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Synthesis of polycarbonate containing in-chain 4-*N*,*N*-dimethylamino-4′-nitrostilbene via ring-opening polymerization

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Summary

We have successfully synthesized a new NLO chromophore based on 4-*N*,*N*-dimethylamino-4'-nitrostilbene which contains bisphenol functionality for polycarbonate preparation. Chromophore-**4** was used to make macrocyclic carbonate oligomers and the oligomers were converted to polycarbonate via ring-opening polymerization in solution.

Introduction

The processability of polymers make them promising candidates for second-order nonlinear optical (NLO) materials. NLO polymers have been prepared using a variety of methods including guest-host, covalent attachment of the chromophore as a pendent group, or incorporation of the chromophore into the polymer backbone (1-3). In order for these materials to exhibit a significant χ^2 (bulk second order NLO coefficient) the chromophore must possess a high value for β (molecular hyperpolarizability). A second requirement is a noncentrosymmetric ordering of the chromophore dipoles which is usually accomplished by electric field poling of the polymer at temperatures slightly above the glass transition temperature(T_g).

We have initiated a program to explore the use of polycarbonates for NLO materials. Gulotty and co-workers (4) described the synthesis NLO polycarbonates based polymerization of nitro-substituted bisphenol A (BPA) using the conventional route of phosgenation. The good optical properties, relatively high T_g and resistance to optical damage make polycarbonates good NLO materials (5). Brunelle and co-workers (6) reported the ring-opening polymerization of macrocyclic oligomers as an alternate route for the preparation of BPA polycarbonates. Advantages of the cyclic oligomer approach include better control of molecular weight; low viscosity precursors; solvent-free processing; and no volatile by-products or volume change during polymerization. We are interested in exploring this method to prepare and process NLO polycarbonates. Our long-term goal is simultaneous poling and polymerization of macrocyclic oligomers which contain covalently incorporated NLO chromophores. We predict that the low viscosity of the cyclic oligomers may enhance dipolar ordering during poling.

Our synthetic strategy is to prepare chromophores which possess bisphenol functionality. In a previous report, we described the synthesis of macrocyclic carbonates containing 4,5-bis(4-hydroxyphenyl)-2-(4-nitrophenyl)oxazole (7) and 6-nitro-2,3-bis(4-hydroxyphenyl)phenylquinoxaline (8). The ring-opening polymerization of these cyclic oligomers was successfully performed in the melt using titanium-based catalysts. While the macrocyclization chemistry was successful, the electro-optic coefficient (r_{33}) of the polycarbonate containing 13 mole % of the oxazole-chrom-ophore was only 0.6 pm/V. This result was obtained for a polycarbonate which was poled in the conventional manner. This low value for the electro-optic coefficient is consistent with the low molecular hyperpolarizability of the oxazole system.

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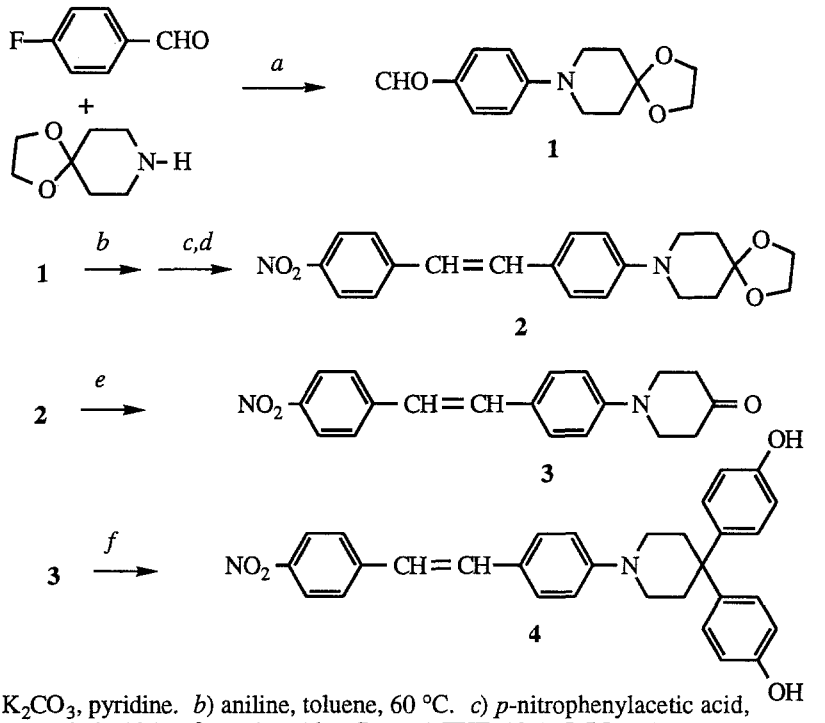
As a result of these earlier investigations, we decided to synthesize chromophores which have bisphenol functionality and higher β values. This report describes the synthesis of a system based on 4-*N*,*N*-dimethylamino-4'-nitrostilbene (DANS) (10). The reported value of β for DANS is several-fold higher than the oxazole-chromophore system which was the subject of our previous studies. Here, we describe the synthesis of this new chromophore, the preparation of cyclic oligomers and the subsequent ring-opening polymerization.

