Organic NLO Polymers. 2. A Study of Main-Chain and Guest–Host $\chi^{(2)}$ NLO Polymers: NLO-phore Structure Versus Poling

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ABSTRACT: Several new dipolar main-chain $\chi^{(2)}$ nonlinear optical (NLO) polymers were prepared. The NLO-phores, based on alkoxy substituted α-cyanoacrylates, were also placed as monomeric guests within a poly(methyl methacrylate) host. Polar alignment of the NLO-phores by corona poling and their relaxation behavior was monitored by detecting the optical signal resulting from the second harmonic generation. The study revealed that two dipolar rigid-rod main-chain NLO polymers (NLOPs), having solubilizing side chains, were not responsive to alignment by corona poling. We found that each main-chain NLOP prepared in the study showed a strong resistance to alignment, whereas virtually the same NLO-phore as a guest within a polymer host responded well to corona poling. When small variations were made in the structure of the NLO-phore, it was found that when hydrogen-bonding groups are rigidly coupled to the NLO-phore they were very effective for retaining polar asymmetry induced by poling and induced no deleterious effects on the alignment process. For main-chain NLOPs, it appears for optimum alignment the bonding axis and the polar axis should not be parallel.

Introduction

There exists a tremendous challenge in designing and preparing $\chi^{(2)}$ nonlinear optical (NLO) materials which can meet or exceed the stringent optical, mechanical, and temporal standards necessary for NLO-device fabrication.[1] Studies covering a rational approach to creating efficient NLO-phores, the molecular structure responsible for NLO activity, have been approached by several groups and is still a subject of great interest.[2] Because of the noncentrosymmetric polar orientation required of the NLO-phore in $\chi^{(2)}$ materials, numerous strategies for aligning the NLO-phores in the polymer matrix have been explored,[3] of which the most common is the application of an external electric field (*e.g.* corona poling or contact poling).[4] Some researchers have elegantly assembled polymeric materials in the presence of an electric field[5] or employed mechanical forces to induce orientation (*e.g.* Langmuir–Blodgett deposition).[6]

A particular area of interest to our synthetic program is the design and synthesis of organic and organometallic main- and side-chain NLO polymers (NLOPs).[7] Work by Katz and co-workers has demonstrated that linking dipolar units together provides an increase in the net dipole moment, albeit not in a linear fashion.[8] To date, attempts to attain a high degree of alignment in head-to-tail dipolar polymers has met with only limited success, when compared to that achieved in side-chain polymers with identical NLO-phores.[9] Several explanations have been offered, one is that the long flexible spacers used in the polymer backbone (to obtain processability) have deteriorated the additive effect of each NLO-phore dipole moment.[10] Recently, an outstanding advance was made in the alignment of main-chain NLO polymers by Dalton and co-workers where they reported a randomly oriented (*i.e.* head-to-tail, head-to-head, etc.) main-chain polyurethane displayed significant second harmonic generation (SHG) activity.[11]

In the present study we report on our continuing synthetic efforts in the area of main-chain NLO polymers, including the synthesis of the first "hairy" [12] rigid main-chain NLOP, in an effort to understand the optimum design criteria for constructing efficient $\chi^{(2)}$ NLOPs. In particular, can head-to-tail NLOPs be designed in such a way as to take advantage of the dipolar, oriented nature of the polymer backbone?

Studies involving second order NLO techniques such as SHG are sensitive in probing orientation and relaxation phenomena at the molecular level in glassy polymers. The SHG technique is sensitive to small degrees of NLO-phore rotational mobility. The initial local free volume/mobility surrounding the NLO-phore and changes with time in the local glassy microenvironment thus affect the SHG intensity. Electric field-induced NLO-phore orientation during poling occurs in regions of sufficient local free volume and segmental mobility. The disorientation of the NLO-phores is caused by mobility of the polymer chains and local free volume present in the vicinity of the NLO-phore; the relaxations of the polymer chains and the presence of local free volume prevent the "freezing in" of the imposed orientation. NLO-phore orientation is examined over a wide range of time and temperature scales as a function of the local free volume and segmental mobility in the glassy polymer matrix. Thus, by examining the second order NLO properties of polymeric materials as a function of time, information can be obtained about the mobility and relaxation phenomena of the polymer microenvironment surrounding the NLO-phore.

