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Syntheses and Characterization of Heteroatom-Bridged Metal-Free Phthalocyanine Network Polymers and Model Compounds

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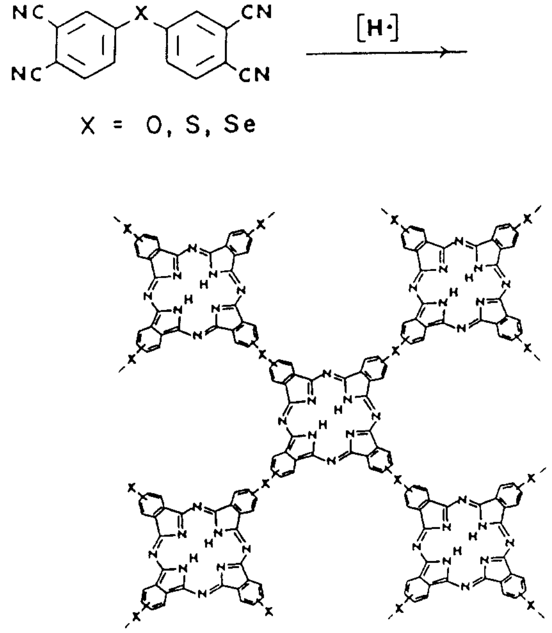
ABSTRACT: Procedures for the preparation of metal-free phthalocyanine network polymers from oxygen-, sulfur-, and selenium-bridged bis(phthalonitrile) monomers were investigated on the basis of phthalocyanine model compounds derived from phenoxy-, (phenylthio)-, and (phenylseleno)phthalonitrile compounds. The oxygen- and sulfur-substituted phthalonitrile compounds could be converted in high yield to the corresponding metal-free phthalocyanine compounds by reaction with tetrahydropyridine, hydroquinone, or 4,4′-biphenol. With an optimum quantity of coreactant, the phthalocyanine yield ranged from near-quantitative to 65% to no conversion for the respective oxygen, sulfur, and selenium phthalonitriles. A side reaction to a triazine structure was also investigated. The model phthalocyanine compounds were characterized by IR, electronic, ^{1}H NMR, and X-ray diffraction spectroscopies and TGA, from which an analysis of the corresponding phthalocyanine network polymers was made. Spectroscopic analysis and sulfuric acid insolubility indicated a significantly higher phthalocyanine content in the oxygen-bridged network polymer. Both phthalocyanine model compounds and network polymers had very high electrical resistivities, and the polymers were not dopable with iodine.

Introduction

As a polymer-forming reaction, the cyclotetramerization of a phthalonitrile functional group to a phthalocyanine macrocycle presents a route where, ideally, a bis(phthalonitrile) monomer is transformed to a phthalocyanine network polymer. Energetically, the high aromatic character of the phthalocyanine ring[1] makes this reaction very favorable. This polymerization was first studied by Marvel and Martin, who used 3,3′,4,4′-tetracyanodiphenyl ether in a heterogeneous fusion reaction with copper bronze at 275 °C.[2] Numerous subsequent polymerizations of bis(phthalonitriles) under fusion reaction conditions with metals or metal salts have been reported[3] although structural characterization of the products has been lacking. Marvel and Martin initially cautioned that the polymerization progresses beyond the dimer and trimer stage only with difficulty. Boston and Bailar have demonstrated by careful model compound work that a 1,2,4,5-tetracyanobenzene–cupric chloride polymerization does not progress beyond the formation of monomeric phthalocyanine complexes.[4] While these reaction conditions have been developed by Linstead and co-workers for conversion of simple phthalonitrile to phthalocyanine compounds,[5] an incomplete molecular dispersal of the metal or metal salt coreactant in a network-forming organic polymer system can set a limit on the degree of conversion obtainable. This coreactant dispersion problem may be circumvented by use of a compatible soluble organic coreactant for conversion of the phthalonitrile to the metal-free phthalocyanine. The patent literature, while lacking analytical characterization, contains claims of several examples of such reagents, which include alcohols, amines, and amides.[6] We have recently found that metal-free phthalocyanine compounds can be prepared in high yield from phthalonitriles in the presence of an appropriate proton-donating organic reducing agent such as hydroquinone and that such coreactants are very useful for curing bis(phthalonitrile) monomers to phthalocyanine resins.[7]

In the present work the objective is to prepare phthalocyanine network polymers from heteroatom (oxygen, sulfur, and selenium) bridged bis(phthalonitrile) monomer melts (eq 1) and to investigate their potential as electrically



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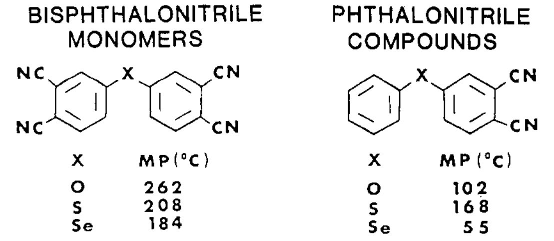


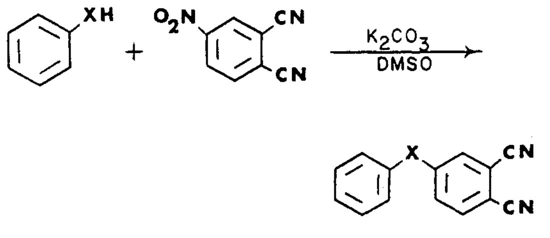
Figure 1. Structures and melting points of bis(phthalonitrile) monomers and monofunctional phthalonitrile compounds.

conducting materials. Since most polymeric systems with high electrical conductivity are structurally characterized by unsaturated repeat units either directly bonded (e.g., polyacetylene and polyphenylene) or bridged by single-atom units of oxygen or sulfur (e.g., poly(phenylene oxide) or poly(phenylene sulfide)),[8] the approach of converting a bis(phthalonitrile) ether, thioether, or selenoether to the corresponding phthalocyanine network polymer appeared promising. The synthetic advantage in using an ether-linked bis(phthalonitrile) as opposed to a rigid monomer such as 4,4′-bis(phthalonitrile) or 2,3,4,5-tetracyanobenzene is the flexibility of the ether linkage permits monomer melt formation at subdecomposition temperatures, and, with increased functional group mobility, it would facilitate a higher conversion to phthalocyanine. Since each phthalocyanine linkage is a tetrafunctional interunit junction, high conversion to phthalocyanine may not be required to attain high molecular weight or network formation. In the ideal case, such a network structure would have a high phthalocyanine structure unit density connected by bridging atoms which are known to permit electron delocalization and moderate electrical conductivity in linear polymer systems after a doping reaction. Iodine has been reported to be an effective doping reagent for phthalocyanine compounds[9] and polymers.[10]

The approach is to use a model compound strategy as an analytical tool for structural analysis and as an evaluation method for determining coreactant efficiency in conversion of phthalonitriles to phthalocyanines. The structures and melting points of the bis(phthalonitrile) monomers and phthalonitrile compounds are presented in Figure 1. In this paper the syntheses of the phthalonitrile compounds and monomers, their conversion to phthalocyanine structures by hydroquinone, 4,4′-biphenol, and tetrahydropyridine, and the characterization of the phthalocyanine products are described.

Results and Discussion

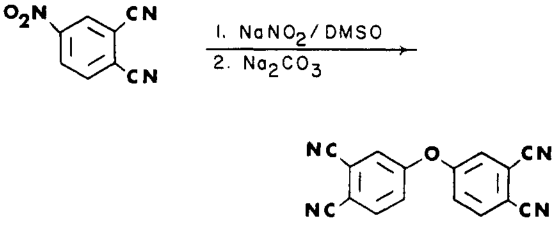
Phthalonitrile Compound and Bis(phthalonitrile) Monomer Synthesis. The base-catalyzed nucleophilic aromatic nitro displacement of 4-nitrophthalonitrile with phenol, thiophenol, or selenophenol yielded the corresponding oxygen-, sulfur-, or selenium-substituted phenyl phthalonitrile ether in good yield as depicted in eq 2. This



(2)

X = O(1), S(2), Se(3)

reaction has been very useful in the preparation of a variety of ether-substituted phthalonitriles and bis(phthalonitriles).[11] However, the oxygen-, sulfur-, and selenium-bridged bis(phthalonitrile) monomers could not be synthesized by simply substituting the hydroxide, sulfide, or selenide sodium salts for the corresponding phenol in a double-displacement reaction. The reaction can be made to proceed by activating the nitro group of 4-nitrophthalonitrile by complexation with anhydrous sodium nitrite in Me_2SO. The oxygen-bridged bis(phthalonitrile) ether is obtained in a single-step synthesis by using the carbonate anion as the nitro-displacing nucleophile.[12] The carbonate–phthalonitrile adduct is not isolated but decarboxylates to the phenolate, which rapidly reacts with a second nitrophthalonitrile to yield the 3,3′,4,4′-tetracyanodiphenyl ether (4) (eq 3). This compound has very



(3)

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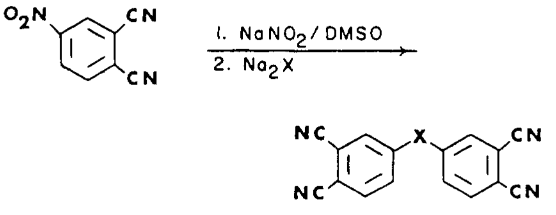
low solubility in most organic solvents but could be purified in anhydrous form by passing a Me_2SO solution through a neutral alumina column. Marvel and Martin prepared this bis(phthalonitrile) ether by a five-step synthesis and found *N,N*-dimethylformamide recrystallization yielded a product with 0.25 mol of water cocrystallized.[2] The anhydrous bis(phthalonitrile) ether slowly absorbs water from the air, and the presence of this water may catalytically divert the bis(phthalonitrile) to form a triazine structure instead of the phthalocyanine structure (vide infra).

