# Film Polymerization − A New Route to the Synthesis of Insoluble Polyimides Containing Functional Nickel(II) Schiff Base Units in the Main Chain

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The synthesis and characterization of a new, amino-derivatized functional bis(salicylaldiminato)Ni$^{II}$ complex is reported. It is a useful and reactive precursor in the synthesis of polyimide thermosets. Thus, the first synthesis of a polyimide containing a nonlinear optical Ni$^{II}$ Schiff base complex in the main chain is achieved by thermally controlled film polymerization. Polymerization was monitored on silicon substrates by FT-IR spectroscopy. The polymer film possesses characteristics analogous to those of the insoluble polymer obtained by polymerization in solution, as evidenced by FT-IR spectroscopy and TGA analysis. The present approach might represent a general strategy for achieving thin films of insoluble, functional polymers.

## Introduction

The development of easily processable, functional molecular materials is of central interest in the emerging field of molecular electronics.[1] In this regard, functional polymers are amongst the most promising materials, by virtue of their facile processability into composites,[2] as well as in thin films.[3] The exploration of new polymers with functional transition metal complexes in the main chain is intriguing and the unique electronic properties associated with the metal center certainly deserve to be investigated, especially the distinct or combined, optical (linear and nonlinear), electrical, and magnetic properties.[4]

The very high thermal stability and high glass transition temperature of polyimides makes them well suited for plastic electronics,[2,3,5] although in some cases their low solubility prevents the application as thin-film materials. An alternative synthetic strategy to polyimides is the in situ film polymerization, with the potential to obtaining better thermal and mechanical characteristics of thin films. This strategy involves the choice of suitable and reactive monomers, in order to achieve a thermally controlled polymerization. The appropriate derivatization of starting monomers is thus of relevance for the design and synthesis of new functional thermoset materials.

We report here on the synthesis and characterization of novel polyimide thermosets by thermally controlled, film polymerization, which might represent a general method for accomplishing films of insoluble, functional polymers. Moreover this contribution represents the first example of a co-polyimide containing a nonlinear optical Ni$^{II}$ metal complex unit[6] in the main chain.[7,8] To this end, the amino-derivatized Schiff base bis(salicylaldiminato)Ni$^{II}$ complex (**1**) and the bis(maleimide) (**2**) were chosen as starting monomers (Scheme 1).

## Results and Discussion

### Synthesis of the Derivatized Schiff Base Complex 1

The synthesis of bis(salicylaldiminato), amino-derivatized compounds represents a difficult task. In fact, since these Schiff bases necessarily involve salicylaldehydes as starting compounds, the latter are chemically incompatible with the concurrent existence of free amines. On the other hand, nitrosalicylaldehydes, which could be used as starting materials, give rise to very low soluble Schiff bases. Actually, both the free ligand and the Ni$^{II}$ complex of the related 5-nitro Schiff base, synthesized by standard procedures,[6b,6c] have a very low solubility in most solvents. Consequently, all attempts to obtain the diamine by reduction failed. We have thus developed an alternative route to the synthesis of amino-derivatized, Schiff base Ni$^{II}$ complexes. The adopted synthetic approach is sketched in Scheme 2. It involves protection of the aldehyde function of the starting 5-nitrosalicylaldehyde by acetic anhydride to afford **3**; $H_2$-catalyzed reduction of the 5-nitro group to the free amine **4**; protection of the amine group with $Boc_2O$, followed by hydrolysis of the phenol and aldehyde func-

