Soluble and Electroactive Nickel Bis(dithiolene) Polymers Prepared via Metal Complexation Polymerization

Fei Wang and John R. Reynolds*

Center for Advanced Polymer Research, Department of Chemistry, The University of Texas at Arlington, Arlington, Texas 76019-0065

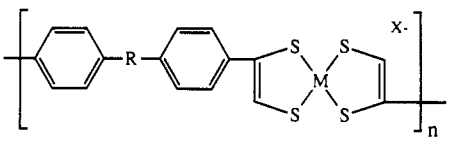
Received October 30, 1989

ABSTRACT: A new series of polymers containing nickel bis(dithiolene) linkages along the polymer main chain have been prepared. A variety of flexible linkages have been utilized to separate the nickel bis(dithiolene) complexes and include –O–, –S–, $-CH_2-$, $-(CH_2)_{10}-$, $-(CH_2)_{22}-$, and $-(OCH_2CH_2)_3O-$. The polymers with short flexible linkages in this series are highly soluble in both aqueous and organic solvents in the reduced (dianionic) form and are slightly soluble in the oxidized or neutral form. Increasing the length of the organic flexible linkage in the polymer main chain increases the solubility of the polymers in the oxidized form. Three different oxidation states of the nickel complex are observed electrochemically with the $[NiL_2^{2-}]_n \rightleftarrows [NiL_2^{-}]_n$ and $[NiL_2^{-}]_n \rightleftarrows [NiL_2^{0}]_n$ redox processes. UV–vis–near-IR spectra show features commonly associated with nickel bis(dithiolene) complexes. The position of the near-IR peak of the metal complex is significantly affected by solvent polarity with a maximum shift of 94 nm observed when changing from a nonpolar (toluene) to a highly polar (DMSO) medium.

Introduction

A variety of metal complex polymers incorporating square-planar MS_4 metal centers into conjugated ligands have been prepared with the goal of preparing materials with elevated electrical conductivity, along with novel magnetic and optical properties. These include poly(metal tetrathiooxalates),[1-3] poly(metal ethylenetetrathiolates),[4-6] poly(metal tetrathiosquarates),[7] poly(metal tetrathiafulvalenetetrathiolates),[8,9] poly(metal tetrathianaphthalenes),[10] and poly(metal benzenetetrathiolates).[11] These materials tend to be insoluble and infusible powders that precipitate during complexation polymerization of transition-metal ions with highly reactive thiolate ligands. In addition, they have a very low crystallinity, tend to be paramagnetic, and are strong absorbers of infrared radiation, making structural characterization by X-ray diffraction, NMR spectroscopy, and IR spectroscopy difficult, if not impossible. During synthesis some of these systems possess solubility, which can be attributed to the high charge density along the polymer backbone, but precipitation to amorphous powders prohibits resolubilization. When these planar conjugated ligands are complexed in a square-planar coordination with transition-metal ions [e.g., Ni(II), Pd(II), or Pt(II)], the molecular structure is quite rigid and "ribbon-like". In fact, for the specific case of poly(metal tetrathiooxalates), which can have conductivities as high as $10^2\ \Omega^{-1}\ cm^{-1}$, we find low degrees of polymerization and stacked/sheetlike model structures.[3]

In order to circumvent the low solubility of these fully conjugated polymers, we have been incorporating square-planar metal complexes, specifically metal bis(dithiolenes), into the main chain of polymers that contain flexible units. Our initial work in this field was recently communicated by reporting the synthesis of poly[[4,4'-oxybis[benzeneethenedithiolato]]nickel(II)] (PBOSD-Ni).[12] This polymer, as illustrated in structure 1, where R = O and M = Ni, is highly soluble in a variety of solvents in the as-prepared, reduced, form with two negative charges associated with each nickel bis(dithiolene) unit. In this form the polymer can be redissovled repeatedly. The oxidized and neutral form of the polymer, with a zero net charge on each metal bis(dithiolene), is only



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sparingly soluble (10^{-5} M) in DMF and completely insoluble in most other solvents.

Here we report on the synthesis and characterization of a series of polymers having the general form of structure 1 via transition-metal complexation polymerization. In this instance we vary the flexible linkage (R) to include –O–, –S–, $-CH_2-$, $-(CH_2)_{10}-$, $-(CH_2)_{22}-$, and $-(OCH_2CH_2)_3O-$. Both the nature of the flexible linkage and the oxidation state of the metal complex are found to impact both the solubility and optoelectronic properties of the polymers.

Results and Discussion

Ligand Syntheses. The synthesis of a series of bis(aryl dithiocarbonates) was carried out as outlined in Scheme I with *p*-phenyl dithiocarbonate moieties separated by a variety of flexible linkages. The –O–, –S–, and $-CH_2-$ linkages were introduced by beginning with diphenyl ether (**2a**), diphenyl sulfide (**2b**), and diphenylmethane (**2d**), respectively. The $-(CH_2)_{10}-$, $-(CH_2)_{22}-$, and oligomeric ether chain $-(OCH_2CH_2)_3O-$ linkages were introduced by preparation of **2c**, **2e**, and **2f** as outlined in Scheme II. Compound **2c** was prepared by a conventional Williamson etherification from phenol and 1,2-bis(2-chloroethoxy)ethane. Compound **2e** was prepared via a Friedel–Crafts acylation of benzene with sebacoyl chloride, followed by a Wolff–Kishner reduction. The synthesis of **2f** was also carried out in two steps. The first reaction was effected by initially reacting benzylmagnesium chloride with 1,10-dibromodecane in the presence of a catalytic amount of lithium tetrachlorocuprate,[13] which proved to be a convenient route to preparing monobromo-terminated alkanes. Wurtz coupling of **7** gave the required product **2f**, separating two phenylenes with 22 methylene carbons.

The bis(dithiocarbonates) were then prepared by using a modification of methods developed for the synthesis of

substituted styryl dithiocarbonates.[14,15] Starting with **2**, Friedel–Crafts acylation with chloroacetyl chloride in the presence of $AlCl_3$ led to **3**. Bromoacetyl bromide and bromoacetyl chloride were also used as acylating reagents, but significantly lower yields of product were obtained. In the case of **2c** as starting material, the polyglycol ether chain could potentially complex with the $AlCl_3$, and we found that an extra amount of $AlCl_3$ and more vigorous conditions of refluxing were required to force the reaction to completion. Compound **3** was subsequently reacted with the potassium salt of *O*-ethylxanthic acid in acetone to give **4**. The potassium chloride that precipitated from the reaction mixture facilitated driving the reaction to high yield. The final step involves a cyclization reaction of the xanthate ester, **4**, with HBr in acetic acid to give the desired dithiocarbonates **5**. Both 30% HBr in acetic acid and 48% HBr in water were used, with the acetic acid–HBr solution giving better results. In the case of **5c**, the polyether tended to cleave with HBr. Milder reaction conditions were employed in this case but lower yields of product were obtained.