The 3,3′,4,4′-tetracyanodiphenyl thioether (5) and selenoether (6) were prepared by substituting anhydrous sodium sulfide and sodium selenide for sodium carbonate (eq 4). It is important that the Me_2SO and sodium salts



(4)

X = S(5), Se(6)

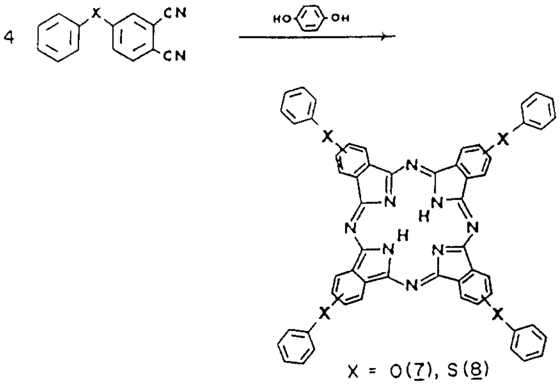
be anhydrous and that the 4-nitrophthalonitrile be used in slight excess. A small quantity of water causes the bis(phthalonitrile) ether (4) to be the major product. Excess sulfide or selenide ion slowly reacts with the nitrile groups, as verified in a control experiment with phthalonitrile.[13]

Phthalocyanine Model Compound Syntheses. Phthalocyanine model compounds were synthesized for the purposes of using structural characterization data to analyze the network polymer system and to determine optimal polymerization conditions for conversion of phthalonitrile to phthaloanine. The oxygen, sulfur, and selenium phenyl phthalonitrile ethers were selected to mimic the corresponding bis(phthalonitrile) monomers in both molecular structure and chemical reactivity.

A classical Linstead preparation of metal-free phthalocyanine from phthalonitrile proceeds through a dilithium phthalocyanine intermediate followed by proton–lithium ion exchange.[14] Phthalocyanine ring formation requires 2 electrons from a redox reaction in addition to the 16 π

electrons from the 8 nitrile groups to yield the 18-π-electron aromatic system. In the Linstead synthesis, the lithium amyl alkoxide/amyl alcohol reaction medium is the source of the reducing agent.[5] Under more severe reactions conditions, the reaction of an alcohol with a phthalonitrile to yield a phthalocyanine will occur in the absence of the lithium alkoxide salt as was reported for methanol and (4-cumylphenoxy)phthalonitrile at 300 °C.[7] If an easily oxidizable alcohol such as hydroquinone is used in stoichiometric quantity, the temperature may be reduced from 300 to 165 °C. Nucleophilic reagents that undergo a facile reduction to aromatic products such as 1,2,3,6-tetrahydropyridine, piperidine, piperazine, and thiazolidine are also effective coreactants for the conversion of phthalonitrile to metal-free phthalocyanine.[15] These reactions are conducted as a uniphase fused melt of phthalonitrile and coreactant.

The tetraphenoxy- and tetrakis(phenylthio)phthalocyanine model compounds, 7 and 8, respectively, were prepared by reacting the corresponding phenyl phthalonitrile ether with a stoichiometric quantity of hydroquinone or tetrahydropyridine in a sealed tube (eq 5). The tetrasubstituted phthalocyanine products were soluble in tetrahydrofuran and were chromatographed on neutral alumina to give elemental analysis consistent with the product structure. Subsequently, yields were conveniently determined by optical density measurement of the reaction mixture in tetrahydrofuran solution (Figure 3). The highest yield obtained for the tetraphenoxyphthalocyanine was 98% while that for the tetrakis(phenylthio)phthalocyanine was 60%. The phenyl phthalonitrile selenoether yielded no phthalocyanine product. It was also inert to reaction with activated copper bronze, which is known to produce copper phthalocyanine in high yield from phthalonitrile.[16] A similar inertness was observed with the bis(phthalonitrile) selenoether monomer. There appears to be a correlation between phthalonitrile bonded oxygen, sulfur, and selenium modification of phthalocyanine-forming reactivity and their descending positions in group 6 of the periodic table.[41]



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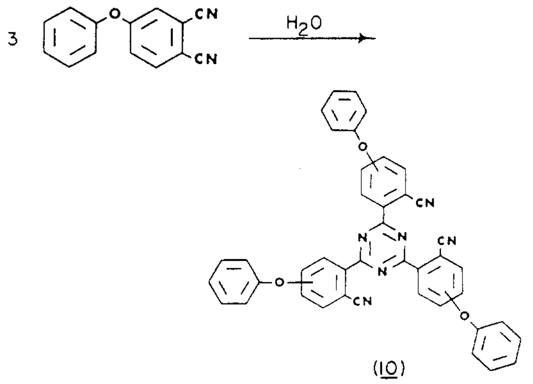

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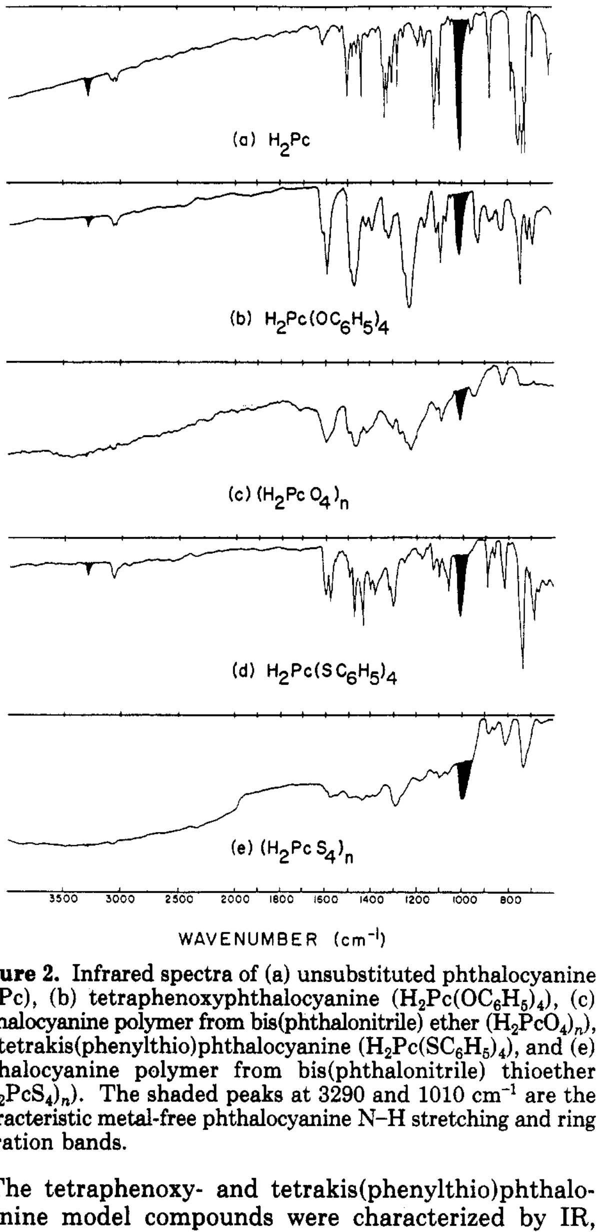

Figure 2. Infrared spectra of (a) unsubstituted phthalocyanine (H_2Pc), (b) tetraphenoxyphthalocyanine ($H_2Pc(OC_6H_5)_4$), (c) phthalocyanine polymer from bis(phthalonitrile) ether ($(H_2PcO_4)_n$), (d) tetrakis(phenylthio)phthalocyanine ($H_2Pc(SC_6H_5)_4$), and (e) phthalocyanine polymer from bis(phthalonitrile) thioether ($(H_2PcS_4)_n$). The shaded peaks at 3290 and 1010 cm^{-1} are the characteristic metal-free phthalocyanine N–H stretching and ring vibration bands.