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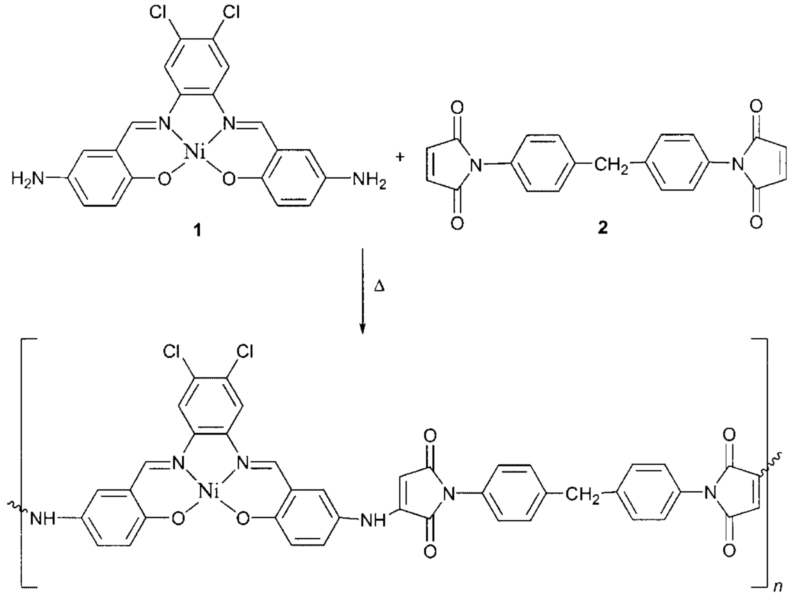
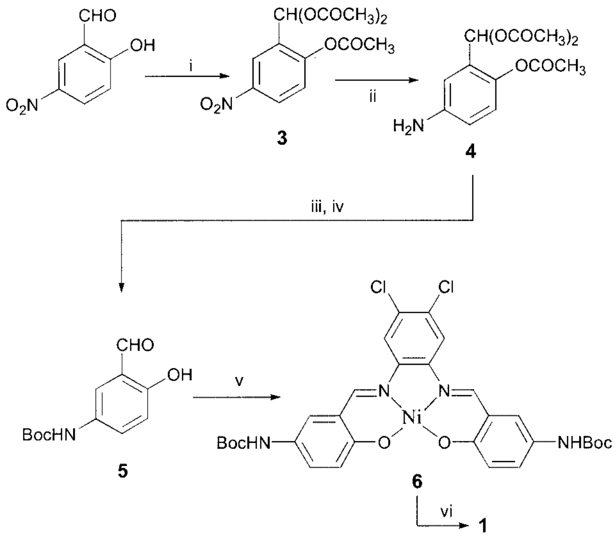


Scheme 1

tionalities with NaOH to get the salicylaldehyde derivative **5**; template reaction with the appropriate 1,2-diamine and $Ni^{II}$ ion affords the 5-amino protected, Schiff base complex **6**; deprotection with trifluoroacetic acid of the amine groups of **6** leads to the 5-amino derivatized Schiff base $Ni^{II}$ complex **1**. All these intermediate precursors **3−6**, as well as the amino-derivatized, Schiff base $Ni^{II}$ complex **1**, were obtained in high yields (> 82%), except compound **5** (65%), and fully characterized by mass spectrometry and $^1H$ NMR spectroscopy, and gave satisfactory microanalyses.



Scheme 2. Reagents and conditions: (i) $(CH_3CO)_2O$, $H_2SO_4$ cat., room temp.; (ii) $H_2$ (45 psi), 10% Pd/C, EtOH; (iii) $Boc_2O$, $CH_2Cl_2$, room temp.; (iv) $MeOH/H_2O$, NaOH, reflux; (v) 4,5-dichloro-1,2-phenylenediamine, $NiOAc_2{\cdot}4H_2O$, MeOH; (vi) $CF_3COOH$, DCM, PhOMe, room temp.; then NaOH, $H_2O$

INDO/SCI-SOS calculations[9] on **1**, upon geometry optimization, indicate a molecular quadratic hyperpolarizability ($\beta_\mu = -22.8 \times 10^{-30}$ $cm^5{\cdot}esu^{-1}$), which can be compared with the calculated ($\beta_\mu = -17.3 \times 10^{-30}$ $cm^5{\cdot}esu^{-1}$)[6c] and experimental ($\beta_\mu = -20.5 \times 10^{-30}$ $cm^5{\cdot}esu^{-1}$)[6c] values for the unsubstituted Ni(salophen) derivative. The derivatized functional complex **1** is thus a potential candidate for nonlinear optical applications.

