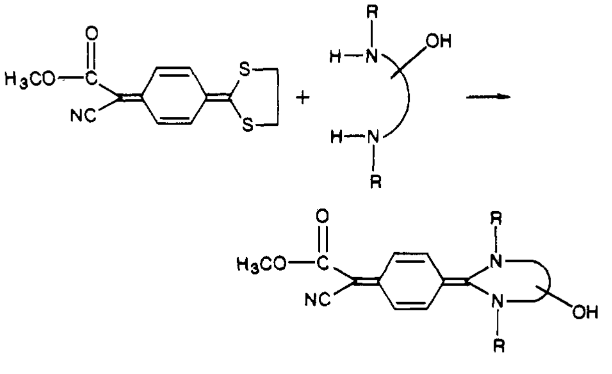
Results and Discussion

Monomer Synthesis. The donor–acceptor quinodimethane monomers were synthesized by condensation of 7,7-(ethylenedithio)-8-carbomethoxy-8-cyanoquinodimethane (DTQ) and a hydroxy diamine.



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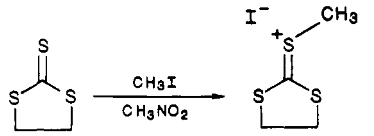
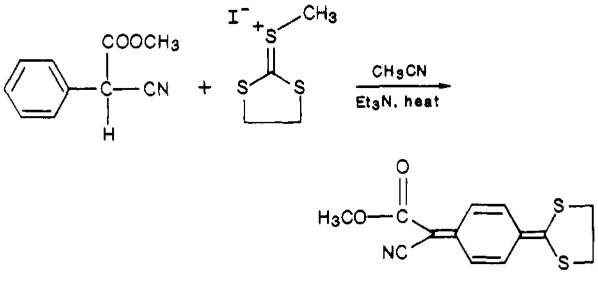
Synthesis of DTO. 1,3-Dithiolan-2-ylidenemethylsulfonium iodide was prepared by the procedure of Harrison.[6]



(4)

Modifying Gompper's procedure,[4,5] we synthesized DTQ via the trimethylamine-promoted condensation of 1,3-dithiolan-2-ylidenemethylsulfonium iodide with methyl α-cyanophenylacetate in refluxing acetonitrile.



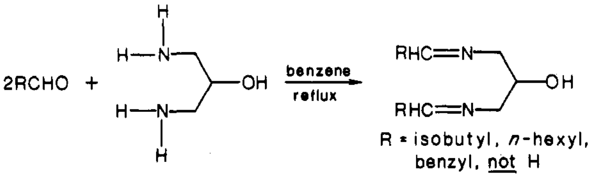
(5)

DTQ

This proved to be a very sensitive reaction. We experimented with various solvents, bases, temperatures, and reagents before deciding on the conditions described in the Experimental Section. The major byproduct derived from this reaction is formed via dealkylation of the *S*-methyl salt as evidenced by the recovery of large amounts of 1,3-dithiolane-2-thione.

DTQ is a dark-purple crystalline dye with multiple ultraviolet (UV) absorptions above 450 nm. Infrared and NMR spectra are in agreement with the proposed structure.

Synthesis of Bis-Substituted Diamines. 1,3-Bis-substituted imines were prepared by the condensation of 2 equiv of aldehyde with 1,3-diamino-2-propanol (eq 6). The imine formation was spontaneous and essentially quantitative. The bis imines were reduced via catalytic hydrogenation over Raney nickel (eq 7); chemical reduction with metal hydrides or dissolved metals is also possible.



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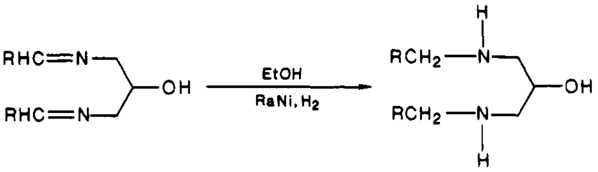
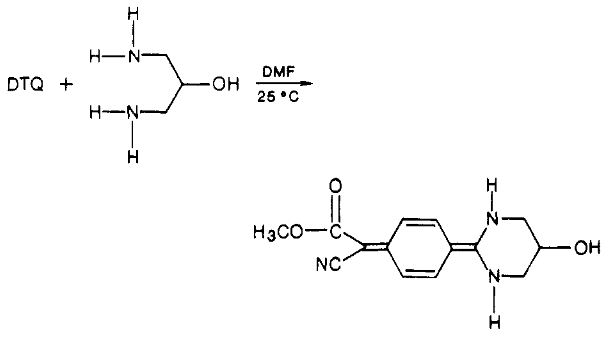


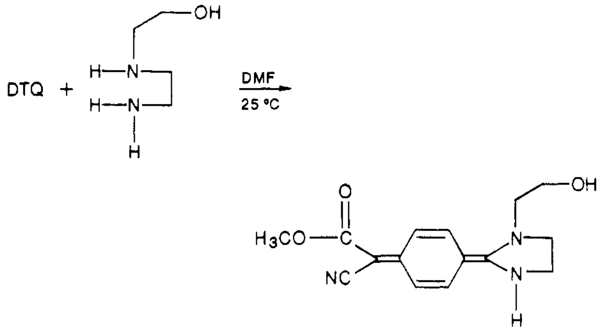
(7)