The tetraphenoxy- and tetrakis(phenylthio)phthalocyanine model compounds were characterized by IR, electronic, and ^{1}H NMR spectroscopies. IR spectra of unsubstituted, phenoxy, and phenylthio metal-free phthalocyanines are presented in Figure 2. IR bands characteristic of the metal-free phthalocyanine ring[17] are a ring vibration at 1010 cm^{-1} and an N–H stretching at 3290 cm^{-1}. These bands are particularly useful for characterization of polymeric metal-free phthalocyanines since there is little frequency dependence on ring substitution and they are not overlapped by strong bis(phthalonitrile) monomer absorptions. The electronic spectra of these compounds are presented in Figure 3. The unique spectral absorption shape is characteristic of the metal-free phthalocyanine chromophore.[18] Tetrasubstitution in the 2- or 3-benzo positions with phenoxy and phenylthio groups causes a respective 13- and 21-nm red shift from the 684-nm maximum at the unsubstituted metal-free phthalocyanine. This absorption deviates from Beer's law as indicated in Figure 3. The most interesting feature of the ^{1}H NMR spectra of the model phthalocyanine compounds is the extraordinarily high upfield shift of the cavity proton signal, which occurs at $\delta = -8.0$ for tetraphenoxyphthalocyanine and at $\delta = -9.0$ for tetrakis(phenylthio)phthalocyanine (Figure 4). This is a much higher upfield chemical shift than that for the porphyrins, which ranges from $\delta = -3$ to $\delta = -5$.[19] Phthalocyanine compounds

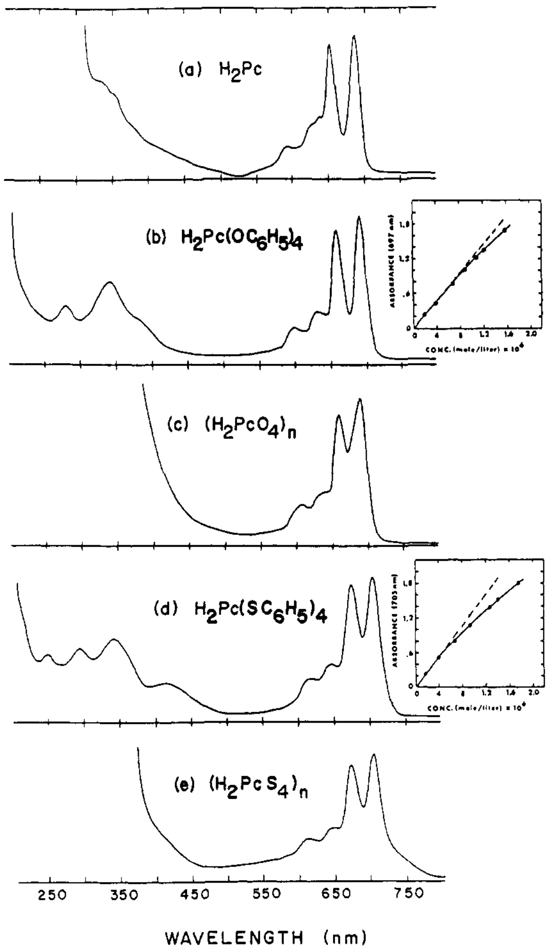

Figure 3. Electronic spectra of tetrahydrofuran solutions of (a) unsubstituted phthalocyanine (H_2Pc), (b) tetraphenoxyphthalocyanine ($H_2Pc(OC_6H_5)_4$; Beer's law plot of 697-nm absorption inserted), (c) partially polymerized bis(phthalonitrile) ether ($(H_2PcO_4)_n$), (d) tetrakis(phenylthio)phthalocyanine ($H_2Pc(SC_6H_5)_4$; Beer's law plot of 705-nm absorption inserted), and (e) partially polymerized bis(phthalonitrile) thioether ($(H_2PcS_4)_n$).

are known to associate as dimers and as higher order complexes in solution,[20] and a cofacial complex structure would promote a stronger ring current effect.[21] The association in solution also accounts for the Beer's law deviation. This cavity proton assignment was verified by deuterium exchange with D_2O. Deuterium exchange also causes the N–H absorption in the infrared to shift from 3290 to 2490 cm^{-1}, confirming the IR assignment.[17] The metal-free phthalocyanine ring may then be detected and analyzed in solution by the electronic spectrum line shape and the cavity proton ^1H NMR signal and also in the solid state by the IR 3290-cm^{-1} N–H stretching and 1010-cm^{-1} ring vibration bands.

To determine the coreactant–phthalonitrile stoichiometry for maximum conversion of phthalonitrile to phthalocyanine, the phthalocyanine yield was measured with variation of the coreactant to phthalonitrile molar ratio in a neat sealed tube reaction. The considerations in coreactant selection were a high conversion to phthalocyanine, thermal stability at the bis(phthalonitrile) monomer melting point (200–275 °C), and a lowest weight fraction of coreactant to minimize the coreactant byproduct occluded in the polyphthalocyanine network. The coreactants selected were hydroquinone, 1,2,3,6-tetrahydropyridine, and 4,4′-biphenol. A previous study had shown hydroquinone to be the most effective dihydroxybenzene for the conversion of (cumylphenoxy)phthalonitrile to the phthalocyanine.[7] However, hydroquinone decomposes to quinhydrone at 160 °C.[22] Tetrahydropyridine is a more effective coreactant,[15] thermally stable for at least 1 h at 275 °C and lower in molecular weight. If oxidized to pyridine, it can generate four electrons and protons for the formation of two phthalocyanine rings as opposed to half that number for hydroquinone. However, both hydroquinone and tetrahydropyridine are volatile compounds above 100 °C and require sealed vessels for polymerization reactions. 4,4′-Biphenol is nonvolatile, is stable, and melts at 265 °C but a much larger weight fraction is required. If quantitative oxidations of the coreactants for phthalocyanine formation are assumed, stoichiometric additions of hydroquinone, tetrahydropyridine, or biphenol to the oxygen-bridged bis(phthalonitrile) monomer would require coreactant weight fractions of 17, 6.8, or 25%, respectively, in a polymerization reaction. The phthalocyanine yield profiles for the phenoxy- and (phenylthio)phthalonitriles with varying quantities of the coreactants are presented in Figure 5. In both cases there is an optimum quantity of coreactant for a maximum phthalocyanine yield, and higher yields, in one case near-quantitative, were obtained for the phenoxyphthalonitrile. With the tetrahydropyridine coreactant the phthalocyanine yields were highest, and the maximum is very close to the stoichiometric 8:1 phthalonitrile:tetrahydropyridine molar ratio. On the basis of this result tetrahydropyridine was selected as the coreactant for network polymer preparation.

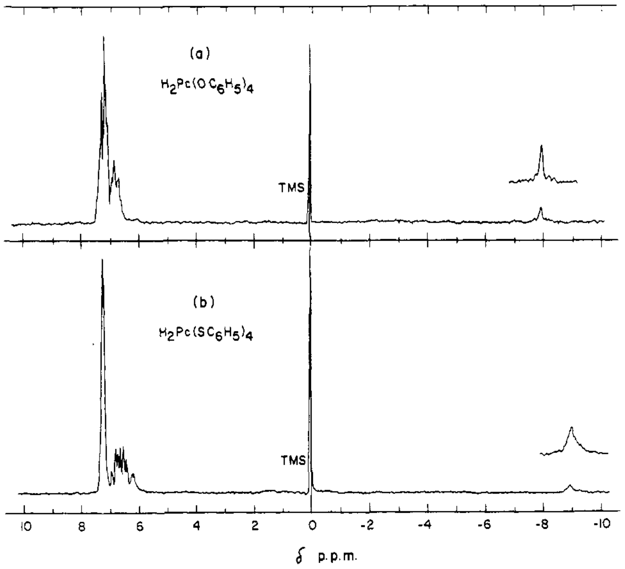

Figure 4. ^1H NMR spectra of (a) tetraphenoxyphthalocyanine ($H_2Pc(OC_6H_5)_4$) and (b) tetrakis(phenylthio)phthalocyanine ($H_2Pc(SC_6H_5)_4$).

Triazine Model Compound Syntheses. In addition to phthalocyanine formation, conversion of phthalonitrile to dehydrophthalocyanine, isoindoline, and triazine structures is possible (Figure 6). Dehydrophthalocyanine has been reported but not isolated in pure form or characterized[23] and is of questionable stability.[24] The isoindoline structure is a known and isolable intermediate in the alkoxide- or ammonia-catalyzed conversion of phthalonitrile to phthalocyanine.[3,23,25] Regarding triazine formation, it was shown by Ross and Fineman that a 45% yield of tris(2-cyanophenyl)-1,3,5-triazine (**9**) could be obtained by heating phthalonitrile with a 0.1% by weight quantity of added water in a sealed tube at 325 °C.[26] This work was reproduced with phthalonitrile and with the phenoxyphthalonitrile compound (eq 6). Since the bis(phthalonitrile) monomers absorb small quantities of water after standing several hours in air, triazine formation is

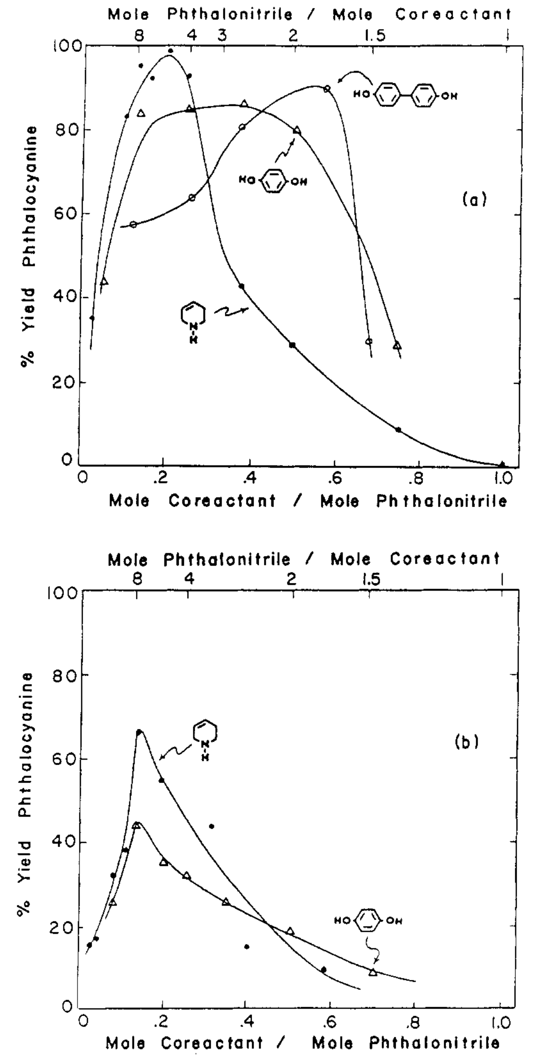

Figure 5. Phthalocyanine yield profiles from (a) phenoxyphthalonitrile and (b) (phenylthio)phthalonitrile with the hydroquinone, tetrahydropyridine, and biphenol coreactants as designated.