## Polymerization in Solution

Polymerization was first carried out in solution. This allows for verification of the chemistry involved, by means of the synthesis and analysis of the prepolymer. Partial polymerization was performed by heating a solution of **1** and **2** (0.034 M in each component) in 1-methyl-2-pyrrolidone (NMP) for 1 h, at 90 °C. The prepolymer, that precipitated from chloroform, was analyzed by $^1H$ NMR and FT-IR spectroscopy. The 500 MHz $^1H$ NMR of the crude prepolymer in [D$_6$]DMSO solution shows a partial disappearing of the sharp resonance at $\delta = 7.15$ ppm (olefinic protons of **2**)[10] and the broad resonance ($D_2O$ exchangeable) at $\delta = 4.57$ ppm, assigned to the primary amine protons of **1**. Moreover, the spectrum reveals the presence of new signals, with respect to the starting monomers. In particular, the peaks at $\delta = 2.80$, 3.85, 4.95, and 5.95 ppm, are evidence for the formation of the succinimide ring[11] and the secondary (−NH−) proton of the nitrogen bridge,[10] respectively (see Exp. Sect.). Along with the typical absorption bands,[12] the FT-IR spectrum of **2** also shows a strong absorption at 688 $cm^{-1}$, from the maleimide ring deformation, and the 1150 $cm^{-1}$ absorption due to asymmetric C−N−C stretching. They represent the reference absorptions used to monitor the reaction between **1** and **2**. The comparison of the FT-IR spectrum of a 1:1 mixture of **1** and **2** with that of the prepolymer indicates an increase of the transmittance of bands at 688 and 1150 $cm^{-1}$, and the formation of a new band at 1175 $cm^{-1}$ due to the asymmetric C−N−C stretching of the succinimide ring.[13] In summary, both the $^1$H NMR and FT-IR spectroscopic experiments on the prepolymer enable us to establish that the reaction between **1** and **2** involves a Michael addition reaction, as sketched in Scheme 1.

Polymerization was performed by curing a solution of the prepolymer in NMP for 2 h, at 140 °C. The resulting brown material has a low solubility in most solvents, typical of the polyimides, thus preventing, in principle, its application as a functional material. Longer reaction times and higher reaction temperatures did not result in appreciable changes in polymer properties (see infra). Thermogravimetric analysis of the polymer indicates a high thermal stability with a decomposition onset of 380 °C. In comparison with monomers (**2** melts at 157 °C, while **1** starts to decompose, without melting, at 330 °C) the higher thermal stability of the polymer is in agreement with its rigid structure. Accordingly, differential scanning calorimetry analysis indicates the absence of a transition glass temperature in the 30−400 °C range.

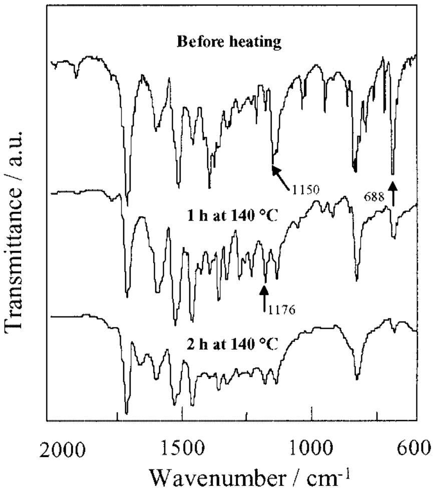


Figure 1. FT-IR spectra of a polyimide thermoset cast film on a silicon substrate at different polymerization stages, using as a reference sample the same substrate before casting. The arrows at 1176, and 1150, 688 cm$^{-1}$ indicate the emerging succinimide function and the disappearing maleimide function, respectively

### Film Polymerization

Casting of filtered chloroform solutions of **1** and **2** monomers (0.034 M in each component) on silicon substrates [Czochralsky-grown Si(100), optically transparent in the 600−4000 cm$^{-1}$ IR region of interest, transmittance ≥ 0.90][14] followed by heating, allows the degree of film polymerization to be monitored by FT-IR analysis (Figure 1). When a film of cast monomers is heated at 140 °C for 1 h, the peaks at 688 and 1150 cm$^{-1}$ associated with the maleimide ring decrease, while the peak at 1176 cm$^{-1}$ associated with the succinimide function appears. After the polymer film is further heated at 140 °C for 2 h, the peak at 688 cm$^{-1}$ almost completely disappears, and a band broadening in the range 1100−1600 cm$^{-1}$ is observed, thus indicating an almost complete polymerization. This is also evident from the comparison of this spectrum with the almost identical one of the polymer obtained by polymerization in solution. The further heating of the film does not produce further changes in the FT-IR spectra. The polymer film possesses almost indistinguishable characteristics with respect those of the polymer obtained by polymerization in solution, as confirmed by the TGA analysis.

The polymer films were also characterized by optical spectroscopy. The optical absorption spectrum of the cast film, before heating, shows a band at 380 nm, and two shoulders at about 450 and about 560 nm (Figure 2). After polymerization is complete, the optical spectrum remains almost unchanged, except for a red-shift (≈ 10 nm) of the band at 380 nm along with a better defined structure. This is consistent with a more homogeneous film upon polymerization and good optical quality. These spectral features are similar to those of the optical spectrum of **1** in chloroform solution, thus indicating that the electronic structure of monomer **1** remains essentially unchanged upon polymerization.