In functionalized systems, it is expected that the temporal stability of the NLO-phore orientation following poling would be improved due to the decreased mobility of the dye in the matrix.[13,14] Local mobility will be defined here as small scale motions that allow the NLO-phore to rotate. Recent studies have attempted to relate the observed thermal dependence of the SHG intensity to information about mobility and relaxations obtained using thermally stimulated current techniques and dielectric relaxation for pendant and main-chain NLO polymers.[15]

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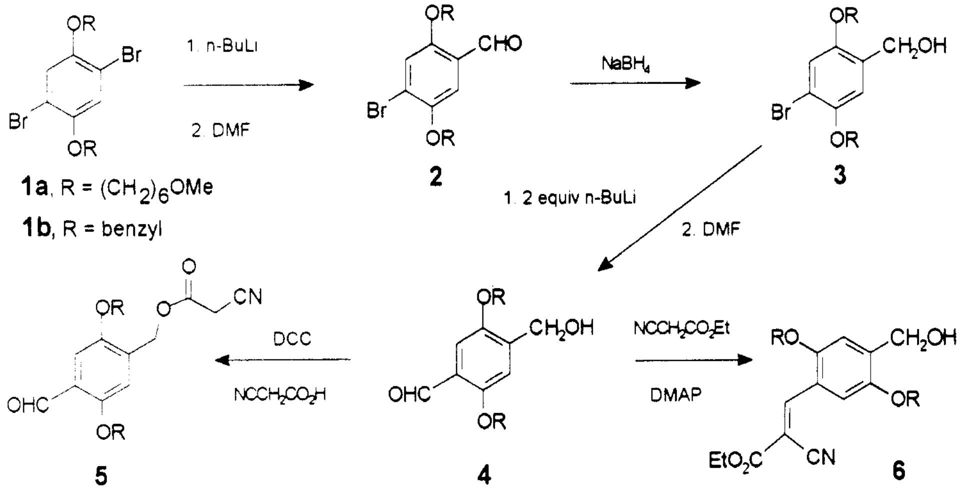
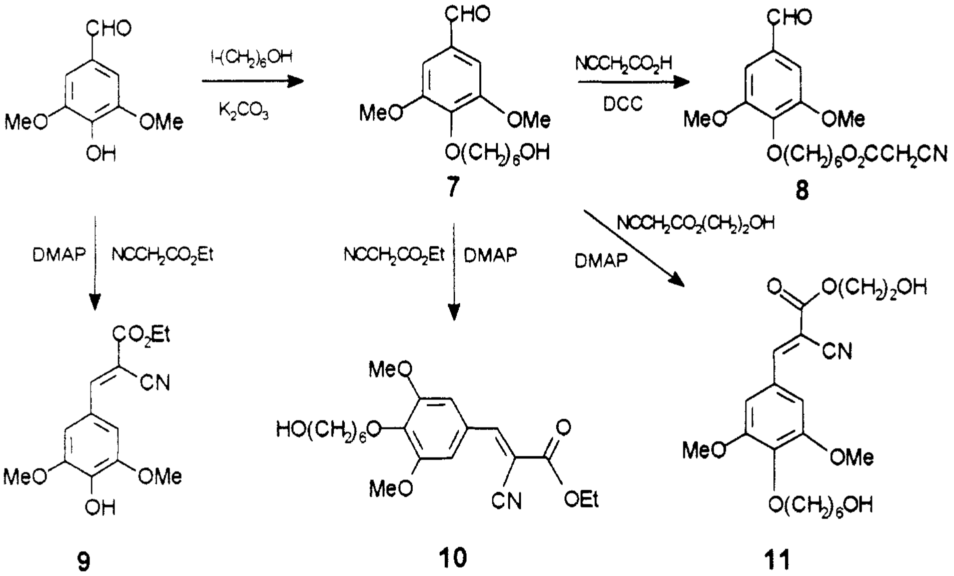
Scheme 1



Scheme 2



This study suggested that the relaxation of a polymer with polar NLO-phores functionalized to the side-chain occurs through local orientation, but if the NLO-phores are placed in the polymer backbone, then a local rotation and reorientation of the end-to-end vector of the chain are detected. Dielectric relaxation studies show that, in addition to local relaxation modes of the NLO-phores found in all systems, an additional relaxation mode attributed to global reorientation of the end-to-end vectors of the chains is found for main-chain NLO polymers. In this study, we will attempt to determine how the movement of the dipolar axis of the NLO-phore relates to its ability to be oriented during poling and its temporal stability following poling.

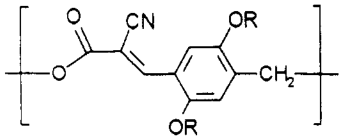
Results and Discussion

Monomer Synthesis. Monomers required for the synthesis of the hairy rigid-rod NLOPs, **5** and **6**, were prepared by starting from hydroquinone through a relatively straightforward and efficient synthetic route (Scheme 1). The synthesis of compounds similar to **1** has recently been reported by Giesa and Schulz.[16] Critical to the synthetic strategy was the selective halogen–metal exchange followed by conversion to the aldehyde.[17] Reduction with sodium borohydride and then treatment with excess *n*-BuLi followed by DMF affords the unsymmetrical and highly functionalized benzene derivative **4**. From **4**, monomers **5** and **6** are prepared in high yield; however, the monomers prove quite difficult to purify. Even at ambient temperature and under neutral conditions monomer **5** homopolymerizes. Flash chromatography on deactivated alumina is somewhat effective, but we always observe some polymer byproduct. The method of choice to purify the monomers is by crystallization from a mixture of ethyl acetate and hexanes.