The structures of all bis(dithiocarbonates) **5a–f** were confirmed by IR, ^1H NMR, ^{13}C NMR, and elemental analysis. All of the IR spectra of **5** exhibit a band at ca. 1635 cm^{-1} for the C=O stretch, confirming formation of the dithiocarbonate. Common features in the ^1H NMR spectra are one singlet at $\delta = 6.8$ corresponding to the olefinic proton and an AA'XX' and AA'BB' system in the aromatic range corresponding to the 1,4-substituted benzene ring. Compound **5b** exhibits only one singlet for all the aromatic protons. Common features in the ^{13}C NMR spectra are a peak at 192 ppm assigned to the carbonyl and six peaks in the aromatic and olefinic range.

Tetrathiolate Formation. The preparation of polymeric metal bis(dithiolenes) via transition-metal complexation polymerization first requires the formation of a highly reactive tetraanionic ligand as shown in Scheme III. As described previously,[12] we have determined the experimental conditions necessary for complete cleavage of the bis(dithiocarbonates) to the tetrathiolates by synthesizing the tetramethylated species (**8**). In fact, we have obtained **8** in quantitative yields as described in the Experimental Section. This is important in that incomplete conversion may limit molecular weight or possibly lead to monodentate as opposed to bidentate chelating ligands. Up to four monodentate ligands could potentially react with each transition-metal ion, leading to a highly cross-linked, and completely insoluble, structure.

These problems were observed for the case of tetrathiapentalenedione (**9**), which serves as a precursor to ethylenetetrathiolate (**10**) as outlined in Scheme IV. One study[6] described the "half-opening" versus "full-opening" of the tetrathiapentalenedione. Gel formation has also been observed in the synthesis of metal complex polymers of ethoxide-treated **9**, with elemental analysis indicating that stoichiometric formation of **10** did not occur.[16]

All results point to the fact that the tetraanionic ligands are extremely sensitive to oxidation. Even when small amounts of oxygen are present during ethoxide cleavage reactions, insoluble polymeric product forms, most likely through the formation of bisulfides. For this reason, all thiolate ligand formation and metal complex polymerizations were carried out in degassed ethanol and with scrupulously deoxygenated nitrogen.

Metal Complexation Polymerizations. Polymerization reactions were carried out at 60 °C by conversion of **5** to tetrathiolate, followed by reaction with a stoichiometric amount of $NiBr_2$ overnight as shown in Scheme V. In the cases of **5a**, **5b**, and **5d**, in which short spacers (–O–, –S–, or $–CH_2–$) were present in the ligands, a homogeneous dark brown solution of polymer was obtained. On the other hand when **5c**, **5e**, and **5f** were used, a small amount of dark brown solid precipitated out of solution, and thus the longer spacers reduced the solubility of these polymers in ethanol. All of the reaction solutions were found to exhibit a typical nickel bis(dithiolene) complex UV–vis–near-IR spectrum [λ_{max}(ethanol) 215, 270, 310, 490, 930 nm][17–19] which indicates that the polymers formed contain the desired nickel bis(dithiolene) units. We term these the reduced form of the polymers. For the poly-

mer from **5a**, the reduced form of the polymer is also soluble in water, acetonitrile, acetone, and DMF.

The reduced forms of all polymers have proven to be air unstable and were oxidized by either air or iodine to yield black solid powders (oxidized form) that are insoluble in most solvents. The oxidized forms of all of the polymers do slightly dissolve in DMF to form brown solutions, but **11d–f** (containing nonpolar linkages) have a lower solubility in DMF than **11a–c** (containing polar linkages) and cannot completely dissolve. Polymer **11c**, containing the polyglycol chain, exhibits a better solubility in DMF than all of the other polymers investigated and is also slightly soluble in THF. The alkane linkages in the polymer chains of **11e** and **11f** reduce their solubilities in DMF but increase their solubilities in toluene, xylene, and THF. When dissolved in these solvents, green solutions are obtained. Thus, as expected, the nature of the flexible linkage plays an important role in controlling the solubility of these polymers, with nonpolar linkages improving solubility in nonpolar solvents and polar linkages improving solubility in polar solvents. Polymers **11e** and **11f** were fractionated by extraction with hot THF, showing ca. 20% of polymer to be soluble while the other 80% remained insoluble. A GPC analysis on these THF solutions shows a series of separated peaks corresponding to different chain length oligomers. Comparison of these GPC retention times with those found for monomeric model compounds prepared in our laboratory suggests the soluble fraction to contain up to hexamers. We expect the 80% remaining insoluble fraction to have a higher degree of polymerization. Elemental analyses of all polymers (**11a–f**) were found to differ somewhat from that calculated for a neutral polymeric repeat unit (see Experimental Section). This is not surprising considering end-group contributions in these oligomers and the possibility of incomplete oxidation of each metal center.

One explanation for the low solubilities of these polymers in the oxidized state is the strong potential for metal–metal and metal–sulfur interactions between molecules. In order to reduce the regularity of the spacer in the ligand along the polymer chain we prepared mixed-ligand polymers using equal amounts of **5e** and **5f** in the polymerization process. Unfortunately, the resulting polymers had no significant improvement in solubility.

All of the polymers in the oxidized form have intense IR bands at 1367 ± 3 and 1190 ± 2 cm^{-1}. These absorptions are attributed to the nickel bis(dithiolene) complex and are combination bands. A qualitative assignment for the 1367-cm^{-1} peak is a vibration predominantly from the perturbed C=C stretch, and the 1190-cm^{-1} peak is that of the perturbed C=S stretch.[20] These IR results further confirm that the formation of nickel bis(dithiolene) units in the polymer chain and retention of the nickel complex in the oxidized (neutral) form.