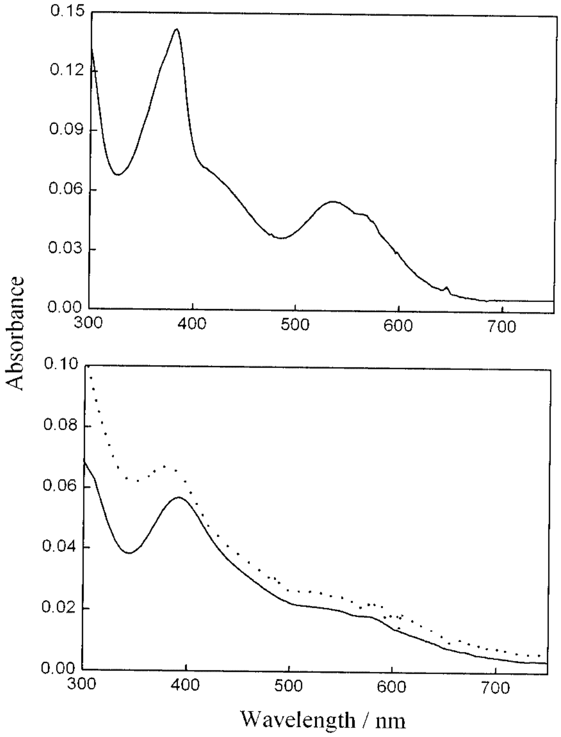


Figure 2. Optical absorption spectra (bottom) of a polyimide thermoset cast film on a glass substrate before heating (- - -) and after 3 h of heating at 140 °C (−). The absorption spectrum of complex **1** (top) in chloroform solution is reported for comparison

## Conclusion

In this contribution we have achieved a convenient synthesis for novel functional, amino-derivatized Ni$^{II}$ metal complexes. These complexes can be easily incorporated in the main chain of polyimides and *thermally controlled* film polymerization can be obtained by heating the monomers, as monitored by FT-IR spectroscopy. Such an approach might represent a general method for accomplishing films of insoluble, otherwise rather intractable, functional polymers.

Further work is currently in progress with the aim of identifying more flexible monomers, in order to obtain copolymers with definite transition glass temperatures.

## Experimental Section

**Materials:** Nickel(II) acetate tetrahydrate, 2-hydroxy-5-nitrobenzaldehyde, and all the other reagents (Aldrich) were used without purification. 4,5-Dichloro-1,2-phenylenediamine (Aldrich) was purified by sublimation in vacuo. 1,1′-(Methylenedi-4,1-phenylene)bis(maleimide) (**2**) (Aldrich), was purified by recrystallization from toluene. Dichloromethane (DMC) was distilled from $CaH_2$.

### Physical Measurements

Elemental analyses were performed with a Carlo Erba 1106 elemental analyzer. $^1$H NMR spectra were recorded with a Varian Unity Inova 500 MHz spectrometer, using TMS as internal standard. ESI MS were recorded with an Agilent 1100 Series ESI/MSD spectrometer. Experimental conditions were as follows: Capillary voltage, 3.5 kV; fragmentor, 100 V; source temperature, 350 °C; drying gas, $N_2$ (10 L/min), carrier solvent, methanol (0.4 mL/min). Samples were dissolved in methanol. For complex **1** the methanol solution was acidified with trifluoroacetic acid. Infrared spectra were recorded with a JASCO FT-IR spectrometer. Thermal measurements were performed with a Mettler Toledo TGA/SDTA85$^e$ system. Thermal analyses were made both in air and under prepurified nitrogen (30 mL/min) using a 10 °C/min heating rate. DSC measurements were obtained from a Mettler DSC 20 calorimeter, under nitrogen atmosphere using a 20 °C/min heating rate. UV-vis spectra were recorded with a Beckman DU 650 spectrophotometer.