Condensation Reactions of Diamines with DTQ. Condensation of the hydroxy bis amines with DTQ was highly dependent upon the structure of the diamines. For unhindered diamines, the reaction was spontaneous at room temperature, giving high yields of the 7,7-(alkanediyldiamino)-8-carbomethoxy-8-cyanoquinodimethanes: DAQ (eq 8) and DEQ (eq 9) precipitated from the reaction mixture as brown powders that were then purified via recrystallization from Me$_2$SO/dichloromethane. For hindered diamines, however, the reaction was sluggish even at elevated temperatures, giving a complex mixture of the desired product with side products. DIQ (eq 10) was



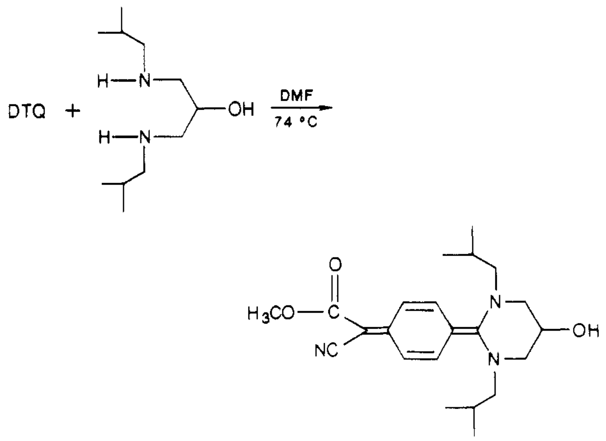
(8)

DAQ



(9)

DEQ



(10)

DIQ

isolated in 12% yield after column chromatography and recrystallization from dichloromethane. The products obtained (DAQ, DIQ, and DEQ) are crystalline materials with very low solubility and intense UV absorptions in the region of 340–400 nm. The IR spectra revealed a large amount of electron delocalization into the ester and cyano groups (Table I). Note the very low carbonyl stretching frequency of the diamino products.

The 270-MHz ^{1}H NMR spectra of the various quinoid products are summarized in Table II. The high multiplicity of the DTQ and DIQ quinoid protons is a result of the superimposed ortho and meta couplings between the quinoid protons. Long-range meta coupling is not seen in either DEQ or DAQ.

Comparison of the IR and ^{1}H NMR spectra of the quinoid products indicates an important feature of these systems: the 7,7-diamino substituents present on DAQ, DEQ, and DIQ are better electron donors via resonance than the 7,7-diethylenedithio substituent in DTQ[7] (Scheme I).

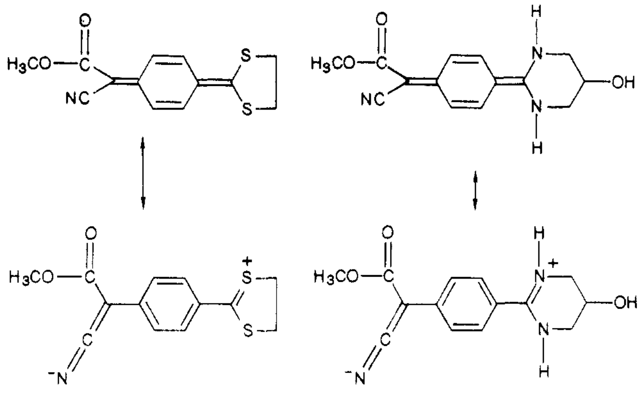
A higher degree of electron donation by nitrogen than that by sulfur is observed in the difference of the CN stretch of DTQ and DAQ. An even better example of this is seen in the comparison of the carbonyl C=O stretching frequencies of DTQ and DAQ. The DAQ ester appears to have almost no double bond character. This extreme amount of delocalization is corroborated by the ^{1}H NMR spectrum of DAQ. Whereas the four quinoid protons of DTQ were distinctly different, those of DAQ appeared as two doublets, each slightly distorted. This phenomenon may be rationalized two different ways:

Table II
^{1}H NMR Spectral Properties of the Quinoid Region of Donor-Acceptor-Substituted Quinodimethanes[a]

compd	chem shift[b]	multiplicity	no. protons
DTQ	8.20	dd	1
	7.60–7.48	m	2
	7.01	dd	1
DAQ	7.67	d	2
	7.41	d	2
DEQ	7.69	d	2
	7.41	d	2
DIQ	7.72	t	2
	7.00	dd	1
	6.90	dd	1

[a] IBM WP270SY spectrometer; Me$_2$SO solvent. [b] Given in parts per million from Me$_4$Si.

Scheme I



(1) If DAQ and DEQ are best represented by charge-separated resonance forms, then the exocyclic carbon–carbon double bonds possess a large amount of single bond character. This lowers the energy of rotation around these bonds enough to allow fast rotation on the NMR time scale.

(2) By shifting the position of the proton(s) attached to nitrogen, both DAQ and DEQ may be drawn in several different tautomeric forms. All of these other tautomers have a central aromatic ring with carbon–carbon single bonds at the exocyclic positions. Even a small equilibrium concentration of one or more of these tautomers could lead to a signal coalescence observed, if the tautomerism is fast on the NMR time scale (Scheme II).