We prepared a series of NLO-phores and monomers **8** and **10** starting from the readily available syringaldehyde (Scheme 2). The crude product was obtained as a reddish-orange oil. Purification was again difficult due to homopolymerization of the material. Purification of **8** is best achieved by oiling the material out of ethyl acetate with hexanes. We now have in hand a series of NLO-phores for incorporation into polymer hosts, assimilation into oriented head-to-tail polymers, or placement into randomly oriented NLOPs through the synthesis of polyurethanes.

Compound **10** is treated with methacryloyl chloride to produce a methacrylate monomer, 4-{$CH_2{=}CMeCO_2(CH_2)_6O$}-3,5-$(MeO)_2C_6H_4CH{=}C(CN)CO_2Et$ (**12**). Although this compound is poised for the synthesis of a side-chain NLOP we have not carried out the homo- or copolymerization chemistry.

Polymer Synthesis and Characterization. Monomers **5** and **6** were homopolymerized by employing Knoevenagel and transesterification polycondensation techniques, respectively, to generate the hairy rigid-rod NLOPs. Both polymerization techniques are found to produce a bimodal molecular weight distribution. The low molecular weight polymer is found to dominate and represented around 70% of the material (based on UV-vis absorption data in the GPC trace). A typical polymerization run would produce the following materials: **13a**

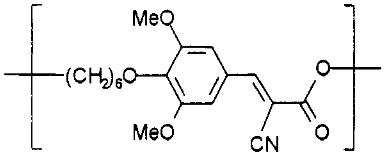


13a, R = $(CH_2)_6OMe$
13b, R = benzyl

M_n = 2700, D_p = 6.0, PD = 2.6 and M_n = ~5 × 10^6, PD = 4.4; **13b** M_n = 2300, D_p = 6.0, PD = 2.6 and M_n = 94 000, PD = 9.8. The materials possess excellent solubility in common organic solvents and are orange in color with λ_{max} absorption bands at 414 and 410 nm (**13a** and **13b**, respectively).

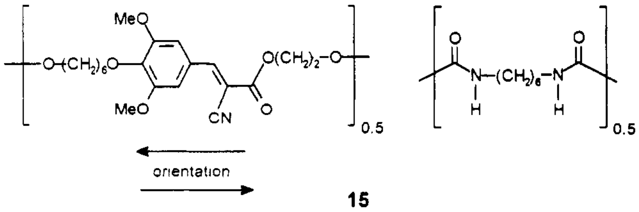
The NMR spectral data for polymer **13** show a single geometry about the double bond and are consistent with the (*E*)-olefin. What is conspicuously missing in the NMR data are sufficient end groups (C*H*O or NCC*H*$_2$CO$_2$) for the average D_p of ~6 (low molecular weight fraction). Analysis of a hexamer by molecular mechanics (MM3) indicates that a helical structure is feasible and that places the termini of the hexamer in very close proximity; hence, a cyclization/condensation appears viable. Attempts to substantiate the idea of cyclic oligomers using FAB/MS analysis failed (no linear or cyclic oligomeric peaks observed).

Homopolymerization of monomer **8** affords polymer **14** possessing a unimodal molecular weight distribution; however, we could never obtain a high molecular weight polymer (M_n = 4300, D_p = 13, PD = 1.9). The ^{1}H NMR spectrum of polymer **14** indicates a 3/100 ratio of end group (CHO/backbone vinyl CH). A value of 8/100 would be expected from the GPC data (D_p = 13). This may reflect that the GPC molecular weights are quite conservative. The polymer is very soluble in organic solvents, will cast high quality films, and has a λ_{max} of 354 nm in dichloromethane.



14

Comonomer **11** was copolymerized with 1,6-diisocyanatohexane in *p*-dioxane over a period of 24 h to yield a random copolymer (**15**). There is no reason to expect the hydroxy moieties to differ in reactivity; so we believe the polymer backbone should not have any kind of extended ordering of the dipolar units. This certainly does not preclude the possibility of small, purely statistical segments of ordered repeating units.



15

PMMA guest–host materials of NLO-phores **9** and **11** have been prepared and characterized. The UV–vis spectra were taken for the guest–host polymers, and we observed no significant shift of λ_{max} when compared to $CHCl_3$ solution data.