Results and Discussion

Chromophore Synthesis Scheme 1 shows the synthesis of chromophore-**4**. Stilbene synthesis was accomplished in a two-step process utilizing a Schiff base intermediate prepared by reaction of **1** with aniline (11) followed by reaction with p-nitrophenylacetic acid. Deprotection afforded cyclohexanone-**3** which was reacted with excess phenol in the presence of HCl (g) and 3-mercaptopropionic acid to give chromophore-**4**. ^{1}H-NMR and IR spectroscopy was used to confirm the structures of the intermediates and products in this synthetic sequence.

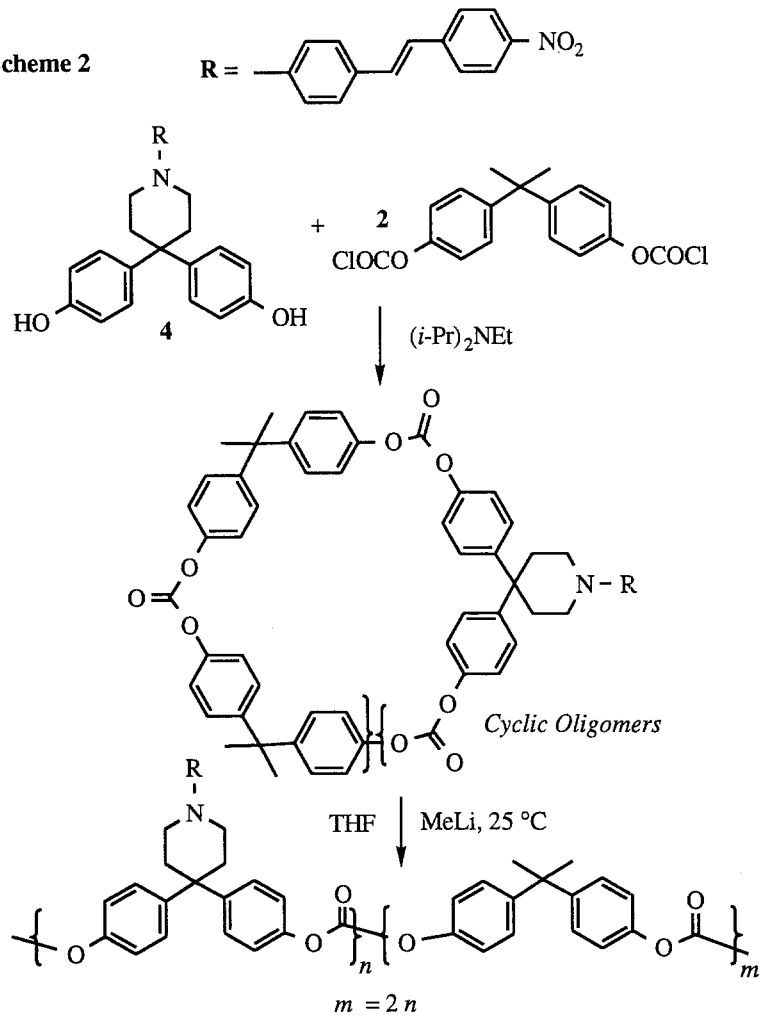
Scheme 1



a) K_2CO_3, pyridine. *b*) aniline, toluene, 60 °C. *c*) *p*-nitrophenylacetic acid, toluene, dark, 10 h. *d*) acetic acid, reflux. *e*) THF, 10% H_2SO_4. *f*) excess phenol, HCl, 3-mercaptopropionic acid.