### Syntheses

**Acetyloxy(2-acetyloxy-5-nitrophenyl)methyl Acetate (3):** A solution of 2-hydroxy-5-nitrobenzaldehyde (1.67 g, 10.0 mmol), acetic anhydride (50 mL), and $H_2SO_4$ (3 drops) was stirred under nitrogen for 1 h at room temperature. The solution obtained was poured into ice cold water (500 mL), and stirred for 30 minutes in order to hydrolyze the anhydride. The white solid was collected by filtration, air dried, and crystallized from an EtOAc/cyclohexane mixture to yield 2.55 g (82%) of a white crystalline solid (m.p. 113−115 °C). ESI MS: *m/z* (%) = 312 (23) $[MH]^+$. $C_{13}H_{13}NO_8$ (311.24): calcd. C 50.17, H 4.21, N 4.50; found C 50.23, H 4.19, N 4.53.

**Acetyloxy(2-acetyloxy-5-aminophenyl)methyl Acetate (4):** A solution of compound **3** (2.49 g, 8.00 mmol) in EtOH (40 mL) and THF (10 mL), was hydrogenated ($H_2$, 45 psi) using 10% Pd/C as catalyst (0.5 g). After 4 h, the filtrate was quickly concentrated to quantitatively give compound **4** (2.25 g) as light brown oil, which was used without any further purification.

***tert*-Butyl (3-Formyl-4-hydroxyphenyl)carbamate (5):** A solution of compound **4** (2.25 g, 8.00 mmol), and di(*tert*-butyl) dicarbonate (1.75 g, 8.00 mmol) in anhydrous DCM (15 mL), was stirred under nitrogen for 8 h. The solvent was evaporated under vacuum, and the oil obtained was dissolved in MeOH (10 mL). Sodium hydroxide (1.6 g, 40 mmol) and water (5 mL) were then added, and the resulting solution refluxed for 5 h. After cooling, the solution was neutralized, and the brown solid was collected by filtration, washed with water, and dried under vacuum. The solid was purified by column chromatography ($SiO_2$, $CHCl_3$, $R_f = 0.22$) and crystallized from cyclohexane, to yield 1.23 g (65%) of pale yellow needles (m.p. 122−123 °C). $^1$H NMR (500 MHz, $CDCl_3$): $\delta = 10.75$ (s, 1 H, O*H*), 9.84 (s, 1 H, C*H*O), 7.82 (d, $J_{meta} = 2.8$ Hz, 1 H, Ar*H*), 7.24 (dd, $J_{ortho} = 9.0$, $J_{meta} = 2.8$ Hz, 1 H, Ar*H*), 6.90 (d, $J_{ortho} = 9.0$ Hz, 1 H, Ar*H*), 6.39 (br. s, 1 H, N*H*), 1.49 (s, 9 H, C*H*$_3$C) ppm. ESI MS: *m/z* (%) = 238 (34) $[MH]^+$. $C_{12}H_{15}NO_4$ (237.25): calcd. C 60.75, H 6.37, N 5.90; found C 60.90, H 6.45; N 5.97.

**{*N*,*N*′-Bis[5-(*tert*-butoxycarbonylamino)-2-hydroxybenzylidene]-4,5-dichloro-1,2-phenylene-diaminato}Ni$^{II}$ (6):** A solution of compound **5** (0.475 g, 2.00 mmol) in 4 mL of methanol was slowly added to a warm solution of 4,5-dichloro-1,2-phenylenediamine (0.177 g, 1.00 mmol) and nickel(II) acetate tetrahydrate (0.250 g, 1.00 mmol) in 10 mL of methanol. The brown suspension obtained was refluxed for 1 h, and then cooled to room temperature. The solid was filtered off, washed with methanol, and dried under vacuum, to yield 0.64 g (95%) of product as red-brown needles. $^1$H NMR (500 MHz, $[D_6]$DMSO): $\delta = 9.11$ (br. s, 2 H, N*H*), 8.87 (s, 2 H, C*H*=N), 8.57 (s, 2 H, Ar*H*), 7.86 (br. s, 2 H, Ar*H*), 7.22 (dd, $J_{ortho} = 9.2$, $J_{meta} = 2.8$ Hz, 2 H, Ar*H*), 6.80 (d, $J_{ortho} = 9.2$ Hz, 2 H, Ar*H*), 1.48 (s, 18 H, C*H*$_3$C) ppm. ESI MS: *m/z* (%) = 671 (12), 673 (13) $[MH]^+$. $C_{30}H_{30}Cl_2N_4NiO_6$ (672.18): calcd. C 53.61, H 4.50, N 8.33; found C 53.93, H 4.66, N 8.27.