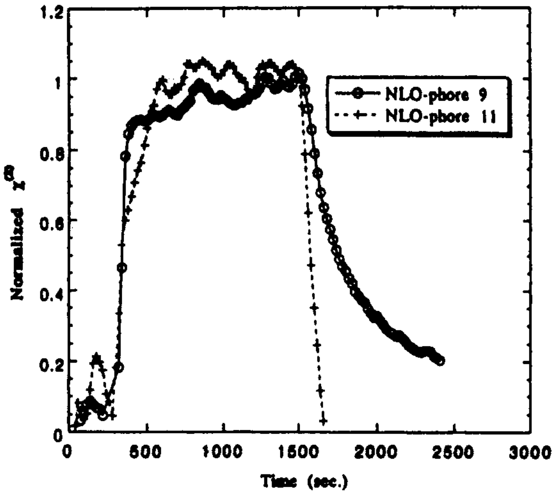


Figure 1. Second order NLO response for guest–host PMMA films containing NLO-phores **9** and **11**. Both films were corona poled (3000 V, 300–1500 s) at (T_g + 10) °C.

SHG Evaluation of Polymeric Materials. Interestingly, none of the main-chain NLO polymers **13**, **14**, or **15** displayed significant SHG activity after being subjected to corona poling under a variety of conditions. The lack of a second order NLO signal for these main-chain NLO polymers is most likely a result of the poling process not breaking down the centrosymmetric nature of the medium. Poling at higher temperatures and field strengths proved ineffective for these head-to-tail (*i.e.* **13** and **14**) and random (*i.e.* **15**) main-chain NLO polymers. Each polymer system was checked for unusual conductivity (in solution), and there was no correlation between the small changes in conductivity measured and the ability to successfully align the polymeric materials.

The PMMA guest–host solutions of **9** and **11** (5% by weight) were prepared and then spin-cast onto ITO slides. The guest–host PMMA films of **9** and **11** were subjected to corona poling and displayed maximum $\chi^{(2)}$ values of 0.96 and 0.52 pm/V, respectively. Figure 1 shows the $\chi^{(2)}$ growth during poling (300–1500 s) and the $\chi^{(2)}$ decay after poling (t > 1500 s) for the guest–host PMMA polymers containing NLO-phores **9** and **11**. Since the uncertainty in the quantitative determination of the magnitude of $\chi^{(2)}$ is approximately 30–40%, the compounds all possess similar second order NLO efficiencies. However, the rise time and the relaxation time of the compounds during and following poling show experimentally significant differences. The rise time of compound **11** (~37 s) is considerably longer than that of molecule **9** (~23 s). This is consistent with NLO-phore **11** being larger than **9**, thus making rotation of compound **11** in the polymer matrix more difficult than that of NLO-phore **9**. However, the relaxation time of NLO-phore **11** is much shorter than that of NLO-phore **9**. These data suggest that hydrogen bonding is most advantageous when in close proximity and rigidly coupled to the NLO-phore.

Concluding Remarks

We successfully prepared hairy rigid main-chain NLO polymers where the flexible spacer used in previous main-chain NLOPs has been removed. The hypothesis that a more rigid polymer backbone could lead to an enhanced additive effect of each dipolar unit was tested. In general, dipolar main-chain NLOPs have shown a strong resistance to alignment and this appears to be the case for these new rigid main-chain polymers. Thus, a more rigid polymer backbone is in itself not a solution to aligning main-chain NLOPs. To further address the issue of alignment, or lack thereof, we prepared a main-chain polymer containing the NLO-phore in a head-to-tail orientation and then in a randomly oriented polyurethane copolymer. Poling followed by measurement of the SHG under carefully controlled experimental conditions showed that the oriented head-to-tail homopolymer and the random copolymer produced no SHG signal (*i.e.* no alignment). We believe this to be a consequence of the NLO-phore having a linear and somewhat symmetrical structure. We suggest that alignment for main-chain NLO polymers is simply a process involving independent dipolar units responding to an external field. Alignment is best achieved with NLO-phores having dipole moment vectors that deviate significantly from that of the polymer backbone.

It can be seen through the guest–host work that indeed NLO-phore **9** is the most responsive to poling and has the best temporal stability for the two related guest–host systems studied. Thus, NLO-phore response time to the electric field appears to be based upon size, as expected; however, the relaxation time is more dependent upon the proximity of hydrogen-bonding sites.[18] Thus, hydrogen-bonding sites rigidly connected to the NLO-phore appear valuable for temporal stability and do not have any deleterious effects on the alignment process. This is not the first study to point out the importance of hydrogen-bonding;[19] however, to our knowledge this is the first time the proximity of hydrogen-bonding has been varied and studied for the same basic NLO-phore.

Study continues in our laboratories on main-chain NLO polymers with a focus on developing an understanding of the mechanism by which these polymers resist or submit to the poling process. In addition, knowledge gained in this study is being applied to the synthesis of interpenetrating polymer networks (IPNs) and new generation main-chain NLOPs.