The ^{1}H-NMR of chromophore-**4** is shown in Figure 1. The aromatic region of the NMR spectrum is complicated but contains resonances attributable to the stilbene hydrogens and the substituted benzene rings. Assignments were made by comparison to the spectra of compounds **1-3**. A full assignment of the NMR resonances is given in the experimental. Thermal gravimetric analysis (TGA) of chromophore-**4** revealed 5% weight loss at 250°C. This is considerably lower than the reported value for DANS (T_d = 290°C) or a DANS derivative in which the diethyl groups are replaced with piperidine, 1-(4'-nitrostilbene)piperidine (T_d = 293°C) (12).

Scheme 2



Macrocyclization The typical procedure for macrocyclization of BPA monomers involves formation of the corresponding bis-chloroformate and a subsequent hydrolysis-condensation reaction under carefully controlled conditions (6). However for exploratory research, we prefer an alternative method to the formation of the bischloroformate (which necessitates the use of phosgene or an equivalent reagent). Reaction of **4** with two mole equivalents of BPA bischloroformate (which is commercially available) produces a trimeric bischloroformate (see Scheme 2) corresponding to 33 mole% chromophore incorporation. Successful formation of trimer-**5** relies on the use of a non-nucleophilic amine catalyst (diisopropyl ethyl amine) which minimizes hydrolysis. Trimer-**5** was used without purification to prepare cyclic oligomers using the standard macrocyclization procedure (6).

The cyclic oligomers were fractionated from linear polymers and linear oligomers by selective dissolution into acetone. GPC analysis confirmed the low molecular weight nature of the cyclic oligomers (Figure 2a); individual peaks for cyclic oligomers can be discerned but we do not have corroborative evidence to make assignments to discrete species. Based on

polystyrene standards, gel permeation chromatography (GPC) analysis of the cyclic oligomers indicated M_n = 600 g/mol and M_w = 3600 g/mol. ^{1}H-NMR analysis (Figure 3) of the cyclics confirmed the presence of BPA and chromophore-**4** in a 2:1 ratio; this is based on the integration of the geminal dimethyl groups for the BPA vs. the piperidino hydrogens of **4**. TGA analysis showed 5% weight loss at 207°C and DSC analysis showed a glass transition temperature at 90°C.

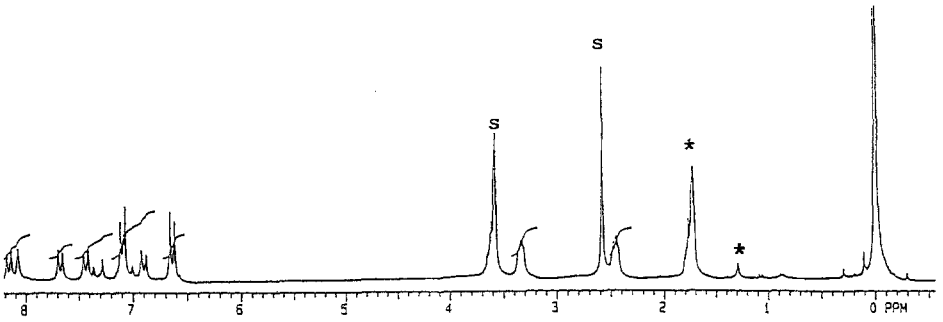


Figure 1. ^{1}H NMR spectrum (in THF-d_8) of chromophore-**4**; s: THF-d_8 peaks, TMS: internal standard, *: unknown impurities.