Polymer Preparation and Characterization. Our experiences with attempted homopolymerizations of DEQ or DAQ established that the relative insolubility of these monomers creates an intractable homopolymer. Therefore, we investigated copolymer systems that should lead to soluble polymers.

The standard high-temperature polyesterification procedure requires that the monomers be heated above their melting point, which enables smooth stirring of the reaction mixture. Both DAQ and DEQ melt above 240 °C with decomposition. In the hope that the comonomers would solubilize the quinodimethane and result in high polymers, several copolymerizations with methyl 12-hydroxydodecanoate (12-HDE) or methyl 4-[(2-hydroxyethyl)oxy]benzoate (2-HEOB) at temperatures ranging from 200 to 250 °C were tried. These failed to produce useful ma-

Scheme II

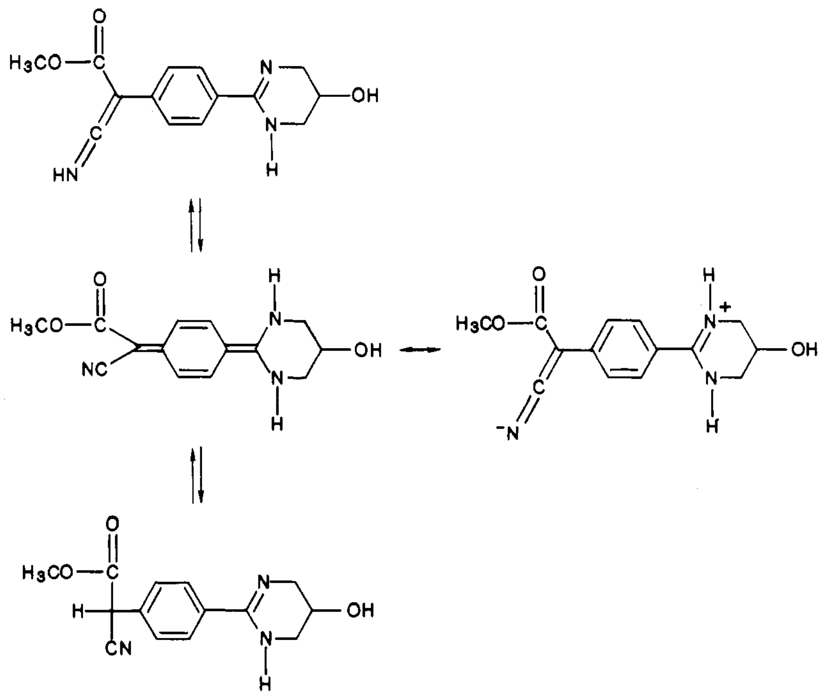


Table III
Physical Properties of Quinodimethane Copolymers[a]

no.	monomer 1	monomer 2	catal	polymn temp	second stage[b]	η_{inh}[c]	T_m[d]
1	DEQ	12-HDE	$Bu_2Sn(OAc)_2$	150	16.0	0.16	85.9
2	DEQ	12-HDE	$Bu_2Sn(OAc)_2$	150	32.5	0.32	85.9
3	DEQ	12-HDE	$Bu_2Sn(OAc)_2$	150	63.5	0.45	87.5
4	DEQ	12-HEOB	$Bu_2Sn(OAc)_2$	150	40.0	0.13	na[g]
5	DAQ[e]	12-HDA	$Ti(O\text{-}i\text{-}Pr)_4$	250	3.0	na	nd[h]
6	DAQ	12-HDA	$Ti(O\text{-}i\text{-}Pr)_4$	200	1.3	0.23[f]	65.0
7	DAQ	12-HDE	$Bu_2Sn(OAc)_2$	150	22.0	na	na

[a] All copolymers are (1/1) unless otherwise noted. [b] Time in hours. [c] Phenol/chlorobenzene (1/1), 25.0 °C. [d] Determined by DSC. [e] 5/1 DAQ/12-HDa. [f] Hexafluoro-2-propanol. [g] NA: not available. [h] ND: not detectable.

terials. A specialized polymerization process was needed to achieve high molecular weight polymers without decomposition of the quinoid structure. An inert solvent that could solubilize our polymerization mixture at low temperatures (100–150 °C) was seen as a potential answer to the problem of thermal degradation.

The first solvents tested were dipolar aprotic compounds, e.g., Me_2SO, DMF, and sulfolane, which dissolve DEQ at low temperatures (100–150 °C). Polymerization attempts in these solvents resulted in oligomer formation with severe discoloration. Utilizing the synthetic strategy outlined by Kantor,[8] we attempted the copolymerizations in benzophenone. Heating a mixture of DEQ and 12-HDE (1:1) in benzophenone (35% by weight) to 150 °C under nitrogen resulted in the formation of a slurry. It was found, after examining various experimental conditions, that utilization of a two-stage polymerization process would allow the formation of a high polymer from the slurry (Scheme III).