Experimental Section

Methods. All manipulations of compounds and solvents were carried out using standard Schlenk techniques. Solvents were degassed and purified by distillation under nitrogen from standard drying agents. Spectroscopic measurements utilized the following instrumentation: ^{1}H NMR, Varian XL 300; ^{13}C NMR, JOEL-270, Varian XL 300 (at 75.4 MHz); infrared, Perkin-Elmer 1750 FT-IR; UV-vis, HP-8452A. NMR chemical shifts are reported in δ versus Me_4Si in ^{1}H NMR and by assigning the $CDCl_3$ resonance at 77.00 ppm in ^{13}C spectra. Dicyclohexylcarbodiimide (DCC), 4-(dimethylamino)pyridine (DMAP), 6-chlorohexanol, sodium hydride, *n*-butyllithium, cyanoacetic acid, and 3,5-bis(methoxy)-4-hydroxybenzaldehyde (syringaldehyde) were purchased from Aldrich Chemical Co. and used as received. K_2CO_3 (granular), methyl iodide, bromine, and sodium borohydride (AR grade, Mallinckrodt) were purchased from Baxter. Hydroquinone was purchased from Baker. Thermal analysis of the polymers was performed using a Perkin-Elmer TGA7 and DSC7 station. GPC data were collected on a Varian 5000 HPLC employing a PL size-exclusion column (300 × 7.5 mm, 5-μm particle size). Molecular weight data are referenced to polystyrene standards. Elemental analyses were performed at Atlantic Microlab Inc., Norcross, GA.

Second Order NLO Measurements. Figure 2 shows a schematic of the experimental apparatus. The laser light is generated by a q-switched Nd:YAG laser (10 Hz, <2 mJ/pulse) at 1.064 μm. The p-polarized beam is split so that the MNA reference, used for monitoring laser power, and the sample are measured simultaneously. A photomultiplier and integrator collect and analyze the emergent SHG light (at 532 nm), and the optical signal is ratioed against the reference. The polymers were dissolved in spectroscopic grade chloroform, and the solutions were mixed well and filtered through a 10-μm filter. The solutions were then spin-coated onto indium–tin–oxide (ITO) glass slides. Spun films, ~3 μm thick, were dried at ambient conditions for 48 h and then under vacuum for 24 h at 25 °C followed by a slow ramp (1 day) to elevated temperature ((T_g + 10) °C) for 8 h. Films were allowed to cool slowly under vacuum and stored in a desiccator prior to use. Films were heated to a poling temperature (T_p) above or below the glass transition and allowed to equilibrate for 1 h in the beam path before measurements were taken.

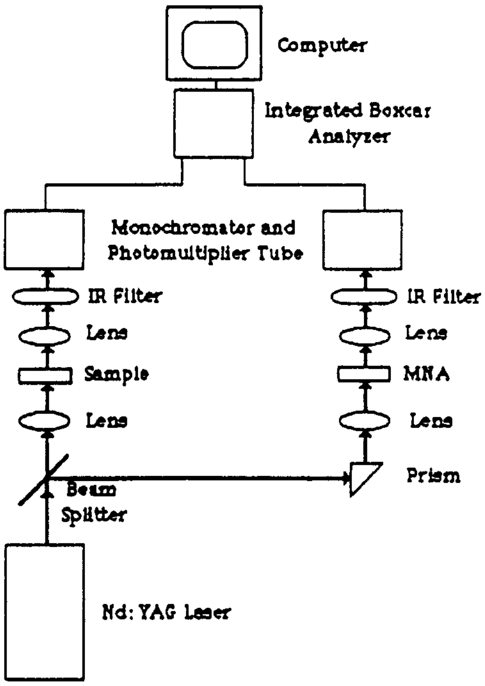


Figure 2. Schematic of the experimental apparatus for SHG measurements. The laser beam is split into sample and reference (MNA) paths. Second harmonic signals from the sample and the reference are detected simultaneously.

Poling was performed under room ambient air. The corona discharge was generated by a tungsten needle (+) biased with 3000 V across a 1.0-cm gap normal to the polymer film. The corona current was limited to <1 μA. The SHG intensity characteristics are a function of poling parameters, including corona polarity, current, gap distance, humidity, and ambient environment.[14] The reported SHG intensity is normalized to the sample thickness to allow comparisons to be made between a variety of films. Error limits due to noise in the SHG intensity measurements are less than or equal to twice the size of the symbols, with greater error at higher temperatures.