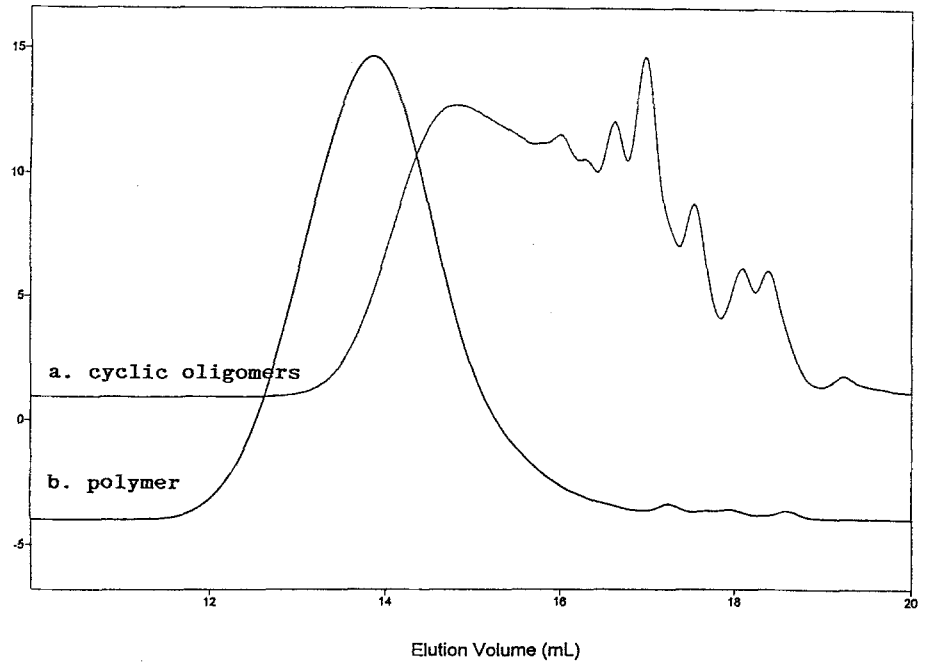


Figure 2. Gel permeation chromatography analysis of (a) macrocyclic oligomers, (b) polymer produced from the ring-opening polymerization.

Ring-Opening Polymerization We elected to perform our initial ring-opening polymerizations in solution. The ring-opening polymerization of macrocyclic carbonates using anionic initiators has been reported (13). The addition of methyl lithium to a THF solution of the cyclic oligomers effected conversion to polymer. Relative to polystyrene standards, GPC analysis of the polymer revealed M_w=18,200 g/mol and M_n = 11,200 g/mol. TGA of the

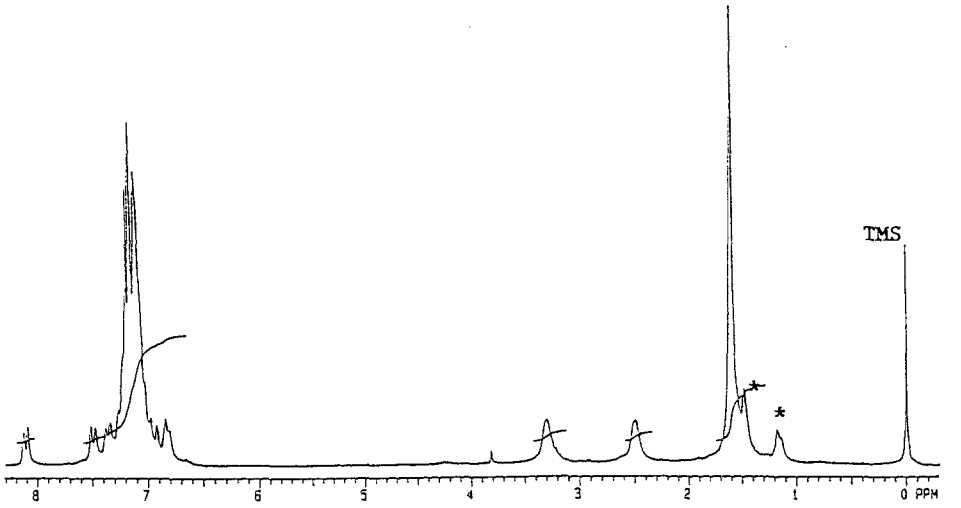


Figure 3. ^{1}H NMR spectrum (in $CDCl_3$) of macrocyclic carbonates composed of 2:1, BPA:**4**; TMS: internal standard, *: unknown impurities.

polymer showed 10% weight loss at 336°C and DSC analysis gave a value for T_g of 152°C, which is only slightly elevated relative to the BPA polycarbonate (150°C).

In summary, we have synthesized a new chromophore based on DANS (**4**) that is functionalized with phenol groups. This new bisphenol chromophore was used to prepared macrocyclic oligomers by a two-step process. Preparation of a linear trimer by reaction of **4** with two equivalents of BPA was followed by macrocyclization. The ring-opening polymerization of these cyclic oligomers was performed in solution using methyllithium as the initiator.