The two-stage polymerization process adopted in this study is a variation of a typical two-stage polyesterification. The first stage, stirring the reagents in the presence of dibutyltin diacetate under nitrogen at 150 °C, involves an initial ester interchange to form oligomers. The second stage, stirring the reaction mixture under a vacuum (0.1–1.0 Torr), allows continuous ester interchange with the removal of methanol driving the polymerization to completion. The molecular weight of the polymers obtained could be controlled by varying the reaction time in the second stage.

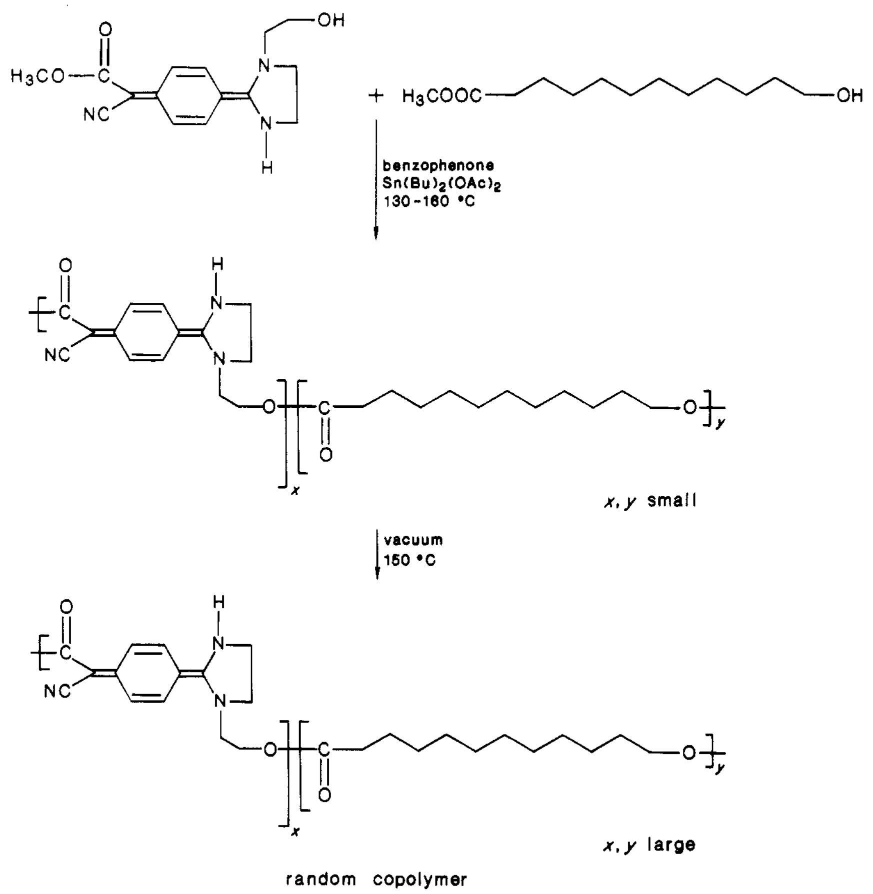
Table IV
Spectral Properties of Quinodimethane Copolymers[a]

copolym no.	IR[b] COOR	IR[b] CN	IR[b] C=C	UV[c]
1	1733, 1628	2160	1582	395
2	1734, 1629	2160	1584	394
3	1733, 1629	2162	1582	396
4	1708, 1622	2155	1575	394
6	1736, 1624	2178	1581	234[d]
7	1731, 1622	2177	1578	386

[a] Copolymer no. refers to Table III. [b] KBr pellet, given in wavenumbers. [c] Me_2SO solvent, given in nanometers. [d] Hexafluoro-2-propanol solvent.

The long polymerization times required are probably due to the inhomogeneity of the reaction mixture. It is believed that the benzophenone solvent originally acts as a transport system for the non-quinoid comonomers, effectively distributing them onto the surface of the solid quinoid particles. Once there, the mobile comonomer may react with the functional groups on the surface of the solid particle. The oligomers formed in this manner are expected to have a lower melting point than the quinoid molecule and to be more mobile. The polymerization temperature is higher than the melting point of the polymer itself. The polymer, although molten, is still highly viscous and remains as insoluble pellets in the reaction flask. The reactive ends of the growing chain are free to move about, very slowly, due to the high viscosity inside the pellet. The lack of mobility of the growing ends is the

Scheme III



cause of the slow overall polymerization process.

The polymerization results are summarized in Table III. DEQ was copolymerized with methyl 12-hydroxydodecanoate using the two-stage process in benzophenone with a dibutyltin diacetate catalyst. Benzophenone was removed from the resultant copolymer by extraction with methanol. The copolymer obtained with this procedure was soluble in phenol/chlorobenzene (1/1) and hexafluoro-2-propanol (HFIP) at room temperature and dipolar aprotic solvents (DMF, Me_2SO, and NMP) at elevated temperatures. The UV absorption spectrum of the polymer was nearly identical with that of DEQ, and IR showed the presence of the two expected carbonyl C═O stretching bands. Inherent polymer viscosities ranged from 0.16 to 0.45. The polymers all had crystalline melting ranges at 86 °C, and glass transition temperatures were not detectable down to −40 °C.