Preparation of 1a. A DMF (40-mL) solution of 1,4-bis[MeO-$(CH_2)_6O]C_6H_4$ (5.0 g, 14.8 mmol) was treated with bromine (7.09 g, 44.4 mmol) and allowed to react at room temperature with stirring for 4 h. The mixture was diluted with water (100 mL) and extracted with ether (2 × 150 mL). The organic layers were combined, washed with aqueous sodium thiosulfate and brine, and then dried over K_2CO_3. The solvents were removed under reduced pressure, and the crude product, obtained as a brown solid, was purified by recrystallization from EtOAc/hexanes (1/2, v/v) to afford pure **1a** as a yellow solid (7.34 g, 93%, mp 93–94 °C). ^{1}H NMR ($CDCl_3$): δ 7.08 (s, 2 H, Ar), 3.95 (t, J = 6.4 Hz, 4 H, CH_2OAr), 3.39 (t, J = 6.5 Hz, 4 H, CH_2OMe), 3.34 (s, 6 H, CH_3), 1.82–1.26 (m, 16 H, CH_2's). ^{13}C NMR ($CDCl_3$): δ 150.0 (Ar C), 118.5 (Ar CH), 111.2 (Ar C), 72.7 (CH_2OAr), 70.2 (CH_2OMe), 58.6 (CH_3), 29.6, 29.1, 25.8 (CH_2's). Anal. Calcd for $C_{20}H_{32}Br_2O_4$: C, 48.40; H, 6.50. Found: C, 48.49; H, 6.52.

Preparation of 1b. A DMF (60-mL) solution of 2,5-dibromohydroquinone (4.0 g, 14.9 mmol) was treated with benzyl chloride (7.56 g, 59.7 mmol) and K_2CO_3 (12.3 g, 89.6 mmol). The reaction mixture was allowed to react at 60 °C with stirring for 12 h. The mixture was diluted with water (100 mL) and extracted with $CHCl_3$ (2 × 150 mL). The organic layers were combined, washed with brine, and dried over K_2CO_3. The solvents were removed under reduced pressure, and the crude product was recrystallized from EtOAc/hexanes (1/2, v/v) to afford pure **1b** as a pink microcrystalline solid (4.5 g, 67%, mp 195–196 °C). ^{1}H

NMR ($CDCl_3$): δ 7.51–7.36 (m, 10 H, Ar), 7.21 (s, 2 H, Ar), 5.11 (s, 4 H, CH_2OAr). ^{13}C NMR ($CDCl_3$): δ 150.0 (Ar C), 136.1 (Ar C), 128.6, 128.1, 127.2, 119.2 (Ar CH's), 111.5 (Ar C), 71.9 (CH_2OAr). Anal. Calcd for $C_{20}H_{16}Br_2O_2$: C, 53.60; H, 3.60. Found: C, 53.65; H, 3.64.

Preparation of 2a. A THF (75-mL) solution of **1a** (3.50 g, 7.1 mmol) was chilled to –78 °C and then treated with *n*-BuLi (2.8 mL, 7.1 mmol). The mixture was allowed to react at –78 °C with stirring for 1 h, and then DMF (2.06 g, 28.0 mmol) was added in one portion. The cooling bath was removed, and the reaction mixture was allowed to warm to ambient temperature over a period of 2 h. The mixture was diluted with water (100 mL) and extracted with ether (2 × 150 mL). The organic layers were combined, washed with brine, and then dried over K_2CO_3. The solvents were removed under reduced pressure, and the crude product was crystallized from EtOAc/hexanes (1/2, v/v) to afford pure **2a** as a light yellow microcrystalline solid (2.2 g, 70%, mp 84–85 °C). ^{1}H NMR ($CDCl_3$): δ 10.43 (s, 1 H, CHO), 7.33 (s, 1 H, Ar), 7.24 (s, 1 H, Ar), 4.05–4.01 (m, 4 H, CH_2OAr), 3.41 (t, J = 6.5 Hz, 4 H, CH_2OMe), 3.36 (s, 6 H, CH_3), 1.86–1.45 (m, 16 H, CH_2's). ^{13}C NMR ($CDCl_3$): δ 188.9 (CHO), 155.7 (Ar C), 149.9 (Ar C), 124.3 (Ar CCHO), 121.0, 118.5 (Ar CH's), 110.0 (Ar C), 72.7 (CH_2OAr), 69.7 (CH_2OMe), 69.4 (CH_2OMe), 58.6 (OCH_3), 29.6, 29.0, 25.9 (CH_2's). IR (CH_2Cl_2): $\nu_{C=O}$ 1683 cm^{-1}. Anal. Calcd for $C_{21}H_{33}BrO_5$: C, 56.65; H, 7.47. Found: C, 56.88; H, 7.54.