Currently, we are studying the ring-opening polymerization of the cyclic oligomers in the melt. One of the issues is the relatively low thermal stability of the cyclic oligomers which necessitates low processing temperatures.

Experimental

General Procedures and Materials ^{1}H NMR spectra were recorded using a Varian Gemini 200 MHz spectrometer. Gel permeation chromatography (GPC) was performed with a Waters system using two PLgel 5 mm MIXED-D columns with THF eluent at a flow rate of 1 mL/min, and molecular weights were determined against polystyrene standards. Thermal gravimetric analysis was performed using a DuPont Model 951 and thermal analysis was performed using a DuPont Model 910 Differential Scanning Calorimeter. UV/Visible spectra were taken using a HP 8453 UV-Visible Spectrophotometer. Unless noted otherwise, all other reagents were used as received from Aldrich chemical company.

4-(1,4-Dioxa-8-azaspiro[4.5]-decane) benzaldehyde (**1**) A round bottomed flask equipped with a condenser was charged with 10.0 g (0.081 mol) 4-fluorobenzaldehyde, 42.66 g (298 mmol) 1,4-dioxa-8-azaspiro[4.5]-decane, 16.69g (120 mmol) potassium carbonate, and 100 mL pyridine. The mixture was heated to 90-100°C with stirring for 3 days. Extraction with methylene chloride, removal of solvent *in vacuo*, and recrystallization from hexane afforded a yellow powder (55 % yield); mp = 116-117 °C; ^{1}H NMR (chloroform-d, TMS, 200 MHz): δ 9.75 (s, 1H, aldehyde hydrogen), 7.7, 6.9 (d, 4H, aromatic hydro-

gens), 3.95 (s, 4H, ethylene oxide protecting group), 3.55, 1.8 (t, 8H, piperidine hydrogens).

1-Methyl (phenyl imine)-4-(1,4-dioxa-8-azaspiro[4.5]-decane) benzene 2.2 g (23.6 mmol) aniline (distilled from KOH), 5 g (21.3 mmol) 4-(1,4-dioxa-8azaspiro[4.5]-decane)benzaldehyde, and 30 mL of toluene were added to a 100 mL round bottomed flask. The reaction mixture was heated to 60 °C until no additional water was collected. Recrystallized from a 1:1 ethyl acetate / ethanol mixture afforded product in 61 % yield; ^{1}H NMR (chloroform-d, TMS, 200 MHz): δ 8.32 (s, 1H, imine methine), 7.7, 6.9 (d, 4H, aromatic hydrogens of 1,4 substituted benzene), 7.15, 7.45 (m, 5H, imine phenyl), 3.95 (s, 4H, ethyl-ene oxide protecting group), 3.55, 1.8 (t, 8H, piperidine hydrogens).

N-(4'-nitrostilbene)-1,4-dioxa-8-azaspiro[4.5]-decane (**2**) 2.84 g (15 mmol) p-nitrophenylacetic acid and 20 mL toluene were combined and stirred for 15 min. 3.8 g (15 mmol) 1-methyl-(phenyl imine)-4-(1,4-dioxa-8-azaspiro[4.5]-decane) benzene was then slowly added and the reaction was allowed to proceed overnight in the dark. 1.70 mL of glacial acetic acid was then added slowly and the solution was refluxed for 2 h. The product was recrystallized from methylene chloride/diethyl ether to afford red crystals (86% yield); mp = 154-155 °C; ^{1}H NMR (chloroform-d, TMS, 200 MHz): δ 8.15, 7.55, 7.4, 6.9 (d, 8H, substituted aromatic hydrogens); 7.25, 7.15, 7.0, 6.9 (2H, stilbene hydrogens); 3.95 (s, 4H, ethylene oxide protecting group); 3.55, 1.8 (t, 8H, piperidine hydrogens).

1-(4'-nitrostilbene)-4-keto piperidine (**3**) 400 mL 10% sulfuric acid was added to a solution of 1.01 g (2.9 mmol) N-(4'-nitrostilbene)-1,4-dioxa-8-azaspiro[4.5]-decane and 200 mL THF in a 1L round bottomed flask. The mixture was heated and allowed to reflux for 20 h. The mixture was allowed to cool and diluted with 150 mL of water. Extraction with methylene chloride and removal of solvent *in vacuo* afforded a red powder (90% yield); mp = 211-213 °C; ^{1}H NMR (chloroform-d, TMS, 200 MHz): δ 8.15, 7.55, 7.4, 6.9 (d, 8H, substituted aromatic hydrogens); 7.25, 7.15, 7.0, 6.9 (2H, stilbene hydrogens); 3.68, 2.65 (t, 8H, piperidine hydrogens).