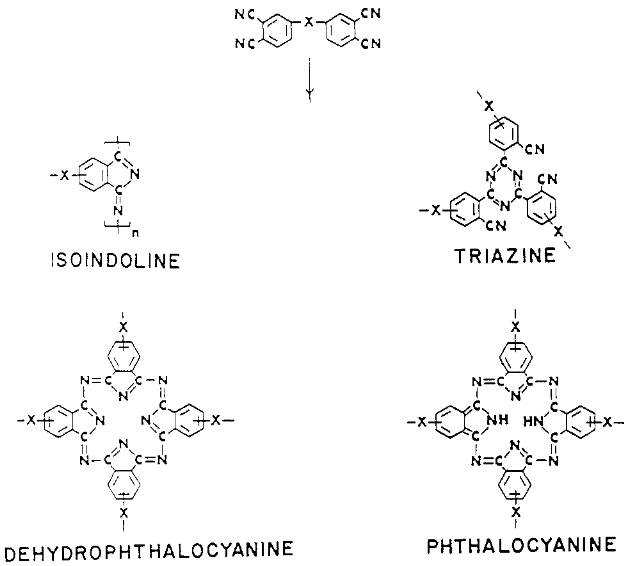

Figure 6. Possible polymeric linking structures from the phthalonitrile functional group.

a distinctly possible side reaction. The triazine products were isolated and characterized by IR, ^{1}H NMR, and mass spectroscopies. The IR spectra are presented in Figure 7. Of primary importance are the weak nitrile band at 2221 cm^{-1} and the strong triazine absorptions at 1520 and 1360 cm^{-1}. Noteworthy is a small but significant shift of the tris(cyanophenyl)triazine nitrile band from that of the phthalonitrile compound (2244 cm^{-1}) or bis(phthalonitrile) monomer (2238 cm^{-1}). Also the strong triazine absorptions do not overlap strong bands in the phthalonitrile compound or bis(phthalonitrile) monomer. In the ^{1}H NMR spectra, the signal corresponding to the protons ortho to the triazine ring is a downfield-shifted doublet at 9.2 ppm (Figure 8). These spectroscopic features are useful for detection of the triazine structure.

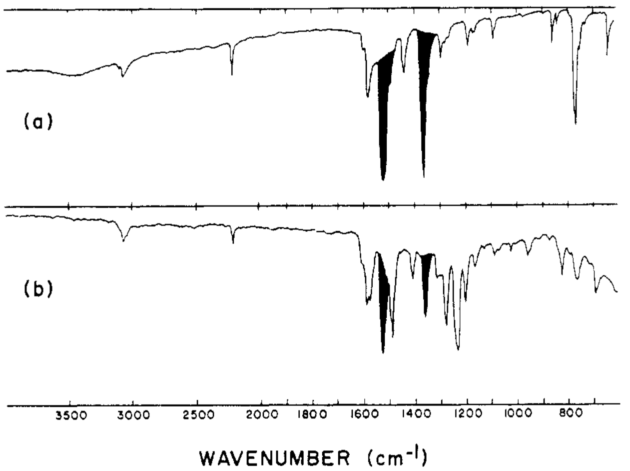

Figure 7. Infrared spectra of (a) tris(2-cyanophenyl)-1,3,5-triazine (**9**) and (b) tris[(4(or 5)-phenoxy-2-cyanophenyl)]-1,3,5-triazine (**10**). The shaded peaks at 1520 and 1360 cm^{-1} are characteristic bands of the 1,3,5-triazine ring.

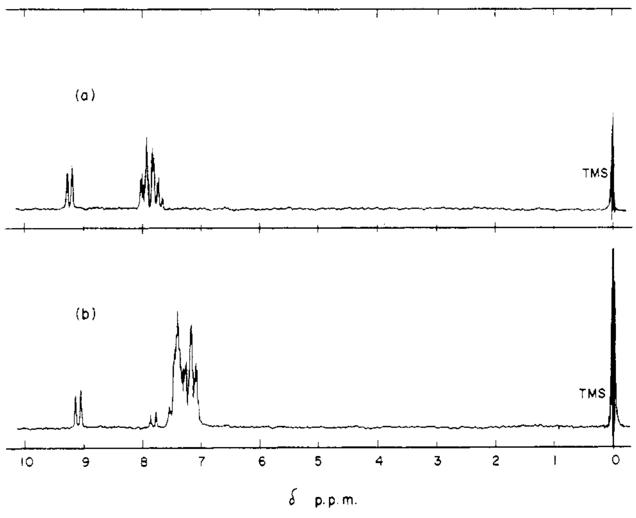

Figure 8. ^{1}H NMR spectra of (a) tris(2-cyanophenyl)-1,3,5-triazine (**9**) and (b) tris[(4(or 5)-phenoxy-2-cyanophenyl)]-1,3,5-triazine (**10**).

Polymerization of Bis(phthalonitrile) Monomers. The purified and degassed bis(phthalonitrile) ether and thioether monomers were polymerized by addition of a stoichiometric quantity of tetrahydropyridine (4:1 mole ratio) in an evacuated sealed tube at 275 °C, which is a melt temperature common to both monomers. The crude products were lustrous purple and very resistant to grinding. Pyridine was detected as a byproduct by IR spectroscopy. After grinding, the samples were purified by Soxhlet extraction with tetrahydrofuran to yield a dark blue-purple powder with a purple reflex. Less than a 1% by weight of the crude product was extracted.

Characterization of the Phthalocyanine Network Polymers. The oxygen- and sulfur-substituted phthalo-

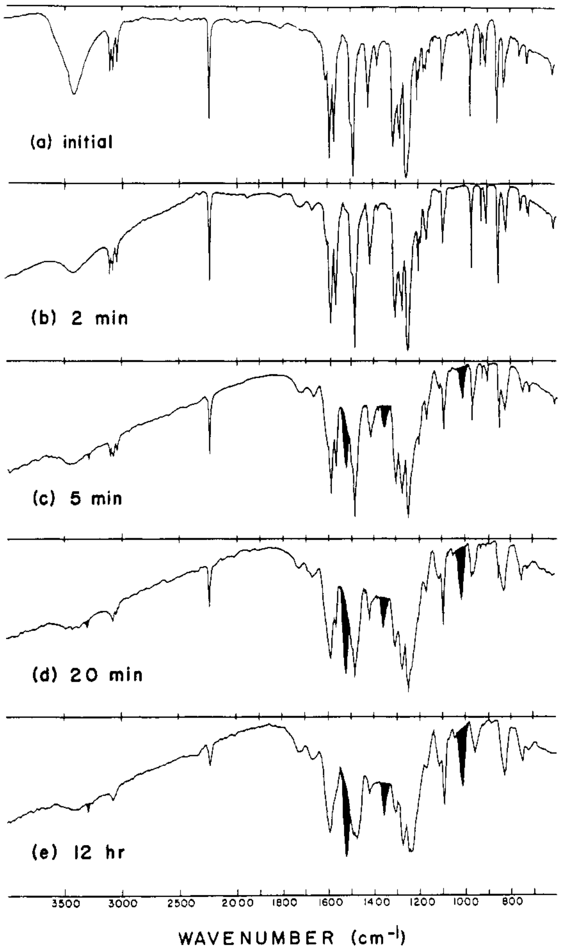

Figure 9. Successive infrared spectra of a KBr matrix polymerization of bis(phthalonitrile) ether with biphenol in a nitrogen atmosphere at 275 °C: (a) initial reagents; (b) 2 min; (c) 5 min; (d) 20 min; (e) 12 h. Shaded peaks at 3290 and 1010 cm^{-1} denote phthalocyanine formation and shaded peaks at 1520 and 1360 cm^{-1} denote triazine formation.

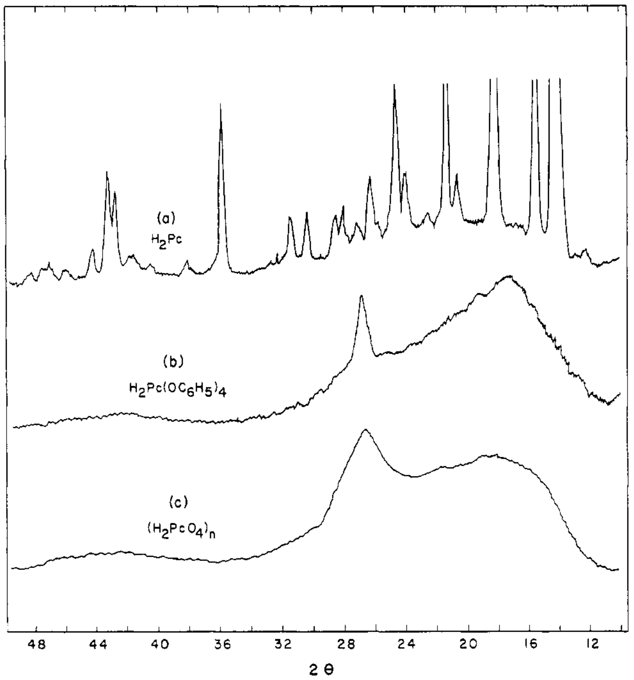

Figure 10. X-ray diffraction pattern of (a) polycrystalline unsubstituted phthalocyanine (H_2Pc), (b) tetraphenoxyphthalocyanine ($H_2Pc(OC_6H_5)_4$), and (c) phthalocyanine polymer from bis(phthalonitrile) ether (($(H_2PcO_4)_n$)).

cyanine polymers were characterized by IR spectroscopy, X-ray diffraction, sulfuric acid solubility, TGA, and electrical conductivity measurements.