Optical Properties. All of the polymer solutions show a near-IR absorption peak maximum at ca. 900 nm, which is assigned to the $2b_{1u} \leftrightarrow 3b_{2g}$ transition.[21,22] This is shown in Figure 1 for polymer **11c**, where the near-IR absorption is separated from the higher energy absorptions by a relatively broad window from 600 to 750 nm. Numerous applications exist for materials that can selectively fiber/absorb near-IR radiation while being relatively transparent in the visible region.[23] These include filters of IR-sensitive materials, heat cut-off materials, and materials addressable by semiconductor (e.g., GaAs based) laser diodes.[24] The ability to directly cast films of polymers containing these near-IR absorbers may ultimately lead to films significantly more homogeneous than dye-impregnated thermoplastics.[23]

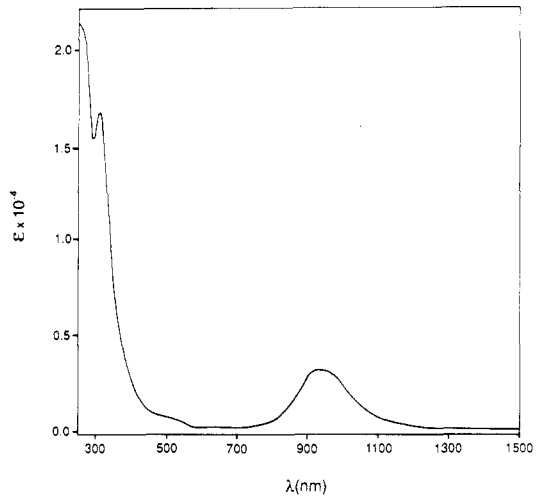


Figure 1. UV–vis–near-IR spectrum of polymer **11c**.

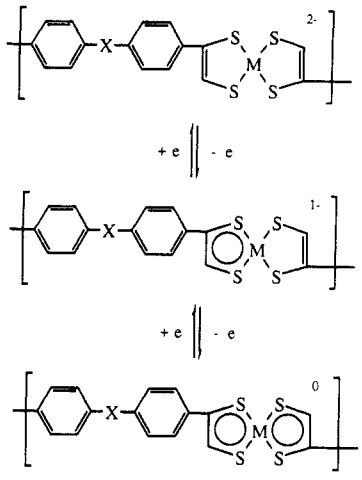
Table I
Near-IR Absorbance Results for Polymer 11e

solvent	dielectric constant	λ_{max}, nm
toluene	2.4	847
THF	7.6	880
HMPA	30.0	927
DMF	36.7	935
DMSO	46.6	941

The position of the near-IR peaks is affected by solvent polarity. For example, Table I shows the near-IR results for the polymer having the nickel bis(dithiolene) complex separated by 10 methylene units. Increasing solvent polarity shifts this absorption significantly further into the near-IR with a maximum shift of 94 nm observed when the solvent is changed from toluene to dimethyl sulfoxide. Simultaneously, a color change is observed as the toluene solutions are green and the HMPA, DMF, and DMSO solutions are brown. Normally, the color of the complex solution indicates the oxidation state of the nickel bis(dithiolene) complex. Neutral forms are usually green while anionic forms are red-brown. Previous studies have shown that the neutral form of the nickel complex can be reacted with a number of nitrogen bases (e.g., pyridine or hydrazine) forming salts of the nickel complex ions.[20] A study on a monomeric model compound shows that the oxidized form dissolved in DMF was green initially but changed to brown in less than an hour. At the same time a shift of the near-IR peak from 855 to 905 nm was also observed. In the case of DMF, the presence of traces of dimethylamine (a degradation product) may account for a partial reduction of the complex and the observed spectroscopic shift. The fact that significant spectral changes are observed in the highly polar, yet nonreducing, solvents HMPA and DMSO verifies that the solvatochromic behavior is due to solvent polarity.

Electrochemical Properties. These polymeric nickel bis(dithiolene) complexes all exhibit two separate redox processes as shown in Scheme VI. As prepared, each metal complex is dianionic and stable in nonoxidizing solvents. A cyclic voltammogram of polymer **11c** is shown in Figure 2 to exemplify the electrochemical behavior of these polymers. At potentials equal to and cathodic of −0.8 V the polymer complex remains in the dianionic state. Scanning anodically, the polymer exhibits two redox processes at $E_{1/2}$ = −0.71 V and at $E_{1/2}$ = +0.19 V. These two processes are reversible as evident by the 60- and

Scheme VI



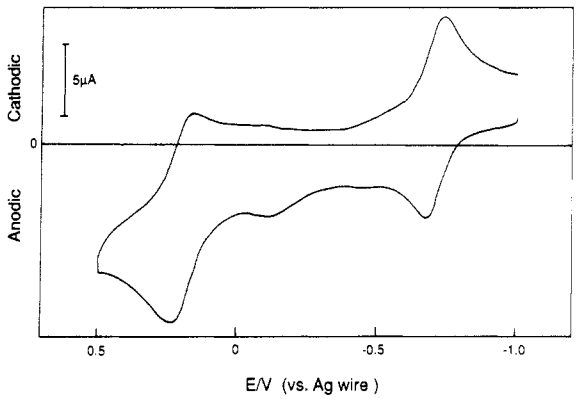


Figure 2. Cyclic voltammogram for polymer **11c** on a carbon button working electrode in a 0.1 M $TBAClO_4$/DMF solution. Potentials are reported versus a silver wire quasi-reference electrode.

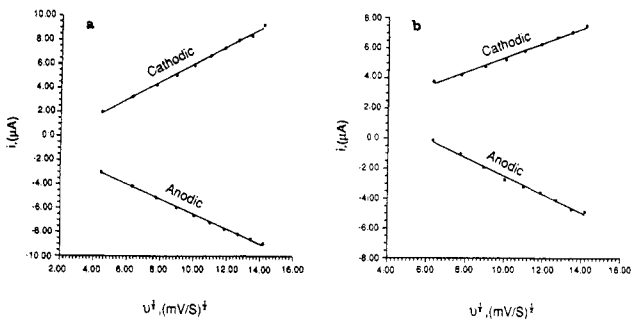


Figure 3. Scan rate (ν) dependence of both anodic and cathodic peak current (i_p) for (a) $[NiL_2^-]_n \rightleftarrows [NiL_2^0]_n$ and (b) $[NiL_2^{2-}]_n \rightleftarrows [NiL_2^-]_n$.