Preparation of 2b. A THF (50-mL) solution of **1b** (2.30 g, 5.1 mmol) was chilled to –78 °C and then treated with *n*-BuLi (2.1 mL, 5.1 mmol). The mixture was allowed to react at –78 °C with stirring for 1 h, and then DMF (2.25 g, 30.8 mmol) was added in one portion. The cooling bath was removed, and the reaction mixture was allowed to warm to ambient temperature over a period of 2 h. The mixture was diluted with water (100 mL) and extracted with ether (2 × 150 mL). The organic layers were combined, washed with brine, and then dried over K_2CO_3. The solvents were removed under reduced pressure, and the crude product was recrystallized from EtOAc/hexanes (1/2, v/v) to afford pure **2b** as a bright yellow microcrystalline solid (1.66 g, 82%, mp 149–150 °C). ^{1}H NMR ($CDCl_3$): δ 10.43 (s, 1 H, CHO), 7.50–7.38 (m, 10 H, Ar), 7.28 (s, 2 H, Ar), 5.17 (s, 4 H, CH_2OAr). ^{13}C NMR ($CDCl_3$): δ 188.6 (CHO), 156.0, 149.9, 136.0 (Ar C's), 128.8, 128.6, 128.5, 128.1, 127.5, 127.2 (Ar CH's), 125.0 (Ac CCHO), 121.5, 119.2 (Ar CH's), 111.5 (Ar C), 71.4 (CH_2OAr). IR (CH_2Cl_2): $\nu_{C=O}$ 1684 cm^{-1}. Anal. Calcd for $C_{21}H_{17}BrO_3$: C, 63.49; H, 4.31. Found: C, 63.59; H, 4.37.

Preparation of 3a. An EtOH (40-mL) solution of **2a** (1.27 g, 2.7 mmol) was treated with $NaBH_4$ (0.22 g, 5.7 mmol) and slightly warmed. The reaction mixture was allowed to react at ambient temperature with stirring for 2 h. The mixture was diluted with water (100 mL) and extracted with ether (2 × 150 mL). The organic layers were combined, washed with brine, and then dried over K_2CO_3. The solvents were removed under reduced pressure, and the crude product was crystallized from EtOAc/hexanes (1/2, v/v) to afford pure **3a** as a white crystalline solid (1.24 g, 97%, mp 85–86 °C). ^{1}H NMR ($CDCl_3$): δ 7.06 (s, 1 H, Ar), 6.94 (s, 1 H, Ar), 4.65 (d, J = 6.4 Hz, 2 H, CH_2OH), 4.01–3.97 (m, 4 H, CH_2OAr), 3.41 (t, J = 6.4 Hz, 4 H, CH_2OMe), 3.36 (s, 3 H, CH_3), 2.34 (t, J = 6.4 Hz, 1 H, OH), 1.84–1.47 (m, 16 H, CH_2's). ^{13}C NMR ($CDCl_3$): δ 152.1, 150.8 (Ar C's), 130.6 (Ar CCH_2OH), 117.7, 115.7 (Ar CH's), 112.4 (Ar C), 73.9 (CH_2OAr), 71.3 (CH_2OMe), 70.0 (CH_2OMe), 62.7 (CH_2OH), 59.7 (OCH_3), 30.7, 30.4, 27.1 (CH_2's); IR (CH_2Cl_2): ν_{OH} 3455 cm^{-1}. Anal. Calcd for $C_{21}H_{35}BrO_5$: C, 56.38; H, 7.88. Found: C, 56.46; H, 7.90.

Preparation of 3b. An EtOH (15-mL) solution of **2b** (0.97 g, 2.5 mmol) was treated with $NaBH_4$ (0.19 g, 4.89 mmol) and slightly warmed. The mixture was allowed to react at ambient temperature with stirring for 2 h. The mixture was diluted with water (100 mL) and extracted with ether (2 × 150 mL). The organic layers were combined, washed with brine, and then dried over K_2CO_3. The solvents were removed under reduced pressure, and the crude product was recrystallized from EtOAc/hexanes (1/2, v/v) to afford pure **3b** as a white crystalline solid (0.87 g, 89%, mp 144–145 °C). ^{1}H NMR ($CDCl_3$): δ 7.50–7.39 (m, 10 H, Ar), 7.20 (s, 1 H, Ar), 7.03 (s, 1 H, Ar), 5.13 (s, 2 H, CH_2OAr), 5.06 (s, 2 H, CH_2OAr), 4.47 (s, 2 H, CH_2OH). ^{13}C NMR ($CDCl_3$): δ 150.8, 149.5 (Ar C's), 136.7, 129.8, 128.7, 128.5, 128.2, 127.9, 127.4, 127.2 (Ar CH's), 117.2, 114.9, 111.4 (Ar C's), 71.8 (CH_2OAr), 71.0 (CH_2OAr), 61.3 (CH_2OH). IR (CH_2Cl_2): ν_{OH} 3393 cm^{-1}. Anal. Calcd for $C_{21}H_{19}BrO_3$: C, 63.17; H, 4.80. Found: C, 63.08; H, 4.82.