IR spectra of the network polymers are presented in Figure 2. Although the polymer spectra are broadened and reduced in intensity, which is attributed to a difficulty in grinding the sample to a small particle size, a good spectral correspondence between the phthalocyanine network polymers and model compounds is observed. The characteristic metal-free phthalocyanine bands at 3290 and 1010 cm^{-1} are present. Also, the 1210- (C–O–C) and 740-cm^{-1} (C–S–C) bands are present in both respective model compounds and corresponding polymers. No evidence of triazine formation is observed, and the nitrile groups are no longer detected.

To circumvent the sample grinding difficulty, an attempt was made to conduct the polymerization of monomer and coreactant dispersed within the KBr disk and monitor the spectroscopic changes at several stages of conversion. The infrared spectra of samples at various reaction times are presented in Figure 9. The 275 °C reaction temperature necessitated the use of biphenol as coreactant to prevent its evaporation from the KBr disk. Easily detectable are the formation of phthalocyanine by appearance and growth of bands at 3290 and 1010 cm^{-1} and the formation of triazine by the appearance and growth of bands at 1520 and 1360 cm^{-1}. Triazine formation was not observed in the model compound system with the biphenol coreactant although the phthalocyanine yield was not as high as with other coreactants (Figure 5). It is possible that the reaction conditions of two high-melting reactants highly dispersed in a solid salt matrix favor triazine over phthalocyanine formation although the presence of adventitious moisture to catalyze triazine formation cannot be ruled out. Precautions to exclude moisture included, in addition to anhydrous storage of the bis(phthalonitrile) monomer, drying the KBr at 400 °C under vacuum, premixing and 180 °C vacuum-drying of the biphenol and KBr immediately before combining with the bis(phthalonitrile) monomer, and pressing the pellet.

In the electronic spectrum metal-free phthalocyanine formation is detected in the initial stages of the bis(phthalonitrile) polymerization before tetrahydrofuran insolubility occurs. The spectral line shapes are similar, and absorption maxima occur at nearly the same wavelength as those of the corresponding phthalocyanine model compounds (Figure 3).

The phthalocyanine ring is a relatively large and symmetrical structure which has a strong tendency to associate in solution.[20] This short-range ordering suggested that an X-ray diffraction spectrum could contain more information than just an amorphous reflection despite the mixed-isomeric nature of the ring substitution. The X-ray diffraction spectra of unsubstituted metal-free phthalocyanine, the tetraphenoxyphthalocyanine, and the oxygen-bridged phthalocyanine network polymer are presented in Figure 10. While the unsubstituted metal-free phthalocyanine has an X-ray diffraction spectrum with many reflections, the purified tetraphenoxyphthalocyanine model compound displays a single well-resolved reflection at a 2θ value of 26.5°. The oxygen-bridged phthalocyanine polymer prepared by reaction with tetrahydropyridine has an X-ray diffraction spectrum nearly identical with that of the tetraphenoxyphthalocyanine model compound. High crystallinity would not be expected in the model compound, since it is in a mixture of geometric isomers, or in the network polymer. However, single X-ray diffraction reflections at this *d* spacing have been observed in other polyphthalocyanine systems. In closely related phthalocyanine systems derived from 2-phenyl-2-[4-(3,4-dicyanophenoxy)phenyl]propane and 2,2-bis[4-(3,4-dicyanophenoxy)phenyl]propane, a well-resolved reflection at $2\theta = 26.3°$ was observed for both model phthalocyanine compound and phthalocyanine network polymer.[27] Other examples of phthalocyanine polymers exhibiting this $2\theta = 26 \pm 1°$ X-ray diffraction reflection may be found in the literature.[28] For the Cu X-ray source, the 2θ value of 26.5° has a corresponding *d* spacing of 3.4 Å. This *d* spacing can be associated with the distance between the planes of two parallel phthalocyanine rings in a cofacial association. This assignment is supported by the following evidence. In crystalline unsubstituted metal-free phthalocyanine the perpendicular distance between planes of parallel molecules is 3.38 Å as determined originally by Robertson.[29] A metal-free phthalocyanine polymorph based on a dimeric complex of cofacial parallel rings with a 4-Å separation distance is also known.[30] In toluene solution tetrakis(cumylphenoxy) metal-free phthalocyanine is a dimeric complex by VPO measurements.[20] Since the polymer solidifies from a monomer melt, a dimeric ordering of phthalocyanine rings is possible. Recently, a cofacial association of an octaalkyl-substituted metal-free phthalocyanine in the liquid crystal state has been reported.[31] The direct correspondence of this $2\theta = 26.5°$ reflection between the purified tetraphenoxy metal-free phthalocyanine model compound and the polymerized oxygen-bridged bis(phthalonitrile) is evidence for significant conversion to a metal-free phthalocyanine polymer. The data are similar for the sulfur-bridged analogue although the intensity of the $2\theta = 26.5°$ reflection is approximately half that of the oxygen system. In summary, we propose that the 26.5° reflection originates from a coplanar association of phthalocyanine rings in the model compound isomer mixture and in the network polymer.

The degree of conversion of phthalonitrile to phthalocyanine in the network polymer in comparison with the model compound system may diverge as the degree of polymerization progresses beyond the oligomer stage since there are differences in functional group density and particularly in functional group mobility. IR spectroscopy indicates all detectable nitrile groups have reacted, a significant quantity have been converted to phthalocyanine, and very little triazine has formed. Considering the phthalocyanine unit to be tetrafunctional, a simple Carother's calculation would predict cross-linking at 50% conversion.

The cross-link density of the phthalocyanine network polymers is assessed by solvent resistance and thermostability characterization. Sulfuric acid is a solvent for monomeric phthalocyanines and has been reported to dissolve many polymeric phthalocyanines.[2,3f-h,4,32] Both the oxygen- and sulfur-bridged phthalocyanine polymers of this work are totally insoluble in either cold or hot sulfuric acid, consistent with a significant degree of cross-linking. Marvel and Martin observed a similar insolubility after prolonged heating of 3,3′,4,4′-tetracyanodiphenyl ether with copper bronze and attributed the result to high molecular weight cross-linked polymer.[2] If the cross-link density approaches the maximum ideal case represented in eq 1, most polymeric linking structures would be the phthalocyanine ring. Such a structure should have a thermal stability far above that of a monomeric phthalocyanine. The TGA thermograms of the oxygen- and sulfur-bridged phthalocyanine network polymers and tetraphenoxy- and tetrakis(phenylthio)phthalocyanine model compounds are presented in Figure 11. In both cases the model compound undergoes a large rapid weight loss at a temperature lower than that of the corresponding network polymer. The rapid weight loss for the tetrakis(phenylthio)phthalocyanine occurs at 440 °C while that for the tetraphenoxyphthalocyanine is at 550 °C, which may be due to an easier thermal scission of the carbon–sulfur bond and elimination of a phenyl pendant group. This compares with a 525 °C sublimation temperature of unsubstituted metal-free phthalocyanine obtained under identical TGA conditions. No sublimed phthalocyanine products were observed in the TGA of the substituted model phthalocyanines. The thermograms of the network polymers are nearly coincident, indicating a bridging oxygen– or sulfur–carbon bond is not a critical determinant of the TGA behavior. The initial weight loss at 500 °C is too low to be phthalocyanine decomposition since it is below the initial sublimation weight loss of unsubstituted phthalocyanine. Sources of the weight loss could be occluded coreactant byproduct or decomposition of linear polyisoindoline structures which lacked sufficient mobility or proper length for phthalocyanine formation. In a very interesting and remarkably simple route to polyphthalocyanines from phthalocyanine monomers, Achar, Fohlen, and Parker report TGA data showing a phthalocyanine polymer to undergo weight loss 150 °C above a monomeric phthalocyanine[32] although sublimation was not distinguished from decomposition of the monomeric phthalocyanine. In summary, sulfuric acid insolubility is consistent with formation of a cross-linked structure, and TGA indicates the presence of structure less stable than the phthalocyanine ring.