DEQ was also copolymerized with methyl 4-[(2-hydroxyethyl)oxy]benzoate (2-HEOB) using the procedure described above. The copolymer obtained was soluble in phenol/chlorobenzene (1/1) at room temperature. The inherent viscosity of the polymer did not exceed 0.13, despite prolonged reaction times. The infrared spectrum of the copolymer displayed the two expected carbonyl C═O stretches, and the ultraviolet spectrum was identical with that of the starting materials.

The copolymerization of DAQ with 12-hydroxydodecanoic acid (12-HDA), in the absence of a solvent, gave poor results. A dark, insoluble material was obtained when a DAQ/12-HDA ratio of 5 was used. When the ratio was lowered to 1, a dark, semicrystalline material was obtained, which was soluble only in HFIP. The inherent viscosity of the polymer was 0.23, although the dark color of the polymer indicated a significant amount of thermal degradation had occurred.

DAQ was copolymerized with methyl 12-hydroxydodecanoate using the two-stage process. The copolymer obtained was soluble only in HFIP, although it was slightly soluble in dipolar aprotic solvents. This polymer was not characterized further.

Conclusion

We successfully incorporated donor–acceptor quinodimethane monomers in condensation copolymers with more flexible α-hydroxy-ω-ester monomers. A procedure using benzophenone for the polyesterification led to 1:1 copolymers with moderate to high viscosities. In these polymers, as well as in the monomers, the IR data indicate that a high degree of electron delocalization occurs from the donor moiety to the acceptor moiety. This proves that the highly dipolar character observed in the monomeric quinodimethanes is preserved in the polymer chain and all these dipoles point in the same direction.

Experimental Section

Methods. Infrared spectra were determined with a Perkin-Elmer 1430 spectrometer. ^1H NMR spectra (90 MHz) were determined with a Varian EM390 spectrometer and 270-MHz spectra were obtained with an IBM WP270SY spectrometer. UV spectra were determined with a Cary 15 UV–vis spectrometer. Melting points were obtained with a Thomas Hoover melting-point apparatus and are uncorrected. Mass spectra, polymer transitions, and elemental analyses were provided by the Analytical Sciences Division of the Research Laboratories, Eastman Kodak Co.

Synthesis of Methyl α-Cyanophenylacetate. This is a modification of Mulvaney's procedure.[9]

Into a 5-L, three-neck flask equipped with a reflux condenser, mechanical stirrer, and dropping funnel were placed sodium hydride (240 g of 50% oil dispersion, 5.0 mol), THF (1500 mL), and dimethyl carbonate (395 g, 4.3 mol). Methanol (0.5 mL) was added to prevent the induction period at the start of the reaction. The dropping funnel was charged with phenylacetonitrile (250 g, 2.1 mol) diluted to 500 mL with THF. The flask was swept with nitrogen and, with vigorous stirring, phenylacetonitrile (30 mL of solution) was added. One should note that this reaction exhibits autoacceleration due to the formation of methoxide as a byproduct. For this reason, a dry ice/ligroine bath was kept ready to control the speed of the reaction. Once the reaction began, as noted by the evolution of hydrogen gas and heat, the phenylacetonitrile solution was added at a rate to maintain a gentle reflux (addition required about 30 min). When addition was complete, the reaction mixture was heated under reflux for 4 h. THF was removed under vacuum, leaving a yellow-brown slurry that was subsequently cooled to 15 °C. As the temperature was maintained at 15 °C, aqueous acetic acid (10%, 1900 mL) was added slowly, with stirring, to hydrolyze the reaction mixture (very exothermic with hydrogen evolution). The resulting solution was then extracted with dichloromethane (4 × 500 mL) and the organic layer was dried with $MgSO_4$. Evaporation of the dichloromethane yielded a two-phase system: a clear oil (NaH protecting oil) and the brown product-containing bottom layer. The protecting oil was removed via extraction with ligroin (2 × 150 mL). The crude material was then vacuum distilled, 78% yield (288 g): bp 110–114 °C (0.5 Torr); ^1H NMR ($CDCl_3$, 90 MHz) 7.32 (m, 5 H), 4.89 (s, 1 H), 3.65 (s, 3 H), identical with authentic material.

1,3-Dithiolan-2-ylidenemethylsulfonium Iodide. *S*-Methyl-1,3-dithiolane-2-thione iodide was prepared according to Harrison.[5]

Synthesis of DTQ. Methyl α-cyanophenylacetate (0.92 g, 0.005 mol) and 1,3-dithiolan-2-ylidenemethylsulfonium iodide (1.44 g, 0.005 mol) were placed in a flask containing 3.4 mL of acetonitrile. Triethylamine (0.5 mL, 0.005 mol) was added and the solution was heated under reflux with a nitrogen blanket. The solution became deep purple in 1 min. After heating for 2 h, the reaction mixture was cooled to room temperature. Dichloromethane (20 mL) was added and the solution was washed thoroughly with water (4 ×20 mL). The organic layer was separated and dried with magnesium sulfate. Evaporation of the solvent under vacuum yielded a purple oil, which was subjected to Kugelrohr distillation at 155 °C and 0.25 Torr for 2 h to remove volatile byproducts. Dichloromethane (10 mL) was added to the tacky purple residue remaining in the distillation pot. The content of the flask was swirled vigorously and filtered through a sintered glass funnel. The addition of dichloromethane and filtration was repeated until all of the product had been transferred to the funnel. The crystalline material was dried at 70 °C under vacuum for several hours, giving 0.27 g (19.4%) of analytically pure product: mp 238–245 °C; IR (KBr, cm^{-1}) 2183 (m), 1683 (s), 1596 (s); mass spectrum *m/e* 277 (M+, parent); ^1H NMR (270 MHz, in Me_2SO-d_6 at 25 °C, ppm) 8.20 (m, 1 H), 7.60–7.48 (m, 2 H), 7.01 (m, 1 H), 3.94 (s, 4 H), 3.70 (s, 3 H); UV (CH_3CN, nm) 480 (19600), 507 (33900), 543 (47500), 588 (40000). Anal. Calcd for $C_{13}H_{11}NO_2S_2$: C, 56.3; H, 4.0; N, 5.1; S, 23.1. Found: C, 56.4; H, 4.1; N, 4.9; S, 23.3.

Synthesis of DAQ. 7,7-(Ethylenedithio)-8-carbomethoxy-8-cyanoquinodimethane (DTQ, 1.4 g, 5.1 mmol) was added to a stirred solution of 2-hydroxy-1,3-diaminopropane (0.5 g, 5.5 mmol) in acetonitrile (150 mL) at room temperature. The dark-purple color quickly faded and a light-purple precipitate formed. After the suspension was stirred at 25 °C for 2 h, it was filtered and the precipitate was washed with ethanol (40 mL), water (40 mL), and ethanol again (40 mL). The product was dried under vacuum at 70 °C overnight, yielding 1.1 g (79%) of brown powdery product. The crude material was recrystallized by dissolving an aliquot in a minimal amount of DMF (25 °C), adding an equal volume of acetonitrile, and cooling to −20 °C for several days. Filtration and washing with methanol yielded a yellow, fine-crystalline product: mp 278–280 °C; IR (KBr, cm^{-1}) 3200 (s, br), 2176 (s), 1623 (s), 1580 (s); mass spectrum *m/e* 273 (M+ parent); ^1H NMR (270 MHz, in Me_2SO-d_6/CF_3COOD at 25 °C ppm) 7.80 (m, 2 H), 7.70 (m, 2 H), 4.26 (m, 1 H), 3.75 (s, 3 H), 3.52 (m, 2 H), 3.38 (m, 2 H); UV (DMF, nm) 397 (32400). Anal. Calcd for $C_{14}N_{15}H_3O_3$: C, 61.5; H, 5.5; N, 15.4. Found: C, 60.8; H, 5.6; N, 14.9.

Synthesis of 1,3-Bis(isobutylideneamino)-2-hydroxypropane. 1,3-Diamino-2-hydroxypropane (40.6 g, 0.45 mol) was placed in a flask containing 250 mL of benzene. Isobutyraldehyde (91 mL, 71 g, 1 mol) was added, and the resulting solution was heated under reflux (18 h) with continual removal of water via a Soxhlet extractor charged with magnesium sulfate. The reaction mixture was then cooled and the solvent stripped under vacuum on a rotary evaporator. The crude, oily product was distilled under vacuum through a 10-cm Vigreux column, giving 79.1 g (89%) of product: bp 85–90 °C (0.4 Torr); IR (neat NaCl plates, cm^{-1}) 3400 (OH str), 1665 (C=N str). The product was used without further characterization.

Synthesis of 1,3-Bis(isobutylamino)-2-hydroxypropane Dihydrochloride. 1,3-Bis(isobutylideneamino)-2-hydroxypropane (11.9 g, 0.06 mol) was hydrogenated over RaNi in ethanol. After the solvent was removed, the crude oil was taken up in ethyl ether. Dry HCl gas was then passed through the stirred solution for 30 min, after which time the suspension was filtered and the precipitate was washed with ethyl ether. The crude material was recrystallized from methanol/isopropyl alcohol, giving 3.9 g (24%) of white powdery product: mp >260 °C; IR (KBr, cm^{-1}) 3400 (m), 2960 (s), 2780 (s), 2400 (w), 1560 (m), 1480 (m); ^1H NMR (90 MHz, in D_2O at 25 °C, ppm) 4.32 (m, 2 H), 3.20 (m, 4 H), 3.13 (s, 1 H), 3.0 (d, 2 H), 2.07 (sept, 2 H), 1.03 (d, 12 H). Anal. Calcd for $C_{11}H_{28}Cl_2N_2O$: C, 48.0; H, 9.9; N, 10.2; Cl, 25.8. Found: C, 47.5; H, 9.5; N, 10.1; Cl, 25.7.