Preparation of 4a. A THF (25-mL) solution of **3a** (1.11 g, 2.5 mmol) was chilled to –78 °C and then treated with *n*-BuLi (6 mL, 15.0 mmol). The mixture was allowed to react at –78 °C with stirring for 1 h, and then DMF (1.10 g, 15 mmol) was added in one portion. The cooling bath was removed and the reaction mixture allowed to warm to ambient temperature over a period of 2 h. The mixture was then diluted with water (100 mL) and extracted with ether (2 × 150 mL). The organic layers were combined, washed with brine, and then dried over K_2CO_3. The solvents are removed under reduced pressure, and the crude product was crystallized from EtOAc/hexanes (1/2, v/v) to afford pure **4a** as a white crystalline solid (0.99 g, 64.0%, mp 98–99 °C). ^{1}H NMR ($CDCl_3$): δ 10.43 (s, 1 H, CHO), 7.26 (s, 1 H, Ar), 7.03 (s, 1 H, Ar), 4.71 (d, J = 6.4 Hz, 2 H, CH_2OH), 4.06 (t, J = 6.4 Hz, 2 H, CH_2OAr), 4.00, (t, J = 6.4 Hz, 2 H, CH_2OAr), 3.37 (t, J = 6.3 Hz, 2 H, CH_2OMe), 3.32 (s, 3 H, CH_3), 2.34 (t, J = 6.3 Hz, 1 H, OH), 1.83–1.41 (m, 16 H, CH_2's). ^{13}C NMR ($CDCl_3$): δ 189.3 (CHO), 152.1, 151.4, 132.9, 123.3 (Ar C's), 113.0, 108.8 (Ar CH's), 72.7 (CH_2OAr), 69.1 (CH_2OMe), 68.5 (CH_2OMe), 61.1 (CH_2OH), 58.6 (OCH_3), 29.6, 29.3, 26.6 (CH_2's). IR (CH_2Cl_2): $\nu_{C=O}$ 1656, ν_{OH} 3378 cm^{-1}. Anal. Calcd for $C_{22}H_{36}O_6$: C, 66.64; H, 9.15. Found: C, 66.35; H, 9.18.

Preparation of 4b. A THF (20-mL) solution of **3b** (0.83 g, 2.1 mmol) was chilled to –78 °C and then treated with *n*-BuLi (3.3 mL, 8.3 mmol). The mixture was allowed to react at –78 °C with stirring for 1 h, and then DMF (1.8 g, 25 mmol) was added in one portion. The cooling bath was removed, and the reaction mixture was allowed to warm to ambient temperature over a period of 2 h. The mixture was then diluted with water (100 mL) and extracted with ether (2 × 150 mL). The organic layers were combined, washed with brine, and then dried over K_2CO_3. The solvents were removed under reduced pressure, and the crude product was crystallized from EtOAC/hexanes (1/2, v/v) to afford pure **4b** as a light yellow crystalline solid (0.58 g, 80%, mp 146–147 °C). ^{1}H NMR ($CDCl_3$): δ 10.49 (s, 1 H, CHO), 7.45–7.36 (m, 10 H, Ar), 7.18 (s, 2 H, Ar), 5.19 (s, 2 H, CH_2OAr), 5.10 (s, 2 H, CH_2OAr), 4.77 (s, 2 H CH_2OH). ^{13}C NMR ($CDCl_3$): δ 189.6 (CHO), 157.0, 151.0 (Ar C's), 138.9 (Ar CH), 137.0 (Ar C), 129.2, 128.9, 128.7, 128.0, 127.9 (Ar CH's), 124.8, 113.9, 109.9 (Ar C's), 72.0 (CH_2OAr), 71.0 (CH_2OAr), 61.9 (CH_2OH). IR (CH_2Cl_2): $\nu_{C=O}$ 1675, ν_{OH} 3425 cm^{-1}. Anal. Calcd for $C_{22}H_{20}O_4$: C, 75.85; H, 5.79. Found: C, 75.63; H, 5.89.

Preparation of 5a. A CH_2Cl_2 (10-mL) solution of **4a** (0.20 g, 0.5 mmol) was treated with $NCCH_2COOH$ (0.04 g, 0.51 mmol) and dicyclohexylcarbodiimide (DCC) (0.11 g, 0.51 mmol). The mixture was allowed to react at ambient temperature with stirring for 4 h. Ether (20 mL) was added, and the reaction mixture was filtered through Celite. The solvents were removed under reduced pressure, and the crude solid was recrystallized from EtOAc/hexanes (1/5, v/v) to afford **5a** as a bright yellow crystalline solid (0.23 g, 96%, mp 79–80 °C). ^{1}H NMR ($CDCl_3$): δ 10.48 (s, 1 H, CHO), 7.32 (s, 1 H, Ar), 7.07 (s, 1 H, