Electroactive, Near-Infrared-Absorbing, Nickel Bis(dithiolene) Complex Polycarbonates and Polyurethanes

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Received August 28, 1990; Revised Manuscript Received February 19, 1991

ABSTRACT: A new series of polycarbonates and polyurethanes, containing nickel bis(dithiolene) (Ni-BDT) complexes in the main chain, have been synthesized via polymerization of a functionalized Ni-BDT complex. These polymers are highly soluble in common organic solvents, and free-standing films can be cast from solution. Gel permeation chromatographic analysis on these polymers indicates hydrodynamic volumes comparable to those of polystyrene standards having weight-average molecular weights (M_w) ranging from 1.35×10^4 to 9.8×10^4. These polymers exhibit a near-IR absorbance between 830 and 940 nm in solution due to the Ni-BDT complex, and solvatochromism is observed with more polar solvents shifting the near-IR absorbance band to higher wavelength. A single glass transition (T_g) is observed for all polymers, suggesting a relatively random polymerization (no phase separation). The T_g's of the polycarbonates decrease with increased Ni-BDT, while the T_g's of the polyurethanes increase, as expected for changes in chain rigidity. Most of the Ni-BDT complex polymers are electroactive with a two-step redox process, typical for Ni-BDT complexes, observed in cyclic voltammograms of the polymers in solution. The results presented herein indicate that the incorporation of Ni-BDT complexes into polymer main chains impart the unique opto-electronic properties of Ni-BDT's to the polymer.

Introduction

Transition-metal dithiolene complexes comprise a large class of compounds that possess unusual chemical properties. These include the ability to undergo a sequence of reversible electron-transfer reactions, interesting magnetic properties, and intense absorbance in the visible and near-infrared region. These complexes have been the subject of many chemical, electrochemical, structural, and spectroscopic studies.[1-3] Due to their molecular nature, only powders or single crystals can be obtained for these compounds, causing limitations to their practical application. The incorporation of such complexes into the main chain of a polymer may then afford a material that exhibits the interesting properties of the metal complex while concurrently retaining useful polymeric properties of processability and mechanical durability.

A variety of metal complex polymers incorporating square-planar MS_4 metal centers into conjugated ligands have been prepared[4-13] and studied theoretically.[14] A common feature of these polymers is that they are all prepared via a metal complexation polymerization with a planar conjugated tetrathio ligand. Upon complexation in a square-planar coordination, the polymer structures are quite rigid and ribbonlike and, thus, these polymers are insoluble and infusible powders which precipitate during the complexation polymerization reaction. The insolubility and infusibility of these tetrathio complex polymers prohibit them from practical application.

To compensate for the low solubility of the fully conjugated metal tetrathio complex polymers, we have previously reported the incorporation of nickel bis(dithiolene) complexes (Ni-BDT) into the main chain of polymers that contain flexible units using metal complexation polymerizations.[15,16] Employing short spacers including -O-, -S-, and $-CH_2-$ and longer units including $-(OCH_2CH_2)_3O-$, $-(CH_2)_{10}-$, and $-(CH_2)_{22}-$, the polymers are highly soluble in a number of solvents in the as-made reduced (anionic) form. Oxidation of the metal centers to the essentially neutral form is found to decrease the overall solubility, while polymers containing long flexible linkages are more soluble than those containing short linkages. Due to the nature of the metal complexation polymerization, problems such as incomplete tetrathiolate formation, nonstoichiometric balance of functional groups during polymerization, and low solubility are limits to obtaining high molecular weight polymers. This limits their mechanical properties, and we were unable to prepare these polymers as free-standing films. In addition, as the flexible linkage in the ligand becomes longer, synthesis of the tetrathiolate ligand precursor becomes more difficult. For example, when the linkage is docosamethylene, the synthesis of the ligand requires multiple steps and therefore the overall yield is low.

Here we report a new synthetic approach to obtaining electroactive polymers containing the Ni-BDT complex along the main chain. This method involved preparing a bifunctionalized Ni-BDT complex which can then be polymerized according to typical step-growth polymerization procedures. Two polymer series, polycarbonates and polyurethanes, have been prepared via this approach and characterized by using FT-IR, UV-vis-NIR, GPC, TGA, and DSC.

Results and Discussion

Synthesis of the Ni-BDT Complex Monomer. The synthesis of bis[4-(2-hydroxyethyl)benzeneethanedithiolato]nickel(II) (5) was carried out as outlined in Scheme I. The aliphatic hydroxy group was chosen as the functional group due to the fact that it is stable during the metal complexation reaction, has a minimum possibility of interfering with the complexation reaction, and could be easily protected and deprotected during the synthetic steps if necessary. Beginning with phenethyl alcohol, a Friedel-Crafts acylation was carried out followed by reaction with potassium *O*-ethylxanthate to form the xanthate ester (2). No interference from the alcohol was observed, though a problem occurred during the cyclization reaction of the xanthate ester. Previously[16] we had utilized HBr in acetic acid to effect the cyclization as initially developed by Mueller-Westerhoff et al.[17] In this instance compound 3 was contaminated with a byproduct produced by the strongly acidic HBr solution, causing dehydration or substitution on the hydroxy group, which

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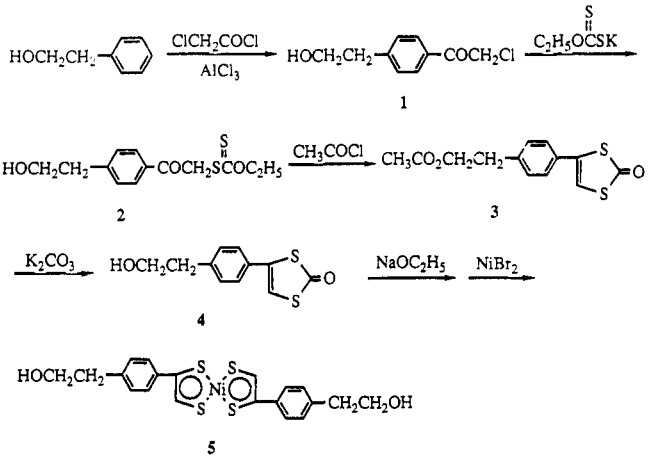
Scheme I



could not be separated by recrystallization. Alternatively, 2 was treated with an excess of acetyl chloride to protect the alcohol, and the released stoichiometric amount of HCl provided a sufficiently acidic environment to promote the cyclization reaction to form the dithiocabonate 3 without further reaction on the alcohol to form the byproduct. To avoid the possible complications caused by deacylation, 3 was deprotected by aqueous K_2CO_3 to 4 prior to the complexation reaction. The complexation reaction of 4 with nickel bromide was carried out as described before.[16]