Synthesis of DIQ. 1,3-Bis(isobutylamino)-2-hydroxypropane (0.29 g, 0.0011 mol) was dissolved in DMF (1 mL), and DTQ (0.4 g, 0.0014 mol) was added. The solution was stirred at 74 °C for 1.5 h with a nitrogen purge and then cooled to room temperature. The reaction mixture was placed under vacuum to remove DMF. The crude, oily material was chromatographed on silica gel using 10% THF/90% dichloromethane to remove nonpolar contaminants followed by 30% MeOH/70% dichloromethane to elute the product mixture. Evaporation of the ethanolic eluent yielded red crystals. The solid was dissolved in a minimum amount of dichloromethane and cooled to −20 °C for 3 days. Filtration yielded analytically pure yellow crystals; 0.05 g, (12%); mp 248–251 °C, IR (KBr, cm^{-1}) 3330 (s), 2161 (s), 1641 (m), 1621 (m), 1592 (s); mass spectrum *m/e* 385 (M+, parent); ^1H, NMR (270 MHz in Me_2SO-d_6 at 25 °C, ppm) 7.72 (m, 2 H), 6.99 (m, 1 H), 6.90 (m, 1 H), 5.68 (d, 1 H), 4.30 (s, 1 H), 3.70 (m, 2 H), 3.45 (m, 5 H), 3.01 (d, 4 H), 1.90 (sept, 2 H), 0.71 (m, 12 H); UV (CH_3CN, nm) 348 (20000), 233 (22400). Anal. Calcd for $C_{22}H_{31}N_3O_3$: C, 68.4; H, 8.0; N, 10.7. Found: C, 68.5; H, 8.1; N, 10.9.

Synthesis of DEQ. 2-(2-(Aminoethyl)amino)ethanol (9.56 g, 0.092 mol) was placed in a 500-mL flask. Acetonitrile (140 mL) was added and DTQ (25.43 g, 0.092 mol) was also added to the solution. DMF (50 mL) was added to the resulting purple slurry and the reaction mixture color quickly changed from deep purple to lavendar. After the reaction was stirred at 25° C for 2.5 h, a distillation head was fitted to the flask. Acetonitrile was removed from the reaction mixture at room temperature under aspirator vacuum, followed by removal of DMF and ethanedithiol at 0.9 Torr and 25 °C. The tacky residue was then triturated with hot acetonitrile (2 × 200 mL). Filtration and drying of the solid yielded 18.1 g (68%) of a brownish-yellow solid: mp 245–248 °C; IR (KBr, cm^{-1}) 3370 (s), 3205 (m), 2160 (s), 1630 (s), 1590 (s), 1501 (s), 1348 (s); ^1H NMR (270 MHz, in Me_2SO-d_6 + D_2O + CF_3COOD at 25 °C, ppm) 7.82 (d, 2 H), 7.73 (d, 2 H), 4.11 (m, 2 H), 4.00 (m, 2 H), 3.79 (s, 3 H), 3.65 (t, 2 H), 3.46 (t, 2 H); UV (DMF, nm) 397 (28900). Anal. Calcd for $C_{15}H_{17}N_3O_3$: C, 62.7; H, 6.0; N, 14.6. Found: C, 62.1; H, 6.0; N, 14.6.

Copolymerization of DAQ with 12-Hydroxydodecanoic Acid. Synthesis of a 5:1 Copolymer. Into a polymerization flask were placed DAQ (0.81 g, 2.9 mmol) and 12-hydroxydodecanoic acid (0.13 g, 0.58 mmol, 20 mol %), and the vessel was flushed with nitrogen. The flask was placed in a 250 °C oil bath and, after a homogeneous melt was achieved, nitrogen was bubbled through the melt. Titanium tetraisopropoxide (2 drops) was added. After 90 min the crusty, viscous mixture was placed under vacuum and stirred at 255 °C for an additional 3 h. After cooling to room temperature, the dark, solid product was scraped out of the flask. The copolymer was insoluble in common laboratory solvents and had a glass transition temperature of 208 °C. Anal. Calcd for 5:1 copolymer: C, 66.1; H, 5.7; N, 14.48. Found: C, 66.0; H, 5.5; N, 13.9.

Synthesis of a 1:1 Copolymer. Into a dry 50-mL polymerization flask were placed DAQ (0.80 g, 2.9 mmol) and 12-hydroxydodecanoic acid (0.63 g, 2.9 mmol). The flask was flushed with nitrogen and then heated to 200 °C. Titanium tetraisopropoxide (1 drop, 0.01 g) was added, and the heterogeneous mixture was heated under nitrogen to 200 °C for 2 h. A mechanical stirrer was fitted to the flask and vacuum (0.3 Torr) was applied. After 80 min, the polymer was a brown, solid crystalline mass. The polymer was insoluble in DMF and Me_2SO and was soluble in 1,1,1,3,3,3-hexafluoro-2-propanol. The inherent viscosity in HFIP at 25 °C was 0.23, the polymer had a glass transition temperature of 27 °C and a crystalline melting point of 62 °C: UV (HFIP, nm) 234 (13 900). Anal. Calcd: C, 68.3; H, 7.5; N, 9.5. Found: C, 65.8; H, 7.5; N, 8.8.

Synthesis of Methyl 4-(Hydroxyethyl)oxybenzoate. Into a flask were placed 4-(hydroxyethyl)oxybenzoic acid, methanol (200 mL) and sulfuric acid (1 mL). The suspension became homogenous when heated under reflux. After the solution was heated for 5.75 h, it was cooled and poured into toluene (100 mL). Water (150 mL) was added and the organic layer was separated. The aqueous layer was extracted with toluene (3 × 100 mL), and the combined organic layers were dried ($MgSO_4$). Evaporation of the solvent yielded a white solid which was recrystallized from CCl_4. White crystals (12.8 g, 59%), mp 65–66 °C, were obtained. Anal. Calcd for $C_{10}H_{12}O_4$: C, 61.2; H, 6.2. Found: C, 68.3; H, 11.0.