**[*N*,*N*′-Bis(5-amino-2-hydroxybenzylidene)-4,5-dichloro-1,2-phenylenediaminato]Ni$^{II}$ (1):** Trifluoroacetic acid (0.81 mL) was added to a suspension of compound **6** (0.540 g, 0.803 mmol) and anisole (0.4 mL) in DCM. The solution obtained was stirred under nitrogen for 24 h, at room temperature. The volatile material was removed under vacuum, and the red solid was collected and washed with diethyl ether. The solid was dissolved in 100 mL of water and filtered. Solid NaOH was added to the aqueous solution (pH ≈ 11), and the dark-brown powder that formed was collected by filtration, washed with water, and dried under high vacuum over $P_2O_5$, to yield 0.36 g (95%) of **1**. $^1$H NMR (500 MHz, $[D_6]$DMSO): $\delta = 8.64$ (s, 2 H, C*H*=N), 8.47 (s, 2 H, Ar*H*), 6.87 (d, $J_{ortho} = 8.5$ Hz, 2 H, Ar*H*), 6.72 (d, $J_{ortho} = 8.5$ Hz, 2 H, Ar*H*), 6.65 (s, 2 H, Ar*H*), 4.57 (br. s, 4 H, N*H*$_2$) ppm. ESI MS: *m/z* (%) = 471 (95), 473 (100) $[MH]^+$. UV/vis ($CHCl_3$): $\lambda_{max.} = 392$, 440 (sh), 544 nm. TGA analysis: $T_{dec.} = 330$ °C (onset). $C_{20}H_{14}Cl_2N_4NiO_2$ (471.95): calcd. C 50.90, H 2.99, N 11.87; found C 51.03, H 3.02, N 11.79.

**Prepolymer:** In a two-necked flask (100 mL), equipped with a reflux condenser, magnetic bar and a nitrogen inlet, a solution of **1** (0.25 g, 0.53 mmol) and **2** (0.19 g, 0.53 mmol) in NMP (16 mL) was stirred under nitrogen at 90 °C for 1 h. The mixture was poured into chloroform to give a brown solid, which was collected by filtration, washed with chloroform, several times, and then dried under vacuum (0.40 g). FT-IR (KBr pellet): $\tilde{\nu} = 3330$ (br. m), 1710 (vs), 1598 (m), 1529 (s), 1460 (s), 1358 (m), 1175 (m), 1136 (m), 825 (s), 688 $cm^{-1}$ (w). $^1$H NMR (500 MHz, $[D_6]$DMSO), in the spectrum are present new peaks, with respect to the starting monomers: $\delta = 5.95$ (s, $D_2O$ exchangeable, Ar−NH succinimide), 4.95, 3.85 and 2.80 (m, succinimide H) ppm.

**Polymer:** A solution of **1** (0.25 g, 0.53 mmol) and **2** (0.19 g, 0.53 nmol) in NMP (16 mL) was placed into a two-necked flask (100 mL) equipped with a reflux condenser and a nitrogen inlet. The solution was stirred under nitrogen at 90 °C for 1 h. The temperature was then raised to 140 °C and stirring continued for 2 h. The dark mixture was cooled to room temperature, and then poured into chloroform to give a brown solid. The solid was collected by filtration, washed several times with chloroform, and then dried under vacuum (0.42 g). FT-IR (KBr pellet): $\tilde{\nu}$ = 3335 (br. m), 1710 (vs), 1598 (m), 1529 (s), 1460 (s), 1358 (m), 1179 (m), 1137 (m), 825 $cm^{-1}$ (s). TGA analysis: $T_{dec.}$ = 380 °C (onset). Anal. calcd. for a polymer structure as in Scheme 1, $C_{41}H_{28}Cl_2N_6NiO_6$: calcd. C 59.31, H 3.40, N 10.12; found C 59.95, H 3.55; N 10.80.

**Film Polymerization:** A filtered (0.2-μm syringe filter) chloroform solution of the monomers (0.034 M, 1:1 molar ratio) was cast on 2 × 2 cm silicon substrates. Polymerisation was achieved by heating the film under nitrogen by curing steps of 1 h at 140 °C. Polymerisation was monitored by FT-IR measurements after each step. FT-IR (silicon substrate, after 3 h heating): $\tilde{\nu} \approx$ 3350 (br. w), 1710 (vs), 1593 (m), 1514 (s), 1452 (s), 1340 (m), 1180 (m), 1142 (m), 826 (s), 689 $cm^{-1}$ (vw). TGA analysis: $T_{dec.}$ = 370 °C (onset).

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