75-mV peak-to-peak separation seen for each process, respectively. Referring to Scheme VI, we may assign these redox processes to the reversible oxidation of the dianion to the monoanion and finally to the neutral state. During both of these processes the polymer remains in solution. This is shown in Figure 3 as the scan rate (ν) dependence of the peak current (i_p). Diffusion-controlled processes typically exhibit an i_p that is linearly dependent on $\nu^{1/2}$, while surface-confined species exhibit i_p dependent on ν. The observed linear dependence of i_p on $\nu^{1/2}$ for both processes and both anodic and cathodic current between 40 and 200 mV s^{-1} shows that the polymer does not deposit on the electrode surface at potentials cathodic of +0.5 V. The pattern of this redox behavior is consistent with nonpolymeric nickel bis(dithiolene) complexes investigated previously,[25] illustrating that, though the metal complexes are contained in the polymer backbone in our case, the metal centers approach the electrode surface close enough for electron transfer.

In the case of polymer **11a** further anodic scanning beyond +0.5 V significantly distorts the symmetry of the $[NiL_2^-] \rightleftarrows [NiL_2^0]$ process by increasing the current during reduction of the neutral form.[12] This was especially evident for the polymer containing only an oxygen flexible linkage as it is precipitating onto the electrode surface in the neutral form.

Electrical Properties. Attempts were made to prepare free-standing films by casting from DMF solutions. The materials were quite brittle, cracking easily. Electrical conductivities were subsequently measured on pressed pellets. As expected for a polymer metal complex system with a low extent of conjugation, the conductivities are quite low. For example, polymer **11a** exhibits a room temperature conductivity of 10^{-6} Ω^{-1} cm^{-1}. It has been found that most metal bis(dithiolenes) have conductivities lower than 10^{-5} Ω^{-1} cm^{-1} independent of the identity of the central metal atom and oxidation state.[26] Recently, Underhill et al. have reported on certain maleonitrile salts that can be metallic.[27-29] The abilities of these complexes to stack, form direct metal–metal bonds, and attain the proper partial oxidation state are all required for high conductivity.

Disorder present in the polymers discussed here prevents significant interchain stacking. In fact, an X-ray powder spectrum of polymer **11a** showed only an amorphous halo centered at about 19°. In addition, the flexible spacers inhibit any conjugation along a single chain, and facile charge transport is prohibited. Thus, the low observed conductivities are as expected.

Conclusions

A series of polymers containing nickel bis(dithiolene) complexes in the main chain have been prepared via metal complexation polymerizations with flexible linkages between the complexes ranging from one atom (–O–, –S–) up to 22 atoms [$-(CH_2)_{22}-$]. The polymers are highly soluble in a number of solvents in the as-made reduced (dianionic) form. While oxidation of the metal centers to the essentially neutral form is found to decrease the overall solubility, polymers containing long flexible linkages are more soluble than those containing short linkages. The electrochemical and spectral properties of the polymers are consistent with a stable main-chain nickel bis(dithiolene) structure where the metal complex can attain –2, –1, and neutral oxidation states. Due to the nature of these metal complexation reactions, especially problems encountered in obtaining stoichiometric balance of functional groups during polymerization, the materials are most likely oligomeric.

Experimental Section

General Procedures. All water- and air-sensitive liquids were transferred either with cannulae or with syringes. Air- and moisture-sensitive reactions were carried out with the use of standard inert-atmosphere techniques. All melting points are uncorrected. Infrared spectra were recorded on a Digilab FTS-40 FT-IR spectrophotometer. Low-field (60 MHz) ^1H NMR spectra were run on a Varian EM 360 spectrometer. High-field (200 and 300 MHz) ^1H and ^{13}C NMR spectra were recorded on a Nicolet NT-200 spectrometer or a Bruker MSL-300 spectrometer in chloroform-*d* solutions. Chemical shifts are reported referenced to tetramethylsilane or chloroform-*d* (77.0 ppm for ^{13}C). HPLC was performed with a Waters 440 HPLC system. UV–vis–near-IR spectra were run on a Varian 2300 spectrophotometer. Powder X-ray diffraction was carried out on a Phill-

ips APD-3600 diffractometer using Cu Kα radiation and a 2θ scanning mode. GPC was performed on a Waters 840 GPC system. Electrochemical measurements were obtained with an EG&G Princeton Applied Research Model 273 potentiostat/galvanostat. Elemental analyses for carbon and hydrogen were carried out on a Perkin-Elmer 2400 CHN analyzer.

Materials. Ethanol was distilled from magnesium and degassed by three freeze–pump–thaw cycles. THF was distilled from potassium benzophenone. All other solvents were distilled from calcium hydride prior to use. Nitrogen was purified by using an Alfa De-Ox deoxygenation catalyst train.

All analogous compounds were prepared in a similar manner so only the **a** series are described in detail. For those compounds prepared with a different procedure, details are included.

Triethylene Glycol Diphenyl Ether (2c).[30] A mixture of phenol (66.9 g, 0.711 mol), KOH (43.9, 0.782 mol), and butanol (300 mL) was stirred and heated to reflux. A solution of 1,2-bis(2-chloroethoxy)ethane (69.2 g, 0.370 mol) in butanol (30 mL) was added dropwise to the mixture over a period of 2 h. The resulting mixture was heated to reflux for 10 h. Concentrated HCl was added to acidify the mixture. After reaction, distillation was used to remove some of the butanol (ca. 120 mL), and water (200 mL) was added to the mixture. The resulting mixture was extracted with ether (3 × 150 mL), and the ether solutions were combined, washed with water (3 × 100 mL), dried (magnesium sulfate), concentrated, recrystallized (hexane), and dried to give 68.3 g (63.6%) of **2c**: mp 37–40 °C; ^{1}H NMR (60 MHz) δ 3.72 (s, 4 H), 3.8–4.0 (m, 4 H), 4.0–4.2 (m, 4 H), 6.8–7.4 (m, 10 H).

1,10-Diphenyl-1,10-decanedione (6).[31] Compound **6** was prepared[32] by reacting sebacoyl chloride (47.8 g, 0.20 mol, 92% pure) with excess benzene (265 g, 3.4 mol) as both reagent and solvent and $AlCl_3$ (60 g, 0.45 mol) as catalyst. Yield of **6**: 45.2 g (76.1%); ^{1}H NMR (60 MHz) δ 1.4–1.8 (m, 12 H), 2.86 (t, 4 H, J = 6.5 Hz), 7.0–7.4 (m, 6 H), 7.6–7.9 (m, 4 H).

1,10-Diphenyldecane (2e).[33] The standard Huang–Minlon modification of the Wolff–Kishner reduction was followed. KOH (50 g, 0.77 mol) was dissolved by warming in diethylene glycol (300 mL) in a 500-mL flask. Compound **6** (45 g, 0.139 mol) and 85% hydrazine hydrate (40 mL) were added to this at 100 °C and refluxed for 1 h. An H_2O/diethylene glycol mixture (60 mL) was distilled away until the temperature rose to 205 °C followed by refluxing for 3 h. After the mixture cooled to room temperature, 50 mL of H_2O was added, the reaction was extracted with ether, and the extract was dried with $MgSO_4$. The ether was removed and the product isolated by vacuum distillation. Yield of **2e**: 23 g (56%); bp 140 °C/3 mm; ^{1}H NMR (60 MHz) δ 1.2–1.7 (m, 16 H), 2.5 (t, 4 H, J = 6.5 Hz), 7.0 (s, 10 H).

1-Bromo-11-phenylundecane (7).[34] Into a 250-mL flask were added magnesium turnings (5.0 g, 0.21 mol) and THF (40 mL). 1,2-Dibromomethane (4.0 g) was added through a dropping funnel. After the vigorous reaction ceased, more THF (80 mL) was added to the flask. Subsequently, a solution of benzyl chloride (12.6 g, 0.10 mol) in THF (20 mL) was added during 30 min. The mixture was allowed to stand for 2 h. 1,10-Dibromodecane (30 g, 0.10 mol), THF (300 mL), and 0.1 M Li_2CuCl_4 solution (10 mL) were mixed in a 500-mL flask and cooled with ice. The Grignard reagent solution was quickly transferred to a dropping funnel, added to the mixture over a period of 3 h, and stirred overnight. Methanol (10 mL) was added, the solvent was removed, and chloroform (250 mL) was added to dissolve the residue. The solution was washed with water and dried with magnesium sulfate. After removal of the solvent, the residue was distilled under reduced pressure to give 15.1 g (48.2%) of **7**: bp 135 °C/1 mm; ^{1}H NMR (60 MHz) δ 1.2–1.9 (m, 18 H), 2.60 (t, 2 H, J = 7 Hz), 3.36 (t, 2 H, J = 6.5 Hz), 7.15 (s, 5 H).

1,22-Diphenyldocosane (2f).[35] Sodium sand was made by heating sodium (3.54 g, 154 mmol) in dry xylene until molten, followed by shaking as the xylene cooled. Compound **7** (23.8 g, 77 mmol) was added in small portions to the reaction, which was controlled by shaking and heating at short intervals. After all of the bromide **7** had been introduced, the mixture was allowed to stand for 3 h. The excess sodium was destroyed by careful addition of ethanol and then water. The mixture was extracted with chloroform (3 × 50 mL). The chloroform solution was washed with water, dried, concentrated, and recrystallized (ethanol) to give 7.12 g (40.2%) of **2f**: mp 58–59.5 °C; IR (KBr) 2916, 2846, 1469, cm^{-1}; ^{1}H NMR (60 MHz) δ 1.1–1.7 (m, 40 H), 2.5 (t, 4 H, J = 7 Hz), 7.1 (s, 10 H).

Bis[4-(chloroacetyl)phenyl] Oxide (3a).[36] The following is a modification of a published procedure.[14] Finely ground $AlCl_3$ (50.0 g, 0.375 mol) was mixed with dichloromethane (50 mL) in a 250-mL flask and cooled to −10 °C. Chloroacetyl chloride (37.3 g, 0.33 mol) was added to the mixture as it was kept cool. Diphenyl ether (25.5 g, 0.15 mol) was dissolved in dichloromethane (10 mL) and charged to a dropping funnel. The diphenyl ether solution was added slowly dropwise to the mixture over 2 h while stirring and keeping the temperature below 0 °C. At the end of the addition, the mixture was left to warm to room temperature and stir overnight. The red solution was poured into a large quantity of ice (about 300 g). The organic layer was separated, the aqueous layer was extracted with dichloromethane (50 mL), and the dichloromethane portions were washed with water until neutral. The organic phase was then dried (magnesium sulfate), concentrated, recrystallized (ethanol), and dried to give 33.8 g (69.7%) of **3a**: mp 108–110 °C; ^{1}H NMR (60 MHz) δ 4.68 (s, 4 H), 7.0–7.3 (m, 4 H), 7.9–8.2 (m, 4 H).

Bis[4-(chloroacetyl)phenyl] Sulfide (3b).[15a] A procedure similar to that described for the synthesis **3a** was used except phenyl sulfide and chloroacetyl chloride were dissolved in dichloromethane and added to the $AlCl_3$ mixture. Phenyl sulfide (16.7 g, 0.090 mol), chloroacetyl chloride (30.6 g, 0.271 mol), and $AlCl_3$ (36.1 g, 0.271 mol) were used. The crude product (19 g, 62%) was decolored by activated charcoal and recrystallized (acetone/ethanol) to give 10.9 g (35.7%) of **3b**: mp 101.5–103 °C; ^{1}H NMR (60 MHz) δ 4.67 (s, 4 H), 7.4–7.6 (m, 4 H), 7.9–8.1 (m, 4 H).

Bis[4-(chloroacetyl)phenyl] Triethylene Glycol Ether (3c). $AlCl_3$ (90.0 g, 0.675 mol) was mixed with dichloromethane (50 mL) and cooled to −10 °C. Chloroacetyl chloride (37.3 g, 0.33 mol) was added to the mixture and cooled to −10 °C. **2c** (45.4 g, 0.15 mol) was dissolved in dichloromethane (30 mL) and slowly added dropwise to the mixture over 2 h. At the end of the addition, the mixture was heated to reflux and stirred overnight. The resulting mixture was worked up as described before. The crude product was recrystallized (THF) and dried to give 42.6 g (62.4%) of **3c**: mp 89–91 °C; IR (KBr) 1689, 1600, 1261, 1219, 1184 cm^{-1}; ^{1}H NMR (60 MHz) δ 3.75 (s, 4 H), 3.8–4.0 (m, 4 H), 4.1–4.3 (m, 4 H), 4.63 (s, 4 H), 6.8–7.1 (m, 4 H), 7.8–8.1 (m, 4 H).