Copolymerization of DEQ with Methyl 12-Hydroxydodecanoate. Into a 10-mL polymerization vessel were placed DEQ (1.00 g, 3.5 mmol), methyl 12-hydroxydodecanoate (0.80 g, 3.5 mmol) and benzophenone (1.0 g). The flask was flushed with nitrogen for several minutes and then placed into a 160 °C oil bath. The dodecanoate and the solvent melted, resulting in a yellow suspension. Dibutyltin diacetate (1 drop, 0.01 g) was added, and the suspension was stirred for 18 h at 150–160 °C. As the same temperature was maintained, vacuum was applied (0.7 Torr) and the stirring was continued for an additional 32 h. The partially solid mass was cooled and collected. The crude polymer was triturated with methanol for 3 days and filtered, resulting in the recovery of 1.45 g of light brown-yellow product. The polymer was soluble in HFIP, 1:1 phenol/chlorobenzene, pyridine, hot Me_2SO, and hot *N*-methylpyrrolidinone, forming bright-yellow solutions. The inherent viscosity, 0.32, was determined with a 0.5% solution in phenol/chlorobenzene (1:1) at 25 °C and the melting point was determined by DSC under an inert atmosphere. Anal. Calcd for 1:1 copolymer: C, 68.8; H, 7.8; N, 9.3. Found after drying at room temperature: C, 66.0; H, 7.6; N, 9.2. Found after drying at 100 °C (above T_m): C, 67.6; H, 8.2; N, 7.3.

General Procedure. In order to obtain a series of polymers with varied inherent viscosities, the above procedure was modified as follows: The reagents were mixed in the polymerization vessel and the vessel was flushed with nitrogen, as before. The first stage was constant for all polymerizations and was begun by placing the flask in a 150 °C oil bath. When a yellow suspension was obtained, dibutyltin diacetate (1 drop, 0.01 g) was added and the mixture was stirred at 150 °C. By allowing the second state to proceed for 15.5 or 63.5 h, after workup as before, one obtains polymer with inherent viscosities of 0.16 and 0.45, respectively (1/1 phenol/chlorobenzene, 25 °C).

The copolymerizations of DEQ/2-HEOB and DAQ/12-HDE were performed by utilizing the benzophenone technique described above.

References and Notes

(1) Iwatsuki, S. *Adv. Polym. Sci.* **1984,** *58,* 93.
(2) Mulvaney, J. E. *Polym. Sci. Technol.* **1984,** *25,* 311.
(3) Hall, H. K., Jr.; Cramer, R. J.; Mulvaney, J. E. *Polym. Bull. (Berlin)* **1982,** *7,* 173.
(4) Gompper, R.; Wagner, H.; Kutter, E. *Chem. Ber.* **1968,** *101,* 4123.
(5) Gompper, R.; Wagner, H.; Kutter, E. *Chem. Ber.* **1968,** *101,* 4141.
(6) Harrison, B. L.; Dolfini, J. E. U.S. Patent 4 131 683, 1978.
(7) Hammett ρ values for dimethylamino (0.83), amino (−0.66), and methylthio (0.00) indicate that nitrogen is a better electron donor via resonance than is sulfur (values taken from: Pine, S. H.; Hendrickson, J. B.; Cram, D. J.; Hammond, G. S. *Organic Chemistry,* 4th ed.; McGraw-Hill: New York, 1980.
(8) Kantor, S. W.; Holub, F. F. U.S. Patent 3 160 602, 1964.
(9) Hall, H. K., Jr.; Cramer, R. J.; Mulvaney, J. E. *Polym. Bull. (Berlin)* **1982,** *7,* 165.

Synthesis of Polyesters Containing a Nonrandomly Placed Highly Polar Repeat Unit

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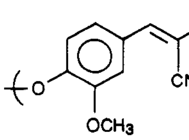
ABSTRACT: Three novel monomers containing the *p*-oxy-α-cyanocinnamate structure were synthesized from ω-hydroxyalkoxy-substituted benzaldehydes and methyl cyanoacetate. These ω-hydroxy-α-cyanoester monomers show a high degree of electron delocalization. Copolyesters were synthesized by copolymerization of these monomers with methyl 12-hydroxydodecanoate by the standard two-stage, high-temperature polyesterification procedure. The copolyesters, incorporating dipolar units all pointing in the same direction, are soluble and solution- and melt-processable.

Introduction

We recently synthesized a series of AB copolyesters with a highly dipolar quinodimethane repeat unit, with all the dipoles pointing in the same direction along the polymer chain.[1] These polymers were not readily soluble in common solvents like dichloromethane and were not meltable, hence were not readily processable. Accordingly, in this work we have synthesized copolyesters with somewhat less dipolar repeats units in order to achieve processability. The group we selected is the *p*-oxy-α-cyanocinnamate unit



Several monomers containing this unit were synthesized and then homo- and copolymerized. The resulting polymers were then characterized.

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