4,4 Bisphenol -1-(4'-nitrostilbene) piperidine (**4**) 2.0 g (21 mmol) phenol, and 10 μL 3-mercaptopropionic acid were combined in a 10 mL flask equipped with a gas inlet and base trap. The system was heated to 45-50 °C and purged with HCl gas for 20 min. The HCl sparge was continued as 1.0 g (3.1 mmol) 1-(4'-nitrostilbene)-4-keto piperidine was added over 2.5 hr. HCl gas was passed through the solution for an additional 0.5 hr. The reaction mixture was allowed to stir overnight. The mixture was allowed to cool and the residue was extracted with 10 % NaOH until extracts were only lightly colored or clear. The washes were filtered and neutralized with HCl (aq) causing a orange solid to precipitate out of solution. The solid was filtered and washed several times with deionized water until water washes were neutral to litmus. The product was then dissolved in THF and filtered. Solvent was then removed *in vacuo* to yield a dark powder (50 % yield); T_d = 250°C (5% weight loss); ^{1}H NMR (THF-d_8, TMS, 200 MHz): δ 8.16, 7.67, 7.43, 6.9 (d, 8H, substituted aromatic hydrogens); 7.36, 7.28, 7.03 (2H, stilbene hydrogens); 7.09, 6.64 (d, 8H, aromatic hydrogens on phenols), 3.32, 2.45 (t, 8H, piperidine hydrogens); 8.07 (2H, OH).

Synthesis of A-B-A trimer of **4** and BPA: 0.5 g (1.02 mmol) **4** and 1.08 g (3.06 mmol) bisphenol-A bischloroformate (recrystallized from petroleum ether) were combined in a round bottomed flask which was purged with argon. 15 mL dry methylene chloride was then added. The reaction was then cooled to 0 °C using an ice bath. To the reaction mixture 535 μl (3.06 mmol) diisopropyl ethyl amine was added. After 5 min, the reaction was washed with acid and twice with water. The reaction mixture was then dried over $MgSO_4$ and filtered. The mixture was used as prepared in the next preparation.

Macrocyclization of BPA-4 trimer A solution of 65 μl 9.75 M NaOH, 60 μL triethylamine, and 5 mL methylene chloride was brought to reflux with vigorous stirring in a 50 mL two neck flask equipped with a condenser. Over a period of 30 min, the trimer solution from the previous preparation was then added via syringe pump so that each drop of solution was instantly dispersed by the stir bar. 1.20 mL 9.75 M NaOH, and 0.18 mL triethylamine were also added over the reaction time (30 min.) After addition of all the reagents, the reaction was allowed to reflux for an additional 5 min. The reaction was then washed with 1N HCl (aq), 0.1N HCl (aq), and twice with water. Solvent was removed *in vacuo* and cyclic product was extracted with several portions of acetone. Solvent was removed *in vacuo* and the resultant cyclics were precipitated from THF/methanol twice and once from methylene chloride/methanol to afford product (40% yield);T_d = 208°C (5% weight loss); T_g = 90°C; GPC: M_n = 600 g/mol, M_w = 3600 g/mol;^{1}H NMR (chloroform-d, TMS, 200 MHz): δ 8.15, 7.55, 7.4 (d, 6H, substituted aromatic hydrogens of dye), 7.15 (m, 12H, phenyl rings in bisphenol-A, stilbene hydrogens, and substituted aromatic hydrogens of dye), 3.35, 2.55 (t, 8H, piperidine hydrogens), 1.65 (s, 6H, isopropylidene hydrogens).

Ring-Opening Polymerization 113 mg macrocycles were dissolved in THF(distilled from Na/benzophenone) in a drybox. 9 μl methyllithium (1.4 M solution in diethyl ether) was added. The reaction mixture was precipitated into methanol to afford a polymer with M_w=18,200 g/mol, M_n=11,200 g/mol; UV/Vis: $\upsilon_{(C=O)}$ = 230 nm, $\upsilon_{(DANS)}$ = 424 nm.

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