Bis[4-(chloroacetyl)phenyl]methane (3d).[36] **3d** was prepared in 70.7% yield: mp 121–122 °C; IR (KBr) 1701, 1600, 1215 cm^{-1}; ^{1}H NMR (60 MHz) δ 4.07 (s, 2 H), 4.63 (s, 4 H), 7.2–7.4 (m, 4 H), 7.8–8.0 (m, 4 H).

1,10-Bis[4-(chloroacetyl)phenyl]decane (3e).[37] A 73.3% yield of **3e** was obtained: mp 85–86 °C; IR (KBr) 2927, 2850, 1701, 1604, 1215, 817 cm^{-1}; ^{1}H NMR (60 MHz) δ 1.2–1.7 (m, 16 H), 2.6 (t, 4 H, J = 6.5 Hz), 4.53 (s, 4 H), 7.0–7.2 (m, 4 H), 7.6–7.8 (m, 4 H).

1,22-Bis[4-(chloroacetyl)phenyl]docosane (3f). **3f** was prepared in 22.4% yield: mp 91–93 °C; IR (KBr) 2920, 2846, 1697, 1604, 1469, 1215, 1164, 995, 817, 790, 756, 721 cm^{-1}; ^{1}H NMR (60 MHz) δ 1.1–1.7 (m, 40 H), 2.6 (t, 4 H), 4.6 (s, 4 H), 7.1–7.3 (m, 4 H), 7.7–7.9 (m, 4 H).

Bis[4-(((ethoxy(thiocarbonyl))thio)acetyl)phenyl] Oxide (4a). A mixture of **3a** (33.8 g, 0.105 mol) and *O*-ethylxanthic acid potassium salt (33.5 g, 0.209 mol) in acetone (450 mL) was heated to reflux for 4 h. The mixture was allowed to cool to room temperature and filtered. The precipitate was washed with dichloromethane (50 mL). The combined organic phase was concentrated to give crude **4a**. The crude **4a** was dissolved in dichloromethane (200 mL) and washed with water (2 × 200 mL). The solution was dried (magnesium sulfate) and concentrated to give 47.2 g (91.4%) of **4a**: ^{1}H NMR (60 MHz) δ 1.44 (t, 6 H, J = 7 Hz), 4.73 (s, 4 H), 4.73 (q, 4 H, J = 7 Hz), 7.1–7.3 (m, 4 H), 8.0–8.3 (m, 4 H).

Bis[4-(((ethoxy(thiocarbonyl))thio)acetyl)phenyl] Sulfide (4b). A 67% yield of **4b** was isolated after recrystallization from acetone/ethanol: ^{1}H NMR (60 MHz) δ 1.41 (t, 6 H, J = 7 Hz), 4.67 (s, 4 H), 4.69 (q, 4 H, J = 7 H), 7.4–7.6 (m, 4 H), 8.0–8.2 (m, 4 H).

Bis[4-(((ethoxy(thiocarbonyl))thio)acetyl)phenyl] Triethylene Glycol Ether (4c). An 88% yield of **4c** was isolated: IR (KBr) 1670, 1600, 1311, 1265, 1238, 1111, 1057 cm^{-1}; ^1H NMR (60 MHz) δ 1.37 (t, 6 H, J = 7 Hz), 3.75 (s, 4 H), 3.8–4.0 (m, 4 H), 4.1–4.3 (m, 4 H), 4.58 (s, 4 H), 4.61 (q, 4 H, J = 7 Hz), 6.8–7.1 (m, 4 H), 7.8–8.1 (m, 4 H).

Bis[4-(((ethoxy(thiocarbonyl))thio)acetyl)phenyl]methane (4d). A 92.8% yield of **4d** was isolated: IR (KBr) 1681, 1600, 1226, 1114, 1053, 995 cm^{-1}; ^1H NMR (60 MHz) δ 1.37 (t, 6 H, J = 7 Hz), 4.07 (s, 2 H), 4.58 (q, 4 H, J = 7 Hz), 4.60 (s, 4 H), 7.2–7.4 (m, 4 H), 7.8–8.0 (m, 4 H).

1,10-Bis[4-(((ethoxy(thiocarbonyl))thio)acetyl)phenyl]decane (4e). A 98.2% yield of **4e** was isolated: IR (KBr) 2916, 2850, 1693, 1604, 1219, 1057, 991, 817 cm^{-1}; ^1H NMR (60 MHz) δ 1.2–1.7 (m, 22 H), 2.6 (t, 4 H, J = 6.5 Hz), 4.5 (s, 4 H), 4.5 (q, 4 H, J = 7 Hz), 7.0–7.2 (m, 4 H), 7.6–7.8 (m, 4 H).

1,22-Bis[4-(((ethoxy(thiocarbonyl))thio)acetyl)phenyl]docosane (4f). A 99% yield of **4f** was isolated: ^1H NMR (60 MHz) δ 1.1–1.7 (m, 40 H), 2.6 (t, 4 H, J = 7 Hz), 4.6 (s, 4 H), 4.6 (q, 4 H, J = 7 Hz), 7.1–7.3 (m, 4 H), 7.8–8.0 (m, 4 H).

Bis[4-(2-oxo-1,3-dithiolyl)phenyl] Oxide (5a). A solution of **4a** (22.0 g, 44.5 mmol) in acetic acid (200 mL) was heated to reflux. A solution of 30% (by weight) HBr in acetic acid (120 mL) was added to the flask. During the addition, **5a** began to precipitate out. The mixture was heated to reflux for 3 h, allowed to cool to room temperature, and filtered. The solid crude product was dissolved in dichloromethane (200 mL) and washed with water until neutral. The solution was then dried (magnesium sulfate), concentrated, recrystallized (dichloromethane/acetone), and dried to give 12.5 g (69.8%) of **5a**: mp 146–148 °C; IR (KBr) 1635, 1496, 1253, 871 cm^{-1}; ^1H NMR (200 MHz) δ 6.77 (s, 2 H), 7.06 (m, 4 H), 7.42 (m, 4 H); ^{13}C NMR (50 MHz) δ 192.22, 157.31, 134.08, 128.31, 128.00, 119.52, 111.21. Anal. Calcd for $C_{18}H_{10}O_3S_4$: C, 53.71; H, 2.50; S, 31.86. Found: C, 53.53; H, 2.49; S, 31.22.

Bis[4-(2-oxo-1,3-dithiolyl)phenyl] Sulfide (5b). The crude product was dissolved in dichloromethane, washed with water, decolored by activated charcoal, and filtered through a silica gel column. The eluate was concentrated to give 32% of **5b**: mp 160–162 °C; IR (KBr) 1635, 1483, 1400, 875, 763 cm^{-1}; ^1H NMR (300 MHz) δ 6.86 (s, 2 H), 7.37 (s, 8 H); ^{13}C NMR (75 MHz) δ 191.94, 136.60, 134.00, 131.68, 131.55, 127.07, 112.22. Anal. Calcd for $C_{18}H_{10}O_2S_5$: C, 51.65; H, 2.41. Found: C, 51.43; H, 2.36.

Bis[4-(2-oxo-1,3-dithiolyl)phenyl] Triethylene Glycol Ether (5c). **4c** (8.5 g, 13.5 mmol) was dissolved in acetic acid (100 mL) and 30% HBr in acetic acid (50 mL). The mixture was heated to reflux for 20 min and then stirred overnight at room temperature. The crude product was purified as described for **5b** to give 0.9 g (12%) of **5c**: mp 125–126 °C; IR (KBr) 1627, 1504, 1257, 1134, 871, 821, 775 cm^{-1}; ^1H NMR (300 MHz) δ 3.75 (s, 4 H), 3.87 (t, 4 H, J = 4.5 Hz), 4.14 (t, 4 H, J = 4.5 Hz), 6.66 (s, 2 H), 6.90–6.93 (m, 4 H), 7.30–7.33 (m, 4 H); ^{13}C NMR (75 MHz) δ 192.63, 159.50, 134.65, 127.59, 125.58, 115.21, 109.79, 70.91, 69.66, 67.60. Anal. Calcd for $C_{24}H_{22}O_6S_4$: C, 53.91; H, 4.15. Found: C, 53.49; H, 3.93.

Bis[4-(2-oxo-1,3-dithiolyl)phenyl]methane (5d). **5d** was isolated in 84.5% yield by using the same procedure described for **5b**: mp 155–156 °C; IR (KBr) 1635, 864, 775 cm^{-1}; ^1H NMR (300 MHz) δ 4.01 (s, 2 H), 6.79 (s, 2 H), 7.20–7.23 (m, 4 H), 7.34–7.37 (m, 4 H); ^{13}C NMR (75 MHz) δ 192.34, 141.68, 134.69, 130.93, 129.66, 126.58, 111.31, 41.22. Anal. Calcd for $C_{19}H_{12}O_2S_4$: C, 56.97; H, 3.02. Found: C, 56.51; H, 2.72.

1,10-Bis[4-(2-oxo-1,3-dithiolyl)phenyl]decane (5e). **5e** was isolated in 83.4% yield by using the same procedure described for **5b**: mp 123–124 °C; IR (KBr) 2924, 2850, 1627, 1504, 871 cm^{-1}; ^1H NMR (300 MHz) δ 1.28 (br s, 12 H), 1.60 (t, 4 H, J = 7.5 Hz), 2.61 (t, 4 H, J = 7.5 Hz), 6.77 (s, 2 H), 7.19–7.22 (m, 4 H), 7.31–7.34 (m, 4 H); ^{13}C NMR (75 MHz) δ 192.68, 144.38, 135.08, 130.11, 129.17, 126.20, 110.71, 35.62, 31.22, 29.48, 29.41, 29.19. Anal. Calcd for $C_{28}H_{30}O_2S_4$: C, 63.84; H, 5.74. Found: C, 63.89; H, 5.53.

1,22-Bis[4-(2-oxo-1,3-dithiolyl)phenyl]docosane (5f). **5f** was isolated in 32% yield by using the same procedure described for **5b**: mp 120–122 °C; IR (KBr) 2920, 2846, 1631, 1504, 871 cm^{-1}; ^1H NMR (300 MHz) δ 1.24–1.57 (m, 40 H), 2.61 (t, 4 H, J = 7.5 Hz), 6.77 (s, 2 H), 7.19–7.22 (m, 4 H), 7.31–7.34 (m, 4 H); ^{13}C NMR (75 MHz) δ 192.64, 144.45, 135.15, 130.14, 129.19, 126.22, 110.67, 35.64, 31.23, 30.86, 29.66, 29.54, 29.43, 29.21. Anal. Calcd for $C_{40}H_{54}O_2S_4$: C, 69.12; H, 7.83. Found: C, 68.39; H, 7.35.

Bis[4-(1,2-bis(methylthio)ethenyl)phenyl] Oxide (8). A mixture of **5a** (0.100 g, 0.248 mmol) and sodium ethoxide (0.101 g, 1.49 mmol) in ethanol (15 mL) was heated at 60 °C and stirred for 40 min. Iodomethane (0.353 g, 2.48 mmol) in ethanol (15 mL) was added to the mixture, the resulting mixture was cooled to room temperature, and the volatile materials were removed by rotoevaporation. The residue was extracted with chloroform (20 mL) and filtered. The filtrate was concentrated to give 0.101 g (100%) of **8**: mp 103–105 °C; IR (KBr) 2997, 2916, 1489, 1249, 810 cm^{-1}; ^1H NMR (300 MHz) δ 2.07 (s, 6 H), 2.40 (s, 6 H), 6.38 (s, 2 H), 6.94–6.97 (m, 4 H), 7.39–7.42 (m, 4 H); ^{13}C NMR (75 MHz) δ 156.42, 133.79, 131.42, 131.36, 128.64, 118.75, 17.46, 16.02. Anal. Calcd for $C_{20}H_{22}OS_4$: C, 59.08; H, 5.45; S, 31.54. Found (after recrystallization from Et_2O/C_5H_{12}): C, 59.26; H, 5.63; S, 31.15.

Poly[[4,4′-oxybis[benzeneethenedithiolato]]nickel(II)] (11a). A mixture of **5a** (0.200 g, 0.497 mmol) and sodium ethoxide (0.203 g, 2.98 mmol) in ethanol (30 mL) was heated at 60 °C with stirring for 40 min. Nickel bromide (0.109 g, 0.497 mmol) dissolved in ethanol (30 mL) was added to the mixture via cannula. The resulting mixture was heated at 60 °C overnight and cooled to room temperature. Iodine (0.252 g, 0.994 mmol) was dissolved in ethanol (10 mL) and added to the mixture. The resulting mixture was stirred for 2 h. The black polymer was collected by filtration and washed thoroughly with water and ethanol. The product was then dried under vacuum to give 0.170 g (84.4%) of polymer **11a**: IR (KBr) 1587, 1498, 1367, 1245, 1189, 1167, 857, 833, 798 cm^{-1}; UV–vis–near-IR (DMF) λ_{max} (ϵ) 265 (48 100), 310 (54 700), 490 (sh, 2500), 930 (13 200) nm. Anal. Calcd for $(C_{16}H_{10}NiOS_4)_n$: C, 47.43; H, 2.49; Ni, 14.49; S, 31.65. Found: C, 47.49; H, 2.91; Ni, 10.80; S, 33.49; I, 2.17; Br, 0.51.

Poly[[4,4′-thiobis[benzeneethenedithiolato]]nickel(II)] (11b). A 79.5% yield of polymer **11b** was isolated: IR (KBr) 1581, 1485, 1365, 1190, 1010, 861, 827, 797 cm^{-1}; UV–vis–near-IR (DMF) λ_{max} (ϵ) 273 (19 700), 316 (25 300), 350 (sh, 18 500), 500 (sh, 1100), 930 (5500) nm. Anal. Calcd for $(C_{16}H_{10}NiS_5)_n$: C, 45.62; H, 2.39. Found: C, 37.59; H, 2.69.

Poly[[4,4′-(triethylene glycol)bis[benzeneethenedithiolato]]nickel(II) ether] (11c). A mixture of **5c** (0.200 g, 0.374 mmol) and sodium ethoxide (0.153 g, 2.24 mmol) in ethanol (30 mL) was heated at 60 °C with stirring for 1 h. Nickel bromide (0.082 g, 0.374 mmol) dissolved in ethanol (30 mL) was added to the mixture via cannula. The resulting mixture was heated at 60 °C overnight and cooled to room temperature. The mixture was opened to air and stirred for 2 h. The black polymer was collected by filtration, washed thoroughly with water and ethanol, and then dried under vacuum to give 0.182 g (90.5%) of polymer **11c**: IR (KBr) 1597, 1508, 1364, 1256, 1191, 1143, 1112, 862, 832 cm^{-1}; UV–vis–near-IR (DMF) λ_{max} (ϵ) 265 (21 100), 310 (16 700), 500 (sh, 500), 935 (3100) nm. Anal. Calcd for $(C_{22}H_{22}NiO_4S_4)_n$: C, 49.17; H, 4.13. Found: C, 43.55; H, 3.82.

Poly[[4,4′-methylenebis[benzeneethenedithiolato]]nickel(II)] (11d). The procedure described for the synthesis of **11a** was followed. Polymer **11d** (0.180 g (89.5%)) was isolated as a black powder: IR (KBr) 1599, 1369, 1191, 861, 781 cm^{-1}; UV–vis–near-IR (DMF) λ_{max} 260, 310, 500, 930 nm. Anal. Calcd for $(C_{17}H_{12}NiS_4)_n$: C, 50.64; H, 3.00. Found: C, 49.20; H, 3.07.

Poly[[4,4′-(decane-1,10-diyl)bis[benzeneethenedithiolato]]nickel(II)] (11e). The procedure described for the synthesis of **11c** was followed. Polymer **11e** (0.171 g (85.0%)) was isolated as a black powder: IR (KBr) 2924, 2850, 1604, 1369, 1323, 1192, 864, 833, 794 cm^{-1}; UV–vis–near-IR (DMF) λ_{max} 260, 310, 490, 935 nm. Anal. Calcd for $(C_{26}H_{30}NiS_4)_n$: C, 58.98; H, 5.71. Found: C, 54.07; H, 5.35.

Poly[[4,4′-(docosane-1,22-diyl)bis[benzeneethenedithiolato]]nickel(II)] (11f). The procedure described for the synthesis of **11c** was followed. Polymer **11f** was isolated in 81% yield as a black powder: IR (KBr) 2920, 2850, 1681, 1604, 1369, 1192, 864, 837, 794 cm^{-1}; UV–vis–near-IR (DMF) λ_{max} 260, 310,

500, 930 nm. Anal. Calcd for $(C_{38}H_{54}NiS_4)_n$: C, 65.41; H, 7.80. Found: C, 64.77; H, 7.63.

Acknowledgment. This work was supported by grants from the Defense Advanced Research Projects Agency monitored by the Office of Naval Research and the Robert A. Welch Foundation.

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Synthesis and Properties of Diacetylenic Glutamate Lipid Monomer and Polymer: Thermochromic Polydiacetylene Free-Standing Films

Thauming Kuo and David F. O'Brien*

C. S. Marvel Laboratories, Department of Chemistry, University of Arizona, Tucson, Arizona 85721

Received July 31, 1989; Revised Manuscript Received December 29, 1989

ABSTRACT: A novel double-chain diacetylene lipid based on a glutamate backbone, bis(docosa-10,12-diynyl) *N*-[6-(triethylammonio)hexanoyl]-L-glutamate bromide, was prepared by a multistep synthesis. Vesicles were formed by room-temperature sonication of the hydrated lipid. At 0 °C, the vesicles were readily polymerized by UV irradiation and the polydiacetylene (PDA) vesicles showed a two-stage thermochromic phase transition as the temperature was elevated. In the first irreversible stage, the PDA vesicles turned from blue to orange-red on warming to room temperature; in the second reversible stage, they turned from orange-red to yellow-orange on warming to 50 °C. Ordered multilayer films of the diacetylene lipid were cast from unpolymerized bilayer vesicles. Photopolymerization of these cast multilayer films yield highly colored polydiacetylenic films, thereby demonstrating that the molecular order inherent in the bilayer vesicles is retained during the casting procedure. The cast, polymerized films of PDA could be stripped from the support to give free-standing thin films of PDA, which were not disrupted by treatment with organic solvents. The PDA films showed reversible thermochromic phase transitions. Treatment of the PDA films with iodine vapors increased the electrical conductivity to 6×10^{-4} Ω^{-1} cm^{-1}.

Introduction

The polymerization of diacetylenes has been of great interest since it was reported[1,2] that the solid-state reaction proceeds by a topochemical 1,4-addition. The reaction is controlled by the packing of monomers in the crystal lattice and leads to the formation of polymeric single crystals. As illustrated, the UV-initiated polymeriza-

0024-9297/90/2223-3225$02.50/0