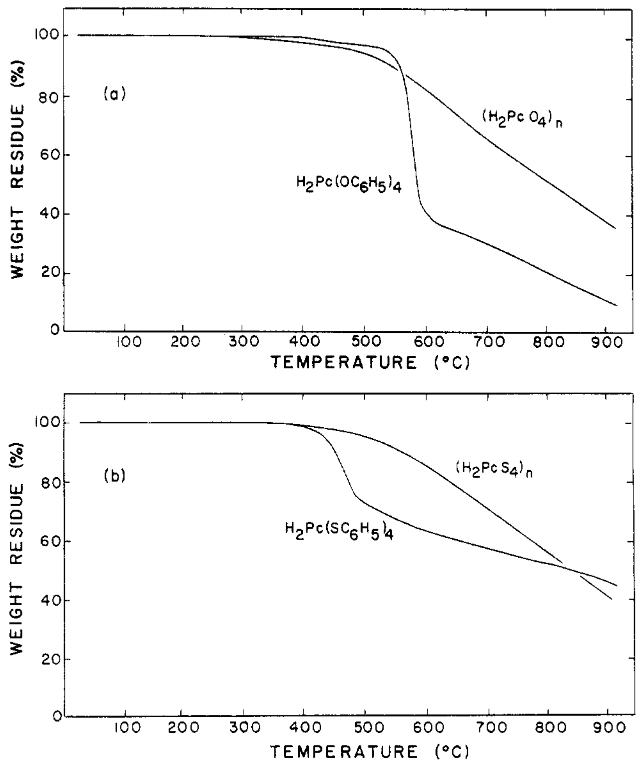

Figure 11. TGA thermograms (nitrogen atmosphere) of (a) tetraphenoxyphthalocyanine model compound ($H_2Pc(OC_6H_5)_4$) and bis(phthalonitrile) ether phthalocyanine polymer ($(H_2PcO_4)_n$) and of (b) tetrakis(phenylthio)phthalocyanine model compound ($H_2Pc(SC_6H_5)_4$) and bis(phthalonitrile) thioether phthalocyanine polymer ($(H_2PcS_4)_n$). Heating rate is 10 °C/min.

Electrical conductivity measurements on bulk samples of the phthalocyanine polymers were unsuccessful. The polyphthalocyanine powders are resistant to high-pressure compression molding (16 000 psi) and required addition of a 10% parafin binder[33] to form a 1-mm-thick disk to which electrical contacts could be made. With such samples, resistivities are too high to obtain meaningful measurements by four-point probe (>10^8 Ω cm) or bulk (>10^{13} Ω cm) measurement techniques.[34] Higher sensitivity may be obtained with surface conductivity measurements using an interdigital microelectrode array consisting of 50 "finger pairs" 7500 μm in length, 25 μm in width, and separated by 25 μm.[35] On a quartz surface the upper measurement limit of this apparatus is 10^{17} Ω/square, which is determined by the electrode spacing, length of the channel between the electrodes, and the sensitivity of the ammeter at a maximum 2.5-V bias. The polymeric samples were applied to the surface conductivity cell as a film by using a poly(vinyl acetate) binder technique.[36] The resistivity was still above the limit of the apparatus. As controls, analogous measurements were made on the phthalocyanine model compounds and on unsubtituted metal-free phthalocyanine. The phthalocyanine model compounds were too highly resistive for a measurement but unsubstituted metal-free phthalocyanine had a surface resistivity of 10^{15} Ω/square, in good agreement with its single-crystal value.[37] The observation that substitution at the benzo positions of the phthalocyanine ring lowers intrinsic conductivity is consistent with recent examples involving noncrystalline films[36] and single crystals.[38] Doping of simple phthalocyanines with iodine has been found to increase electrical conductivity by 10 orders of magnitude.[9] However, iodine doping of the phthalocyanine polymers was attempted but no weight uptake or conductivity was observed. With the phthalocyanine model compounds applied as thin films on the surface electrode, iodine vapor exposure resulted in a resistivity decrease to 10^{14} Ω/square. When an analogous measurement on a sublimed unsubstituted metal-free phthalocyanine film was made, the surface resistivity decreased to 10^7 Ω/square, which is close to the 9–10 order of magnitude change reported for single-crystal and pressed-pellet experiments.[9]

The electrical conductivity of charge-transfer complexes is dependent on the orientation and spacing of the components in the crystal structure of the complex as well as the primary chemical structure of each component. Particularly well-studied and closely related examples are the nickel phthalocyanine–iodine complex[39] and the cofacially linked silicon phthalocyanine polymers doped with iodine.[40] With regard to the phthalocyanine model compound results, a lack of crystallinity (these compounds are isomer mixtures) and a possible steric interference by the phenyl substituent groups toward intermolecular charge carrier transport or toward the redox reaction between the iodine and the phthalocyanine ring could be causes of the small conductivity increase after iodine doping as compared with the unsubstituted phthalocyanine compound results. With regard to the phthalocyanine polymer, the idea behind trying to synthesize a heteroatom-bridged phthalocyanine network was to generate a three-dimensional system of easily oxidizable highly delocalized centers covalently connected by low-energy tunneling barriers. The unmeasurably low level of iodine doping and conductivity could be due to an impermeability of the matrix and or to an insufficient degree of phthalocyanine formation.

Summary

Oxygen-, sulfur-, and selenium-bridged bis(phthalonitrile) monomers and phenoxy-, (phenylthio)-, and (phenylseleno)phthalonitrile compounds were prepared, and their conversions into the corresponding metal-free phthalocyanine polymers and model compounds were investigated. Coreactants for this conversion in order of decreasing efficiency were tetrahydropyridine > hydroquinone > biphenol with optimum phthalocyanine yields ranging from near-quantitative to 65% to no conversion for the respective oxygen-, sulfur-, and selenium-substituted phthalonitriles. Metal-free phthalocyanine ring formation was detected by electronic, IR, ^{1}H NMR, and X-ray diffraction spectroscopies. Triazine byproduct was also detected. The oxygen- and sulfur-bridged phthalocyanine polymers were characterized as highly cross-linked by sulfuric acid insolubility and had very high electrical resistivities that could not be decreased to a measurable value by iodine doping.

Experimental Section

Instrumentation. ^{1}H NMR spectra were obtained with a Varian EM 390 spectrometer using Me_4Si as the reference. IR spectra were recorded with a Perkin-Elmer 267 spectrometer. Electronic spectra were recorded with a Varian 118C spectrometer. TGA data were obtained from 10-mg samples in a nitrogen atmosphere at a 10 °C/min heating rate using a Du Pont 990 thermal analyzer and 951 thermogravimetric analyzer. X-ray diffraction spectra were obtained with a Philips XRG-2600 X-ray diffraction unit. Surface electrical resistivity measurements were made with a gold interdigital microelectrode array deposited on quartz consisting of 50 pairs of "fingers" 25 μm in width, 7500 μm in length, and separated by 25 μm.[35] The upper measurement limit of this apparatus is 10^{17} Ω/square. Samples for bulk electrical resistivity measurements were prepared as disks (1 mm thick, 1-cm diameter) by pressing in a Perkin-Elmer no. 186-0025 potassium bromide die at 16 000 psi in a Carver press for 5 min. Opposite sides of the disk were coated with silver paint (Microcircuit Co.). Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory. Melting points were determined in an electrothermal melting point apparatus. All melting points are uncorrected.

4-Phenoxyphthalonitrile (1). To a 250-mL three-neck flask fitted with a magnetic stirring bar, thermometer, and nitrogen inlet tube was added 100 mL of Me_2SO (purged for 1 h with nitrogen) followed by 9.41 g (0.100 mol) of phenol (Fisher Scientific) and 17.30 g (0.100 mol) of 4-nitrophthalonitrile (Eastman). After 10 min of additional nitrogen purging, 20.7 g of finely ground anhydrous potassium carbonate was added in 2.0-g quantities at 0.5-h intervals over a 5-h period with rapid stirring. The reaction mixture was stirred under nitrogen at 23 °C for 14 h. The reaction was worked up by filtering and concentrating at reduced pressure (60 °C/0.1 torr) to near dryness followed by addition of 100 mL of water and 50 mL of methylene chloride, shaking, and transferring to a separatory funnel. The methylene chloride phase was separated and the aqueous phase was extracted twice with 50 mL of methylene chloride. The combined extracts were extracted with 50 mL of 5% sodium carbonate solution and 50 mL of distilled water followed by drying over anhydrous magnesium sulfate. The color was removed by passing the solution through an alumina column (Woelm, neutral, activity 1); yield 18.2 g (82.5%). The product was recrystallized from CCl_4 and vacuum-dried at 50 °C: mp 101.5–102 °C; NMR ($CDCl_3$) δ 7.0–7.7 (m, 8 H); IR (KBr) 3120, 3100, 3060, 2244, 1613, 1591, 1570, 1484, 1439, 1293, 1259, 1211, 1162, 1095, 1038, 1011, 960, 877, 832, 791, 700 cm^{-1}; *m/e* 220 (P). Anal. Calcd for $C_{14}H_8N_2O$: C, 76.34; H, 3.66; N, 12.72. Found: C, 76.15; H, 3.82; N, 12.30.

4-(Phenylthio)phthalonitrile (2). By a procedure identical with that for 4-phenoxyphthalonitrile (1), 11.0 g (0.100 mol) of thiophenol (Aldrich) was reacted with 17.30 g (0.100 mol) of 4-nitrophthalonitrile (Eastman) with sequential additions of K_2CO_3 (20.7 g) in 100 mL of Me_2SO. After the mixture was passed through the alumina column and the CH_2Cl_2 was evaporated, a 17.59-g (70.0%) yield was obtained. The product was recrystallized from 1:2 CH_2Cl_2–CCl_4 mixture and vacuum-dried at 50 °C: mp 167–168 °C; NMR ($CDCl_3$) δ 7.4–7.8 (m, 8 H); IR (KBr) 3118, 3070, 3040, 2244, 1590, 1548, 1480, 1452, 1223, 1196, 1075, 874, 840, 770, 700 cm^{-1}; *m/e* 236 (P). Anal. Calcd for $C_{14}H_8N_2S$: C, 71.14; H, 3.41; N, 11.86; S, 13.58. Found: C, 71.42; H, 3.44; N, 11.88; S, 13.70.