The IR spectrum of 5 has an intense band at 1371 cm^{-1} and a band at 1193 cm^{-1} which are common features of IR spectra for Ni-BDT complexes.[18] The UV–vis–NIR spectrum of 5 has an intense NIR band at 835 nm, which is typical for nickel bis(dithiolene) complexes in the neutral form.[19] The mass spectrum of 5 shows two molecular peaks at 478 and 480, with the 478 peak having a higher intensity. The natural abundance of ^{58}Ni is 68.27%, and the natural abundance of ^{60}Ni is 26.10%. The calculated molecular weight of 5 with ^{58}Ni is 478 and with ^{60}Ni is 480, accounting for these two peaks. The results are in good agreement with the calculated values, which further confirms the proposed structure. Thermogravimetric analysis of 5 shows the compound has an onset of decomposition temperature of 217 °C, most likely due to dehydration of the alcohols. This will be addressed further later.

Synthesis of Polycarbonates and Polyurethanes Containing the Ni-BDT Unit. Polymerizations were carried out to prepare a series of bisphenol A (BPA) polycarbonates[20,21] containing varied compositions of the Ni-BDT complex along the polymer main chain as outlined in Scheme II by using mole percentages of the Ni-BDT complex in the feed ranging from 0 to 20 mol %.

Pyridine, a good solvent for 5, was used as both the solvent and the base for complexing the HCl produced in the reaction. In some instances, during the workup, some gel-like material formed which was insoluble in chloroform, attributable to some cross-linking during the polymerization process. The insoluble gel was separated from the soluble fraction by centrifugation or filtration. All of the metal-containing polycarbonates are solid green powders with a deeper color with increased content of the Ni-BDT complex.

A similar series of polyurethanes containing the Ni-BDT complex were prepared as outlined in Scheme III. A modified literature procedure was used to yield polyurethanes with a Ni-BDT content ranging from 0 to 20 mol %.[21-23] Polymer 12 is white, while the metal-containing polyurethanes are brown. Again, the intensity of the color increased with increased Ni-BDT content.

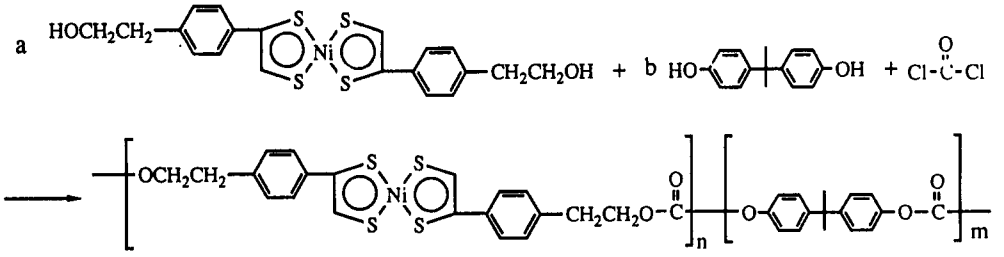
Elemental analysis results for the polycarbonates and polyurethanes are shown in Tables I and II, respectively. The analyses of the polyurethanes are quite close to that expected on the basis of the ratio of diols used in the polymerization. This is as expected as the aliphatic Ni-BDT diol (5) would be expected to have a similar reactivity to urethane formation as 1,10-decanediol. A discrepancy arose in the analysis of the polycarbonates. When 5 and 10 mol % feeds of the Ni-BDT diol relative to bisphenol A were used, the polymers obtained exhibited significantly lower than expected nickel contents. At the same time, the sulfur analyses are within experimental error of the feed composition. Since the Ni-BDT complex has been prepared and fully characterized prior to polymerization, there is most likely a problem in the combustion analyses for nickel in the polycarbonates. This is not surprising, as other investigators have had difficulties obtaining accurate combustion analyses on metal tetrathiolate polymers.[10,11] Incomplete dissolution prior to analysis may have led to these low values for nickel content. Outside of this, all of the combustion analysis results suggest the polymers have the expected composition.

Both ^{13}C and ^{1}H NMR spectra were obtained on all polymers and are consistent with the expected polycarbonate and polyurethane structures detailed in Schemes II and III. Due to the relatively low content of the Ni-BDT units in the polymers, little microstructural information was available. For example, the ^{1}H NMR of polycarbonate 10 exhibits two broad single peaks at 3.1 and 4.4 ppm. Though these can be directly assigned to the two methylene groups of the Ni-BDT unit, the poor resolution does not allow determination of the identity of the alcohol group (BPA or Ni-BDT) on the other side of the carbonate linkage. The presence of the 10 methylene linkages from the 1,10-decanediol in the polyurethanes precludes any use of NMR in structural determination here also.

UV–Vis–Near-IR Spectroscopy. The UV–vis–near-IR spectra of these polymers (Figure 1) show one broad band in the near-IR range which corresponds to the Ni-BDT complex $2b_{1u} \rightarrow 3b_{2g}$ transition. We have previously reported observing this transition in nickel bis(dithiolene) polymers prepared via *metal complexation polymerization*, and this confirms the presence of the Ni-BDT complex in the polymers prepared via *polymerization of a functionalized metal complex*.[16] Again, as shown in Table III, the position of the NIR peak is significantly affected by solvent polarity. In the case of both polycarbonates and polyurethanes, over a 100-nm shift is observed when the solvent is changed from toluene to DMSO. The fact that significant spectral changes are observed in the highly polar, yet nonreducing, solvents HMPA and DMSO indicates that the solvatochromic behavior is due to solvent polarity. These highly polar solvents have the ability to donate an electron pair and are referred to as electron pair donor solvents.[25] The neutral form of a Ni-BDT complex is a good electron acceptor, and presumably, a specific axial interaction of the Ni-BDT metal center with solvent molecules is responsible for this solvatochromic behavior. The solvatochromism for some metal benzene-1,2-dithiolate complexes has been observed previously.[26]

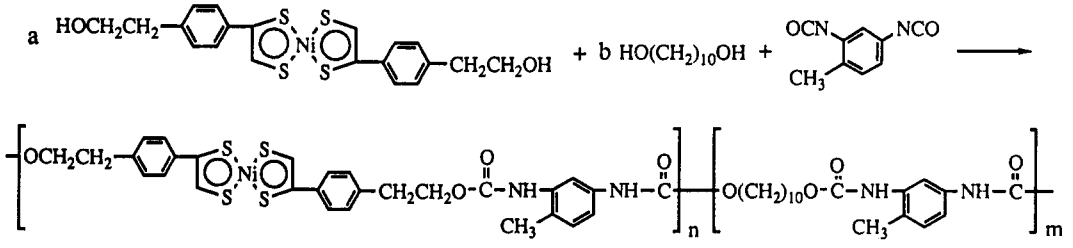
Infrared Spectroscopy. The infrared spectra of these nickel complex polymers is, over most of the spectral range, essentially identical with that of the parent polyurethane and polycarbonates since the highest Ni-BDT content utilized was 20 mol %. The Ni-BDT complex (5) does exhibit an intense band at 1371 cm^{-1} due to a perturbed C=C stretch.

Scheme II



6 a = 0 b = 1
7 a = 0.01 b = 0.99
8 a = 0.025 b = 0.975
9 a = 0.05 b = 0.95
10 a = 0.10 b = 0.90
11 a = 0.20 b = 0.80

Scheme III



12 a = 0 b = 1
13 a = 0.01 b = 0.99
14 a = 0.025 b = 0.975
15 a = 0.05 b = 0.95
16 a = 0.10 b = 0.90
17 a = 0.20 b = 0.80

Table I
Elemental Analysis Results for Polycarbonates

	a	*b*		C, %	H, %	S, %	Ni, %
7	0.01	0.99	calcd	75.07	5.51		
			found[a]	76.34	5.07		
8	0.025	0.975	calcd	74.33	5.45		
			found[a]	75.91	4.92		
9	0.05	0.95	calcd	73.14	5.36	2.40	1.10
			found[a]	74.04	5.45		
			found[b]	72.82	5.43	2.59	0.41
10	0.10	0.90	calcd	70.93	5.20	4.59	2.10
			found[a]	72.54	5.34		
			found[b]	71.49	5.38	4.52	0.56
11	0.20	0.80	calcd	67.06	4.90		
			found[a]	69.78	4.50		

[a] Carried out at UT—Arlington. [b] Carried out at Texas Analytical Laboratories, Inc.

Table II
Elemental Analysis Results for Polyurethanes

	a	*b*		C, %	H, %	N, %	S, %	Ni, %
13	0.01	0.99	calcd	65.26	8.02	7.97		
			found[a]	64.60	7.00	7.93		
14	0.025	0.975	calcd	64.93	7.91	7.87		
			found[a]	64.57	6.89	7.86		
15	0.05	0.95	calcd	64.40	7.73	7.70	1.76	0.81
			found[a]	64.66	7.81	7.68		
			found[b]	63.85	7.76		2.04	0.89
16	0.10	0.90	calcd	63.39	7.39	7.39	3.38	1.55
			found[a]	63.65	7.43	7.41		
			found[b]	62.85	7.32		3.46	1.97
17	0.20	0.80	calcd	61.60	6.80	6.84		
			found[a]	61.44	5.84	6.86		

[a] Carried out at UT—Arlington. [b] Carried out at Texas Analytical Laboratories, Inc.

Fortuitously, in the case of the polyurethanes there is a window of low absorbance between 1350 and 1400 cm^{-1} as shown in Figure 2 for polymer **12**. As the Ni-BDT complex content is increased in the polymer, there is a concomitant increase in absorption at 1370 cm^{-1}, indicating inclusion of the metal complex in the main chain. Similar results are observed for the polycarbonates as detailed in Figure 3. In this case there are interfering absorptions at 1365 and 1385 cm^{-1} which are assigned to the geminal methyl group vibration of BPA. As the Ni-BDT complex content is increased, the absorption at ca. 1370 cm^{-1} is increased to the point that the three peaks merge in the spectrum of polymer **11**.

Molecular Weights. The number-average molecular weight (M_n) and weight-average moelcular weight (M_w) of these polymers were determined by gel permeation chro-

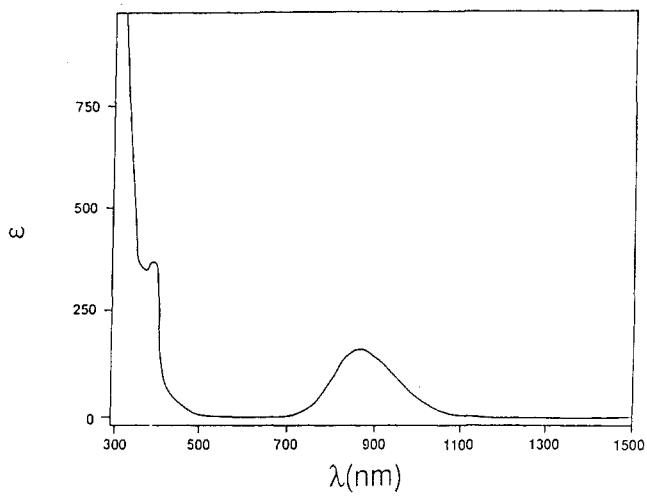


Figure 1. UV–vis–near-IR spectrum of polymer 9.

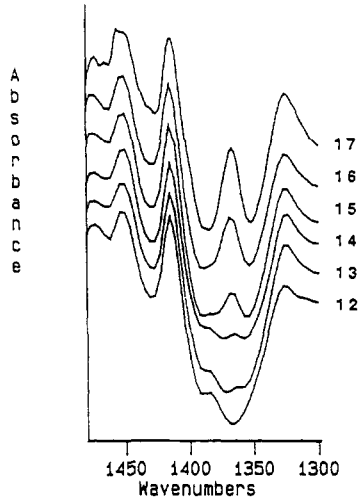


Figure 2. Infrared spectra of polymers 12–17.

Table III
Near-IR Absorbance Results for Polymers 9 and 15

solvent	dielectric constant	λ_{max}, nm of 9	λ_{max}, nm of 15
toluene	2.4	840	840
$CHCl_3$	4.8	845	830
THF	7.6	845	838
HMPA	30.0	930	930
DMF	36.7	932	933
DMSO	46.6	942	942

Table IV
GPC Results for Polymers 6–17

polymer	M_n	M_w	polymer	M_n	M_w
6	24 400	66 200	12	15 600	45 600
7	25 600	97 800	13	14 400	31 900
8	19 000	83 200	14	15 700	50 700
9	14 700	67 100	15	14 800	46 400
10	10 900	52 600	16[a]	11 500	34 100
11	7 400	25 100	17[a]	6 600	13 500

[a] Polymers partially soluble in THF.

matography (GPC) using polystyrene standards, and the results are summarized in Table IV.

In our earlier work[15,16] utilizing metal complexation polymerization, the Ni-BDT polymers were oligomeric in nature and were not fully soluble in THF. Soluble weight fractions exhibited discrete peaks with degrees of polymerization up to about hexamers evident.

The polycarbonates and polyurethanes prepared here exhibit much higher molecular weights. GPC traces are

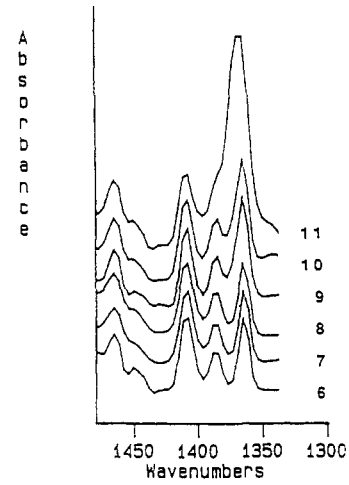


Figure 3. Infrared spectra of polymers 6–11.

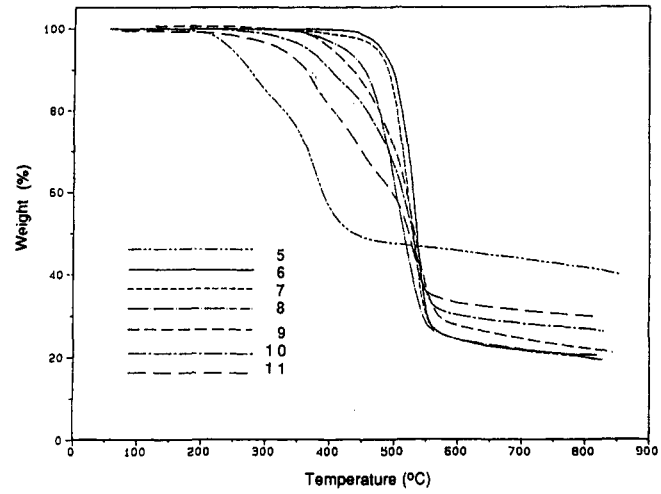


Figure 4. TGA thermograms of polymers 6–11 and monomer 5.

continuous and relatively symmetric. Free-standing films could be cast in all cases, leading to tough solid materials for both the polycarbonates and the polyurethanes.

Examination of the GPC results for the polycarbonates shows a continuous drop in M_n from about 25 000 to 7400 as the Ni-BDT complex content is increased. This can be attributed to a decreased reactivity of the aliphatic Ni-BDT diol to polymerization relative to BPA. Addition of a metal complex to the growing chain yields a chain end less reactive than the phenolic end-group generated when BPA is added.

This problem was not evident in the case of the polyurethanes as polymers 12–15 exhibited essentially the same molecular weights. Polymers 16 and 17 could not be completely dissolved in THF, and the values reported are for the soluble fractions only. This constancy of molecular weight for the fully soluble polymers indicates that the Ni-BDT diol is exhibiting essentially the same reactivity to polymerization as 1,10-decanediol, as expected since they both contain aliphatic alcohol functional groups.

Thermogravimetric Analysis. Thermograms for polymers 6–11 and compound 5 are shown in Figure 4 and for polymers 12–17 in Figure 5. The onsets of decomposition temperatures (ODT) are listed in Table V.

As expected, the polycarbonates are more thermally stable to degradation than the polyurethanes. Examination of the thermal stability of the Ni-BDT diol monomer (5) shows a large initial mass loss between 200 and 300 °C of ca. 20%. This is most likely due to the elimination of

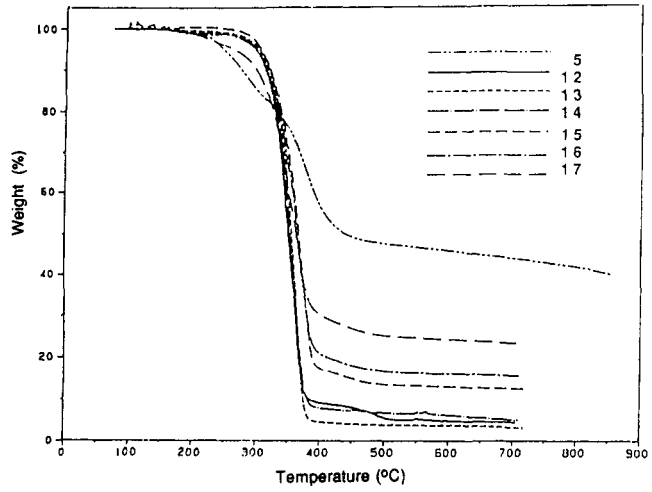


Figure 5. TGA thermograms of polymers 12–17 and monomer 5.

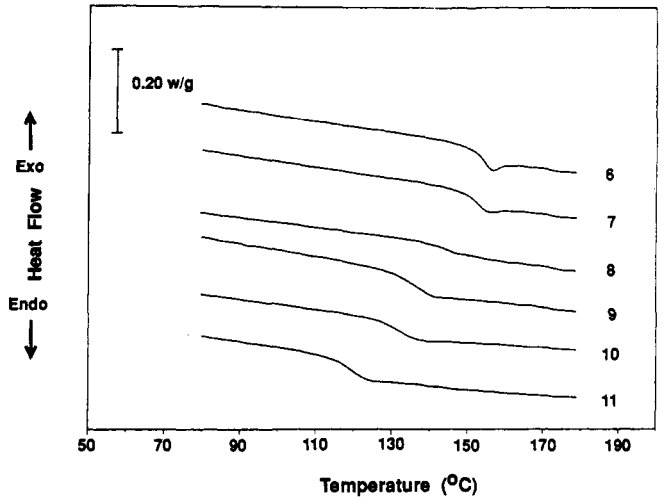


Figure 6. DSC scans for polymers 6–11.

Table V
TGA Results for Polymers 6–17 and Compound 5

sample	ODT, °C	sample	ODT, °C
6	489	12	315
7	479	13	315
8	445	14	313
9	381	15	303
10	347	16	300
11	308	17	278
5	217		

H_2O from the aliphatic diol, a process that is not seen after both carbonate and urethane formation, and thus, the polymers are more stable than the Ni-BDT monomer. There is a second thermal degradation occurring in 5 between 300 and 400 °C which is extended to the polymer degradation. This is evident in the thermograms of the polycarbonates (Figure 4) as increasing Ni-BDT contents lead to decreasing thermal stabilities. In that the onset of decomposition of the polyurethanes, with and without metal complex, occurs between 300 and 315 °C, this process does not lead to a decrease in their thermal stability.

Differential Scanning Calorimetry. DSC was used to determine the glass transition temperatures of these polymer samples. Figure 6 shows the DSC traces of polymers 6–11, while Figure 7 shows the DSC traces of polymers 12–17. All polymers exhibited a single glass transition (T_g) as listed in Table VI. This is suggestive of a relatively random polymerization as substantial blockiness should cause phase separation and the observation

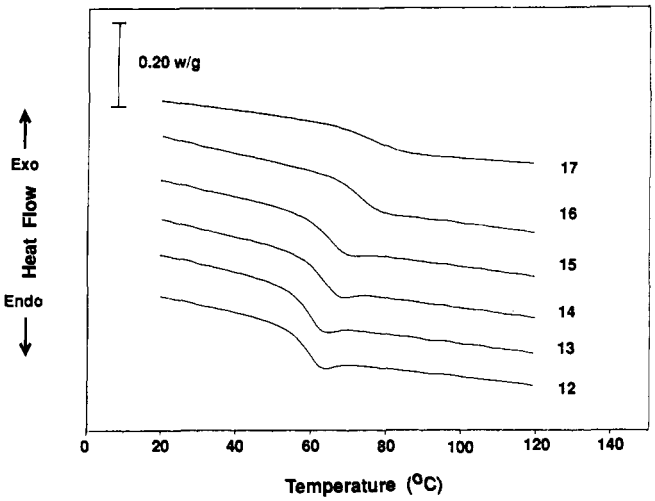


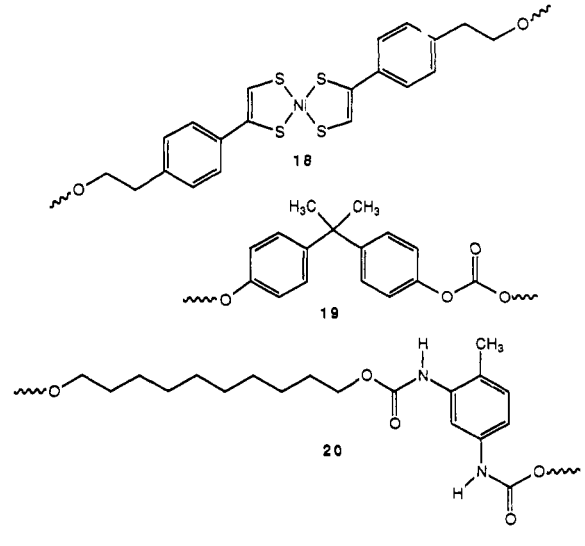
Figure 7. DSC scans for polymers 12–17.

Table VI
DSC Results for Compounds 6–17

sample	T_g, °C	sample	T_g, °C
6	154	12	59
7	152	13	60
8	145	14	63
9	136	15	65
10	132	16	73
11	119	17	76

of two T_g's. Neither set of polymers exhibited melt transitions at temperatures <200 °C, and the polymers are, thus, amorphous as expected. This has been confirmed by X-ray diffraction studies of polycarbonate 11 and polyurethane 17, each prepared by using 20 mol % Ni-BDT in the feed. Amorphous halos peaking at 2θ equal to 18° (4.9 Å) and 21° (4.7 Å) are observed for 11 and 17, respectively.

The inclusion of the Ni-BDT complex into the main chain of these polymers causes a distinct, and opposite, effect on the glass transition properties. For the polycarbonates, the T_g decreases up to 35 °C as the Ni-BDT is increased from 0 to 20 mol %. On the other hand, the T_g of the polyurethanes increases with Ni-BDT. A maximum increase of 17 °C is observed when the polyurethane containing 20 mol % Ni-BDT is compared to pure polyurethane. Examination of the polymer structural units between oxygen atoms, structures 18–20, yields an explanation of these effects. Pure BPA polycarbonate



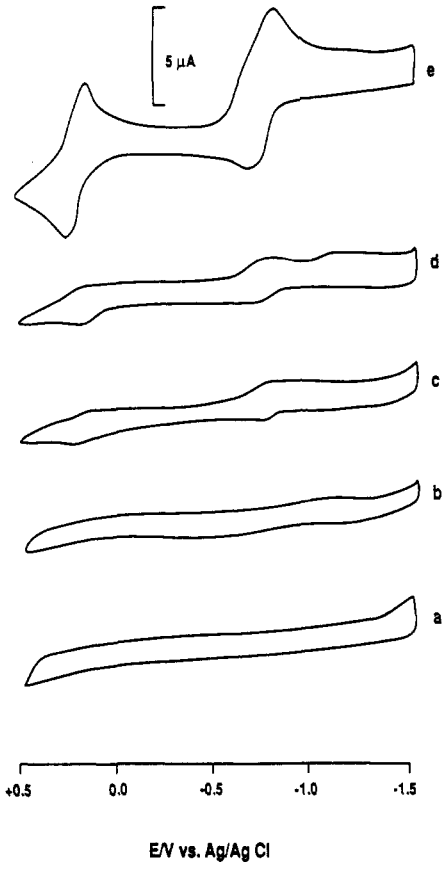


Figure 8. Cyclic voltammograms for Ni-BDT polycarbonates. (a) Polymer 7; (b) polymer 8; (c) polymer 9; (d) polymer 10; (e) polymer 11. Scan rate = 100 mV s^{-1}.

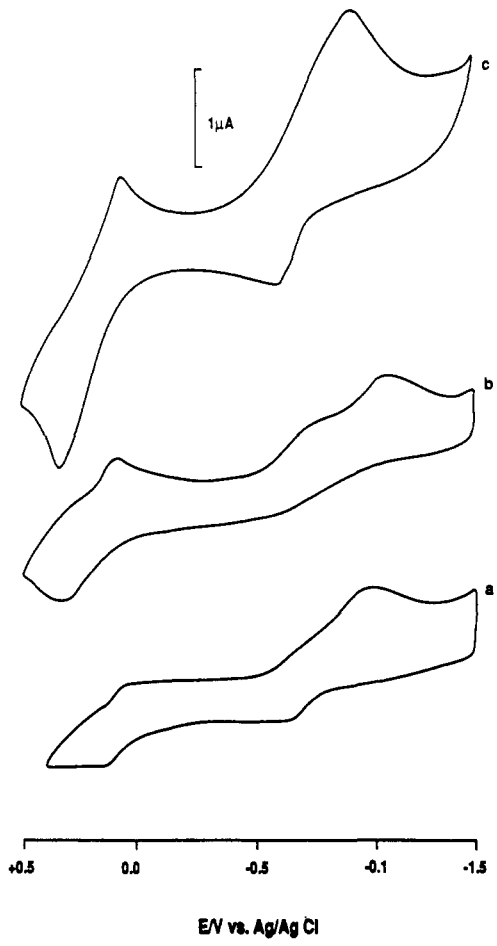


Figure 9. Cyclic voltammograms for Ni-BDT polyurethanes. (a) Polymer 15; (b) polymer 16; (c) polymer 17. Scan rate = 100 mV s^{-1}.

has a rigid structure, with no flexible units on the polymer chain. Bond rotation is thus difficult and leads to the relatively high T_g. Incorporation of the Ni-BDT units along the polymer chain, which in this case contains two methylene groups on each side, introduces flexible and easily rotated sites. The pure polyurethane, on the other hand, contains a highly flexible decanediol unit between each urethane. The diphenyl nickel bis(dithiolene) unit has a relatively rigid structure, comparable to inclusion of a terphenyl along the chain when incorporated into the polyurethane. As such, overall chain rigidity and T_g are increased.

Redox Properties. One of the more interesting properties of metal bis(dithiolenes) in general, and our previously studied nickel bis(dithiolene) polymers prepared by transition-metal complexation polymerization,[15,16] is their ability to be reversibly cycled through various oxidation states. The polymers prepared here allow us to examine the effect of Ni-BDT complex content, and the nature of the polymeric backbone, on electroactivity.

Figure 8 shows a series of cyclic voltammograms for the polycarbonates containing 1–20 mol % Ni-BDT complex. At the lowest compositions of 1 and 2.5 mol %, no electroactivity is apparent. As the Ni-BDT complex content increases, two reversible redox processes become evident. At a potential set to −1.5 V vs Ag/AgCl the metal complex is held in the dianionic state. Scanning anodically the first oxidation, corresponding to $[NiL_2^{2-}] \rightleftarrows [NiL_2^{-}]$, occurs with an $E_{1/2} = -0.73$ V. The second process, with an $E_{1/2} = +0.21$ V, corresponds to the $[NiL_2^{-}] \rightleftarrows [NiL_2^{0}]$ process. The peak potentials are constant as Ni-BDT complex content is increased as the metal centers behave as separated redox sites. The processes are essentially reversible as evidence by their 120- and 79-mV peak separations. The pattern of these redox processes is identical with those observed previously. When the solution of polymer 11 was scanned repeatedly, the cyclic voltammogram was completely reproducible, with no changes in the peak currents up to 15 scans, indicating the Ni-BDT complexes along the chains are electrochemically stable over this potential range. The peak currents are linearly dependent on the square root of scan rate for all processes. This indicates that there is no precipitation occurring during the scan and all redox processes involve solution species.

Quite similar redox processes are observed for the polyurethanes as shown in Figure 9. Only polymers 15–17 are shown as, in the case of the polycarbonates, the polymers with low Ni-BDT complex content were not electroactive. Though the cyclic voltammograms for the polyurethanes exhibit broad peak separations of 1000 mV for the first oxidation and 340 mV for the second, the fact that $E_{1/2}$ values are quite close to those of the polycarbontes indicates that the polymer environment is not expressing a large effect on the electroactivity of the Ni-BDT complex sites. The polyurethanes are significantly less electrochemically stable than the polycarbonates as shown by the multiple cyclic voltammograms in Figure 10 for polymer 17. The peak current for both the $[NiL_2^{2-}] \rightleftarrows [NiL_2^{-}]$ and $[NiL_2^{-}] \rightleftarrows [NiL_2^{0}]$ process decreases rapidly over four sequential scans, showing the polymer to be unstable over this potential range. Though no deposition of polymer was evident, this instability precluded a scan rate analysis of the redox processes.

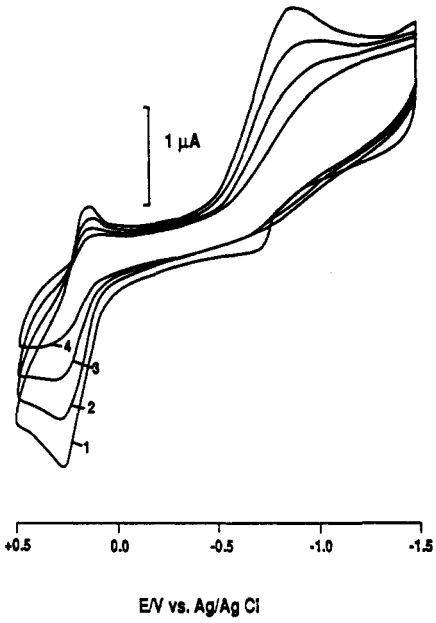


Figure 10. Four consecutive cyclic voltammograms for polymer 17. Scan rate = 100 mV s^{-1}.

Conclusions

The polymerization of an aliphatic diol functionalized nickel bis(dithiolene) complex has been utilized in the preparation of a new series of polycarbonates and polyurethanes containing 1–20 mol % of the metal complex. The polymers are highly soluble in a variety of organic solvents and of sufficient molecular weight to allow free-standing films to be prepared. The reactivity differences between the aliphatic Ni-BDT complex diol and BPA to carbonate formation were evident as polycarbonates with high Ni-BDT complex content exhibited lower molecular weights.

A typical Ni-BDT near-infrared absorption is evident which exhibits solvatochromism. The peak position is affected by solvent polarity with 100-nm shifts observed.

All of the polymers are stable to >250 °C with increased Ni-BDT content imparting a decreased thermal stability to the polycarbonates. The thermal stability of the polyurethanes is not affected by the incorporation of the Ni-BDT complex. The Ni-BDT complex affects the polymer chain rigidity with an increase in the rigidity of the polyurethanes and a decrease in the rigidity of the polycarbonates.

With sufficient Ni-BDT complex content (5–20 mol %) the polymers are electroactive and exhibit the typical $[NiL_2^{2-}] \rightleftarrows [NiL_2^{-}]$ and $[NiL_2^{-}] \rightleftarrows [NiL_2^{0}]$ redox processes. The polycarbonates are quite stable to electrochemical cycling in solution while, conversely, the polyurethanes are not.

Experimental Section

All water- and air-sensitive liquids were transferred by cannula 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 Biorad-Digilab FTS-40 Fourier transform spectrophotometer. For small molecules and brittle polymers, the diffuse reflectance method was used on samples containing 3 mg in 300 mg of KBr. For most polymers transmission methods were used on thin cast films on a KBr plate. Low-field (60 MHz) proton NMR spectra were run on a Varian EM 360 spectrometer. High-field (300 MHz) ^1H and ^{13}C NMR spectra were recorded on a Bruker MSL-300 spectrometer in chloroform-*d* solutions. Chemical shifts are reported referenced to TMS, DMSO-d_6 (2.49 ppm for ^1H and 39.5 ppm for ^{13}C), or chloroform-*d* (77.0 ppm for ^{13}C). UV–vis–NIR spectra were run on a Varian 2300 spectrophotometer. GPC was carried out on a Waters 840 GPC system with UV (300 nm) and refractive index detector accessories. TGA and DSC were carried out on a Du Pont 9900 thermal analysis system fitted with a Model 951 thermogravimetric analyzer and Model 910 differential scanning calorimeter accessory modules. The software supplied by the manufacturer was used for the analyses of data. All TGA experiments were performed with nitrogen flushing through the oven and cell at the rate of ca. 60 mL/min. A typical TGA scan procedure involved (1) equilibrating at 80 °C and holding isothermally for 3 min and (2) heating at a rate of 20 °C/min to 900 °C. The DSC procedure used involved (1) equilibrating at 200 °C and holding isothermally for 1 min, (2) cooling at a rate of 10 °C/min to −100 °C, (3) isothermal holding for 3 min, and (4) heating at a rate of 10 °C/min to 200 °C. Mass spectrometry was performed on a Finnigan MAT TSQ 70 GC/MS instrument. A direct exposure probe method was used. The sample was equilibrated at 50 °C initially, and subsequently heated at a rate of 100 °C/min to 1000 °C. Elemental analyses were determined by using a Perkin-Elmer 2400 CHN analyzer. Powder X-ray diffraction studies were carried out on a Rigaku diffractometer with a θ–θ goniometer. The Cu Kα source was operated at 50 kV and 20 mA. Results were collected by repeated scanning and summed and averaged.

Cyclic voltammetry was carried out on an EG&G Princeton Applied Research Model 273 potentiostat/galvanostat in 0.1 M tetrabutylammonium perchlorate DMF solutions under an argon atmosphere. A Pt button working electrode and Pt counter electrode were employed with a Ag/AgCl reference electrode. The measurements were performed on saturated polymer solutions.

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

4-(Chloroacetyl)phenethyl Alcohol (1). A procedure reported previously[16] was adopted by using $AlCl_3$ (92.0 g, 0.69 mol), dichloromethane (120 mL), chloroacetyl chloride (37.3 g, 0.33 mol), and phenethyl alcohol (36.6 g, 0.30 mol). The phenethyl alcohol solution was added while the temperature was kept at about 10 °C. Crude 1 was recrystallized from ether and dried to give 48.8 g (81.9%) of 1: mp 41–45 °C; IR (KBr) 3477, 3355, 2947, 1702, 1693, 1606, 1218, 1044, 818 cm^{-1}; ^1H NMR (60 MHz) δ 1.96 (s, 1 H), 2.92 (t, 2 H, J = 6.5 Hz), 3.90 (t, 2 H, J = 6.5 Hz), 4.67 (s, 2 H), 7.2–7.4 (m, 2 H), 7.8–8.0 (m, 2 H).

4-[(Ethoxy(thiocarbonyl)thio)acetyl]phenethyl Alcohol (2). A mixture of 1 (48.5 g, 0.244 mol) and *O*-ethylxanthic acid potassium salt (39.1 g, 0.244 mol, Aldrich Chemical Co.) in acetone (250 mL) was heated to reflux for 3 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 2. Crude 2 was dissolved in dichloromethane (200 mL) and washed with water (100 mL). The solution was dried (magnesium sulfate), concentrated, and cooled to give a light yellow solid. The solid was crushed and washed with hexane to give 65.9 g (95.0%) of 2: mp 53–55 °C; IR (KBr) 3329, 2891, 1672, 1605, 1224, 1113, 1054 cm^{-1}; ^1H NMR (60 MHz) δ 1.33 (t, 3 H, J = 7 Hz), 2.90 (t, 2 H, J = 6.8 Hz), 3.85 (t, 2 H, J = 6.8 Hz), 4.60 (s, 2 H), 4.60 (q, 2 H, J = 7 Hz), 7.2–7.4 (m, 2 H), 7.8–8.0 (m, 2 H).

4-(2-Oxo-1,3-dithiolyl)phenethyl Acetate (3). A mixture of 2 (63.4 g, 0.223 mol) and acetyl chloride (70 mL, 0.98 mol) was stirred at room temperature for 24 h. Chloroform (200 mL) was added to the flask, and the mixture was poured over ice (300 g). The chloroform solution was separated and washed with water until neutral, concentrated, recrystallized (ethanol), and dried to give 54.0 g (86.4%) of 3: mp 55–56 °C; IR (KBr) 3079, 2964, 1728, 1632, 1256, 1042, 784 cm^{-1}; ^1H NMR (300 MHz) δ 2.03 (s, 3 H), 2.95 (t, 2 H, J = 6.8 Hz), 4.28 (t, 2 H, J = 6.8 Hz), 6.81 (s, 1 H), 7.24–7.37 (m, 4 H); ^{13}C NMR (75 MHz) δ 192.29, 170.76, 139.20, 134.58, 130.92, 129.57, 126.30, 111.28, 64.28, 34.62, 20.78. Anal. Calcd for $C_{13}H_{12}O_3S_2$: C, 55.69; H, 4.31. Found: C, 55.30; H, 3.97.

4-(2-Oxo-1,3-dithiolyl)phenethyl Alcohol (4). A mixture of 3 (40.0 g, 0.143 mol) dissolved in 500 mL of methanol and 40 g of K_2CO_3 dissolved in 300 mL of water was stirred at room temperature for 1 h. The mixture was extracted with 300 mL of chloroform. The chloroform solution was washed with water, concentrated, recrystallized (methanol/ether), and dried to give 23.8 g (70.0%) of 4: mp 92–94 °C; IR (KBr) 3258, 3060, 2927, 1697, 1632, 1503, 1055, 1046, 868 cm^{-1}; ^1H NMR (300 MHz) δ 1.50 (s, 1 H), 2.89 (t, 2 H, J = 6.8 Hz), 3.89 (t, 2 H, J = 6.8 Hz), 6.80 (s, 1 H), 7.26–7.39 (m, 4 H); ^{13}C NMR (75 MHz) δ 192.58, 140.11, 134.83, 130.93, 129.83, 126.49, 111.22, 63.32, 38.78. Anal. Calcd for $C_{11}H_{10}O_2S_2$: C, 55.44; H, 4.23. Found: C, 56.32; H, 4.56.

Bis[4-(2-hydroxyethyl)benzeneethenedithiolato]nickel-(II) (5). A mixture of 4 (1.500 g, 6.294 mmol) and sodium ethoxide (1.285 g, 18.88 mmol) in ethanol (100 mL) was heated at 60 °C with stirring for 40 min. Nickel bromide (0.687 g, 3.147 mmol) dissolved in ethanol (200 mL) was added to the mixture via cannula. The resulting mixture was heated at 60 °C for 4 h and then cooled to room temperature. The ethanol was removed, and 200 mL of acetone was added to the residue. After the solid residue was filtered and washed with more acetone (2 × 100 mL), the acetone solution was collected and a solution of 50 mL of water with 1 mL of 37% HCl was added. Removing the solvent gave the product which was washed with water and chloroform and then dried under vacuum to give 1.034 g (68.6%) of 5: IR (KBr) 3366, 3022, 2933, 1414, 1371, 1193, 1043, 1017, 864, 793 cm^{-1}; ^1H NMR (300 MHz) δ 2.71 (s, 2 H), 3.56 (s, 4 H), 4.19 (s, 4 H), 7.0–7.5 (m, 8 H), 8.0–9.0 (br s, 2 H); UV–vis–NIR (THF) λ_{max} (ϵ) 295 (24 500), 365 (sh, 9100), 835 (10 150) nm. Anal. Calcd for $C_{20}H_{20}NiO_2S_4$: C, 50.11; H, 4.21. Found: C, 49.84; H, 3.84.

Syntheses of Polymers 6–11: Poly(oxycarbonyloxy-1,4-phenyleneisopropylidene-1,4-phenylene) (6) and Poly{[1-oxyethylene[4-(1,2-dithiolatoethenyl)phenylene]nickel(II)-[(1′,2′-dithiolatoethenyl)-4′-phenylene]-1′-ethyleneoxycarbonyl]-*co*-(oxycarbonyloxy-1,4-phenyleneisopropylidene-1,4-phenylene)} (7–11). The general procedure is as follows. A 50-mL three-neck flask equipped with a mechanical stirrer was charged with 5, bisphenol A, and 10 mL of pyridine. The mixture was then purged with nitrogen for 10 min. Phosgene was admitted into the vapor space of the reaction flask, and the stirring was continued. The temperature was maintained at about 25 °C. Addition time for phosgene was about 1.5 h, during which time the viscosity of the solution increased and pyridinium hydrochloride precipitated. The end point for the polymerization was assured by visual observation that the viscosity of the solution no longer increased as phosgene addition continued. Sometimes a gellike mixture was formed. The polymer solution was then diluted with 10 mL of chloroform and precipitated into 200 mL of methanol and stirred vigorously. The polymer was redissolved in 20 mL of chloroform and filtered. The chloroform polymer solution was reprecipitated into 200 mL of methanol. The polymer was filtered and dried at 65 °C in a vacuum oven overnight. From 0.600 g of BPA was obtained 0.471 g (70.5%) of 6: IR (neat) 2970, 1775, 1505, 1409, 1365, 1227, 1193, 1163, 1014, 831 cm^{-1}. From 0.021 g of 5 and 0.990 g of BPA was obtained 0.994 g (88.4%) of 7. From 0.053 g of 5 and 0.975 g of BPA was obtained 1.054 g (92.4%) of 8. From 0.105 g of 5 and 0.950 g of BPA was obtained 1.064 g (91.0%) of 9. From 0.105 g of 5 and 0.450 g of BPA was obtained 0.523 g (85.5%) of 10. From 0.210 g of 5 and 0.400 g of BPA was obtained 0.577 g (86.5%) of 11. The polymers ranged in color from white to dark green; the solubilities in THF ranged from 5 to 10%.

Syntheses of Polymers 12–17: Poly(oxycarbonylimino-4-methyl-1,3-phenyleneiminocarbonyloxydecamethylene) (12) and Poly{[1-oxyethylene[4-(1,2-dithiolatoethenyl)-phenylene]nickel(II)[(1′,2′-dithiolatoethenyl)-4′-phenylene]-1′-ethyleneoxycarbonylimino-4-methyl-1,3-phenyleneiminocarbonyl]-*co*-(oxycarbonylimino-4-methyl-1,3-phenyleneiminocarbonyloxydecamethylene)} (13–17). The general procedure is as follows. A 50-mL three-neck flask with mechanical stirrer was charged with tolylene 2,4-diisocyanate (TDI) dissolved in 5 mL of DMSO. 5 and 1,10-decanediol were dissolved in 5 mL of DMSO and charged into an addition funnel. The flask was heated to 60 °C, and the DMSO solution of the diol was drop-added to the flask with stirring over 10 min. After the completion of the addition, 5 drops of dibutyltin dilaurate was added as catalyst. The mixture was stirred for 4 h at 60 °C. The polymer solution was then diluted under 5 mL of DMSO and precipitated into 200 mL of methanol with vigorous stirring. The rubbery product was then cut to small pieces, washed with water and methanol, and dried at 70 °C in a vacuum oven overnight. From 1.00 g of 1,10-decanediol and 1.02 g of TDI was obtained 1.823 g (91.2%) of 12: IR (neat) 3312, 2928, 2855, 1706, 1600, 1535, 1229, 1068, 756 cm^{-1}. From 0.027 g of 5, 0.990 g of 1,10-decanediol, and 0.999 g of TDI was obtained 0.926 g (45.9%) of 13. From 0.069 g of 5, 0.975 g of 1,10-decanediol, and 0.999 g of TDI was obtained 1.488 g (72.8%) of 14. From 0.138 g of 5, 0.950 g of 1,10-decanediol, and 0.999 g of TDI was obtained 1.689 g (80.9%) of 15. From 0.138 g of 5, 0.450 g of 1,10-decanediol, and 0.499 g of TDI was obtained 0.716 g (65.9%) of 16. From 0.275 g of 5, 0.400 g of 1,10-decanediol, and 0.499 g of TDI was obtained 0.532 g (45.3%) of 17. The polymers ranged in color from white to dark brown; the solubilities in THF ranged from 5 to 10%.

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 (Y-1012).

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