4-(Phenylseleno)phthalonitrile (3). A 14-mL quantity of THF was distilled from $LiAlH_4$ into a flamed-out 25-mL three-neck flask. The flask was fitted with a magnetic stirring bar, thermometer, and nitrogen inlet tube, and 2.00 g (0.0127 mol) of distilled benzeneselenol (Pfaltz and Bauer) was added followed by 2.20 g (0.0127 mol) of 4-nitrophthalonitrile. The solution was warmed to 53 °C, and 1.3 g of hexamethylphosphotriamide (HMPA) was added followed by addition of 2.63 g of finely ground anhydrous K_2CO_3 in 0.5 g-quantities at 0.5-h intervals. The reaction mixture was refluxed (70 °C) for 14 h under nitrogen. The mixture was concentrated at reduced pressure, and the viscous residue was taken up in a mixture of 15 mL of water and 15 mL of diethyl ether. After filtering, the ether phase was separated and combined with two subsequent 15-mL ether extracts. The ether solution was extracted twice with 10 mL of 5% Na_2CO_3, washed twice with 10 mL of distilled water, and dried over anhydrous $MgSO_4$. The ether was evaporated to yield 2.13 g (59%) of an orange crystalline solid. The product was further purified by vacuum sublimation to yield a bright yellow crystalline product: mp 54–56 °C; NMR ($CDCl_3$) δ 7.15–7.35 (m, 5 H), 7.5–77 (m, 3 H); IR (KBr) 3120, 3095, 3075, 3058, 2240, 1575, 1538, 1474, 1439, 1360, 1023, 1000, 836, 760, 735, 690 cm^{-1}; *m/e* 284, 282 (2:1 intensity, ^{80}Se:^{78}Se) (P). Anal. Calcd for $C_{14}H_8N_2Se$: C, 59.36; H, 2.85; N, 9.90. Found: C, 59.40; H, 3.19; N, 9.48.

4,4′-Oxybis[phthalonitrile] (4). To a 100-mL three-neck flask fitted with a magnetic stirring bar, thermometer, nitrogen inlet tube, and distilling head were added 45 mL of Me_2SO and 5 mL of toluene. The Me_2SO was dried by azeotropic distillation of the toluene under nitrogen until a vapor temperature of 155 °C was observed. After cooling, 6.92 g (0.040 mol) of 4-nitrophthalonitrile was added followed by 2.00 g of anhydrous (fuse dried) sodium nitrite. The $NaNO_2$ was taken into solution with development of a red color. A 11.0-g quantity of finely ground anhydrous K_2CO_3 was slowly added over a 1 h period. The temperature was raised to 120 °C for 2 h followed by 20 min at 170 °C. After cooling, an additional 6.92 g of 4-nitrophthalonitrile was added, and the mixture was stirred 12 h at 90 °C under nitrogen. The reaction was worked up by slowly pouring the cooled reaction mixture into 500 mL of a 2% HCl solution followed by dropwise addition of concentrated HCl until just acidic. The crude product was filtered and vacuum-dried to yield 7.47 g (69%). The product solubility was very low in most organic solvents (chloroform, methylene chloride, acetone, acetonitrile, THF, and dioxane) except Me_2SO where 10% by weight solutions could be prepared. The product was purified by dissolving in Me_2SO and passing through an alumina column (Woelm, neutral, activity 1) packed in toluene and eluted with Me_2SO to yield a colorless product after evaporation of the Me_2SO and vacuum-drying: mp 262–262.5 °C (lit.[2] mp 255 °C); NMR (Me_2SO-d_6) δ 7.7 (d of m, 2 H), 8.0 (d of m, 2 H), 8.25 (d of m, 2 H); IR (KBr) 3103, 3079, 3042, 2238, 1590, 1530, 1486, 1420, 1310, 1280, 1253, 1205, 1097, 971, 853 cm^{-1}; *m/e* 270 (P). Anal. Calcd for $C_{16}H_6N_4O$: C, 71.09; H, 2.24; N, 20.75. Found: C, 71.07; H, 2.24; N, 20.40. Reference 2 analysis of this compound requires 0.25 mol of water of crystallization. Alumina column purification removed this water although it was reabsorbed after the compound was allowed to stand in air for a few hours.

4,4′-Thiobis[phthalonitrile] (5). To a 50-mL three-neck flask fitted with a magnetic stirring bar, thermometer, nitrogen inlet tube, and distilling head were added 24 mL of Me_2SO and 4 mL of toluene. The Me_2SO was dried by azeotropic distillation of the toluene under nitrogen until a vapor temperature of 160 °C was observed. After cooling to 30 °C, 3.46 g (0.020 mol) of 4-nitrophthalonitrile was added followed by 1.38 g of anhydrous (fuse dried) $NaNO_2$. The $NaNO_2$ was taken into solution with development of a red color. A 0.78-g quantity of finely ground anhydrous sodium sulfide (Ventron) was added slowly over a 1-h period with stirring. The temperature was increased to 130 °C for 2 h. After cooling, the reaction mixture was worked up by slow precipitation in 500 mL of water. The stirred suspension was made acidic by dropwise addition of concentrated HCl followed by filtering the vacuum-drying to yield 2.00 g (70%). In contrast to the oxygen analogue, this thioether was soluble in CH_2Cl_2, acetone, acetonitrile, THF, and dioxane and may be recrystallized from methanol. The product was purified by passing through an alumina column (Woelm, neutral, activity 1) packed in CH_2Cl_2 and eluted with THF to yield a colorless product after recrystallization from methanol and vacuum-drying: mp 208–208.5 °C; NMR (Me_2SO-d_6) δ 7.8–8.2 (m, 6 H); IR (KBr) 3100, 3066, 3035, 2239, 1582, 1550, 1480, 1397, 1280, 1252, 1213, 1193, 1137, 1074, 913, 870, 857, 725 cm^{-1}; *m/e* 286 (P). Anal. Calcd for $C_{16}H_6N_4S$: C, 67.10; H, 2.11; N, 19.58; S, 11.21. Found: C, 67.97; H, 2.40; N, 19.30; S, 10.88.

4,4′-Selenobis[phthalonitrile] (6). To a 50-mL three-neck flask fitted with a magnetic stirring bar, thermometer, nitrogen inlet, and distilling head were added 24 mL of Me_2SO and 4 mL of toluene. The Me_2SO was dried by azeotropic distillation of the toluene until a vapor temperature of 155 °C was observed. After cooling, 3.46 g (0.020 mol) of 4-nitrophthalonitrile and 1.38 g of anhydrous (fuse dried) $NaNO_2$ were added and stirred for 1 h under nitrogen with development of a homogeneous red solution. A 1.25-g quantity of finely ground anhydrous sodium selenide (Ventron) was added with minimal air exposure. The temperature was increased to 130 °C for 4 h. The reaction mixture was worked up by concentrating to 5 mL at reduced pressure (65 °C/2 torr) and slowly adding to 300 mL of water to precipitate a flocculant brown product. The suspension was acidified by dropwise addition of concentrated HCl, filtered, and vacuum-dried. The product is soluble in acetone, methanol, THF, dioxane, and acetonitrile and was purified by passing through an alumina column (Woelm, neutral, activity 1) with THF elution: yield 1.98 g (59%); mp 182–186 °C; NMR (Me_2SO-d_6) δ 7.8–8.15 (m, 6 H); IR (KBr) 3090, 3045, 3030, 2239, 1590, 1574, 1487, 1420, 1310, 1280, 1254, 1097, 922, 910, 850 cm^{-1}; *m/e* 334, 332 (2:1 intensity, ^{80}Se:^{78}Se) (P). Anal. Calcd for $C_{16}H_6N_4Se$: C, 57.66; H, 1.82; N, 16.82. Found: C, 57.69; H, 1.97; N, 16.48.

Tetraphenoxyphthalocyanine (Mixed Isomers in 2- and 3-Benzo Positions) (7). To a 10 × 75 mm tube were added 0.500 g (2.27 mmol) of 4-phenoxyphthalonitrile and a Teflon-coated stirring bar. Volatiles were removed by fusion (170 °C) under vacuum until vapor evolution ceased (5 min). After cooling, 0.024 g (0.29 mmol) of 1,2,3,6-tetrahydropyridine (purified by distillation) was added. The tube was cooled with dry ice, evacuated, and sealed. The entire tube was heated at 275 °C with stirring. Solidification occurred within 5 min and the reaction time was 1 h. At 185 °C reaction temperature, solidification occurred in 1 h. The crude product was dissolved in 15 mL of THF and passed through an alumina column with THF elution. The eluted solution was evaporated to a 5-mL volume at 23 °C and precipitated by dropwise addition to 150 mL of stirred methanol. The flocculant blue product was filtered into the thimble of a micro-Soxhlet extractor and extracted with methanol to remove unreacted phthalonitrile. The product was vacuum-dried at 23 °C. Heating this compound in the dry state caused THF insolubilization. Yield 0.40 g (81%); NMR ($CDCl_3$) δ −8.0 (s, 2 H), 8.35, 8.55 (m, m, 32 H); IR (evaporated film on NaCl) 3290, 3050, 1608, 1587, 1470, 1420, 1392, 1320, 1228, 1160, 1092, 1070, 1010, 930, 825, 742, 712, 690 cm^{-1}; electronic spectrum (THF), 695.5 (log ϵ = 5.06), 661, 632, 600, 341, 280 nm. Anal. Calcd for $C_{56}H_{34}N_8O_4$: C, 76.16; H, 3.88; N, 12.70. Found: C, 75.78; H, 4.16; N, 12.31.

Tetrakis(phenylthio)phthalocyanine (Mixed Isomers in 2- and 3-Benzo Positions) (8). By a reaction and workup procedure identical with those of the tetraphenoxyphthalocyanine (7), 0.28 g (1.85 mmol) of 4,4′-thiobis[phthalonitrile] was reacted with 1,2,3,6-tetrahydropyridine to yield 0.12 g (43%) of tetrakis(phenylthio)phthalocyanine: NMR ($CDCl_3$) δ −9.0 (s, 2 H), 8.3 (m, 12 H), 8.6 (m, 20 H); IR (evaporated film on NaCl) 3290, 3060, 1606, 1585, 1481, 1442, 1410, 1391, 1330, 1311, 1138, 1112, 1071, 1019, 900, 824, 744, 691 cm^{-1}; electronic spectrum (THF), 702 (log ϵ = 5.15), 673, 648, 663, 417, 351, 250 nm. Anal. Calcd for $C_{56}H_{34}N_8S_4$: C, 70.99; H, 3.62; N, 11.84; S, 13.55. Found: C, 70.49; H, 3.72; N, 11.63; S, 13.31.

Tris(2-cyanophenyl)-1,3,5-triazine (9).[26] To a 10 × 75 mm tube were added 0.500 g (3.9 mmol) of phthalonitrile (Fisher, recrystallized) and 0.005 g (0.3 mmol) of water. The tube was cooled with dry ice, evacuated, and sealed. The entire tube was heated at 325 °C for 20 h. The crude product was Soxhlet extracted with cyclohexane and then into benzene and collected to yield 0.36 g (72%). The product was further purified by recrystallization from benzene: mp 297 °C (lit.[26] mp 301.5 °C); NMR ($CDCl_3$) δ 8.1 (m, 12 H), 9.2 (d, 3 H); IR spectrum identical with that of ref 26; *m/e* 384 (P).

Tris[4(or 5)-phenoxy-2-cyanophenyl]-1,3,5-triazine (Mixed Isomers in 4- and 5-Phenyl Positions) (10). To a 10 × 75 mm tube were added 0.250 g (1.14 mmol) of 4-phenoxyphthalonitrile and 0.0034 g (0.19 mmol) of water. The tube was cooled with dry ice, evacuated, and sealed. The entire tube was heated at 325 °C for 20 h. The crude product was dissolved in CH_2Cl_2 and passed through an alumina column (Woelm, neutral, activity 1) packed in toluene. Methylene chloride elution yielded the pure product. Dioxane and THF elution yielded small quantities of phthalocyanine (**7**) and hydrolyzed tricyanotriazine. Yield 0.11 g (44%); mp 195–204 °C; NMR δ 7.3 (m, 15 H), 7.75 (m, 6 H), 9.1 (d, 3 H); IR (evaporated film on NaCl) 3070, 2220, 1589, 1522, 1490, 1412, 1360, 1280, 1234, 1204, 826, 767, 693; m/e 660 (P). Anal. Calcd for $C_{42}H_{24}N_6O_3$: C, 76.36; H, 3.64; N, 12.73. Found: C, 75.98; H, 3.75; N, 12.55.

Polymerization of 4,4′-Oxybis[phthalonitrile]. To a 10 × 75 mm tube were added 0.0768 g (0.926 mmol) of 1,2,3,6-tetrahydropyridine and 1.00 g (3.70 mmol) of the bis(phthalonitrile) ether **4**. The tube was cooled in dry ice, evacuated, and sealed. The polymerization reaction was conducted at 275 °C for 4 h. The lustrous purple product was crushed into coarse particles, ground in a Wigg-L-Bug, Soxhlet extracted with THF for 16 h, and vacuum-dried at 180 °C to yield a bluish purple powder: yield 0.986 g (98%); IR (KBr) 3290, 3040, 1592, 1465, 1420, 1310, 1222, 1090, 1010, 945, 825 cm^{-1}. Anal. Calcd for $C_{64}H_{26}N_{16}O_4$: C, 70.96; H, 2.42; N, 20.71. Found: C, 68.28; H, 3.09; N, 15.21. This polymerization was conducted in a KBr matrix, using 4,4′-biphenol as the coreactant by the following procedure. KBr was vacuum-dried at 400 °C before use. Stock solutions of 3.0 mg of bis(phthalonitrile) ether **4** in 1.00 g of KBr and 1.0 mg of biphenol in 1.00 g of KBr were prepared separately with mortar and pestle grinding for dispersal and vacuum-dried at 180 °C for 10 min immediately before KBr disk preparation. The KBr disk was prepared by mixing 0.050 g of each stock solution (2:1 monomer to coreactant or 4:1 phthalonitrile group to coreactant molar ratio) with 0.200 g of dry KBr. After mortar and pestle grinding, the mixture (0.30 g) was transferred to a Perkin-Elmer no. 186-0025 evacuable KBr die, evacuated for 5 min, and pressed at 16 000 psi for 5 min. The disk was removed and heated in a nitrogen atmosphere at 275 °C with interruptions to obtain spectra at initial 2-, 5-, and 20-min and 12-h reaction intervals.

Polymerization of 4,4′-Thiobis[phthalonitrile]. By a reaction and workup procedures identical with those of the 4,4′-oxybis[phthalonitrile] polymerization, 1.00 g (3.49 mmol) of bis(phthalonitrile) thioether (**5**) was reacted with 0.0725 g (0.874 mmol) of tetrahydropyridine to yield 0.989 g (99%) of phthalocyanine polymer; IR (KBr) 3290, 3050, 1583, 1440, 1290, 1105, 1005, 893, 821, 741 cm^{-1}. Anal. Calcd for $C_{64}H_{26}N_{16}S_4$: C, 66.98; H, 2.29; N, 19.54; S, 11.19. Found: C, 64.26; H, 2.67; N, 16.72; S, 9.91.

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Anionic Polymerization of Dienyl Methacrylates[†]

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ABSTRACT: Dienyl (2,4-hexadienyl, 1,3-cyclohexadienylmethyl, 4,7-octadienyl, etc.) methacrylate copolymers were prepared by anionic polymerization. The dienyl methacrylates were prepared by titanate-catalyzed transesterification of methyl methacrylate with dienols. These copolymers are useful new air-drying finish vehicles because they cross-link rapidly in air to give hard, durable films.

Anionic polymerization has been used to synthesize polymers with narrow molecular weight distributions, polymers with functional groups at the chain ends, block copolymers, and star polymers. These syntheses rely on the presence of a reactive carbanion at the end of each polymer molecule throughout the reaction, living polymerization. Another use of anionic polymerization, not yet fully exploited, is to synthesize polymers with radical-sensitive functional groups.

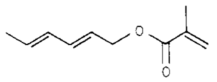
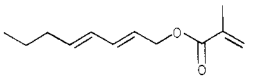
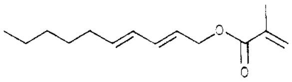
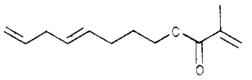
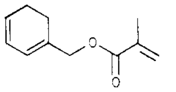
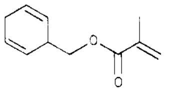
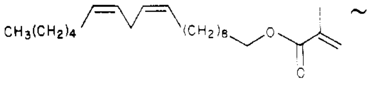
Linear poly(allyl methacrylate) has been prepared by anionic polymerization.[1] We became interested in copolymers of allyl methacrylate for use as air-drying finish vehicles because the high molecular weight homopolymer cross-links in air[1] or with free-radical initiators.[2] However, our initial work showed that the copolymers cross-link too slowly for many applications. The known chemistry of natural drying oils suggested that copolymers of dienyl methacrylates would cure faster.[3] Indeed, the copolymers can be prepared by anionic polymerization, and they cross-link rapidly on exposure to air to form hard, durable coatings.[4]

Results

Dienyl methacrylates can be synthesized by tetraisopropyl titanate catalyzed transesterification[5] of methyl methacrylate with dienols (Table I) in good yields. Diels–Alder reactions between the conjugated dienes and methacrylate vinyl groups do not occur significantly. Titanate catalysts are necessary because standard acidic and basic catalysts do not give good yields. For instance, strong bases convert 2,4-hexadienol to 2-hexenal, which leads to other byproducts.

The chemistry that we used to prepare highly structured methacrylate polymers[6] was used to prepare polymers from dienyl methacrylates. Addition of the monomer or monomer mixture to a solution of (1,1-diphenylhexyl)lithium in tetrahydrofuran at −78 °C produces the polymer in almost quantitative yield (100% conversion by NMR).

Table I
Dienyl Methacrylates Prepared by Transesterification of the Corresponding Alcohol

methacrylate	structure	yield, %
2,4-hexadienyl		71
2,4-octadienyl		78
2,4-decadienyl		65
4,7-octadienyl		87
1,3-cyclohexadienylmethyl		72
2,5-cyclohexadienylmethyl		87
9,12-octadecadienyl		~100

The rate of polymerization if fast enough, relative to the addition time, that effectively random copolymers are produced. Side reactions are absent because the ester–enolate polymer end is not basic enough to polymerize conjugated dienes or isomerize 1,4-dienes. Free-radical polymerization of 2,4-hexadienyl methacrylate leads to insoluble, cross-linked products.

Polymers that we have prepared are described in Table II. The compositions were adjusted to give the copolymers glass transition temperatures near room temperature to improve film appearances. Proton NMR helped to characterize the polymers. The olefinic protons and the protons on methyl or methylene groups attached to oxygen are useful probes of composition. The 10 phenyl protons

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[†] Contribution No. 3171.

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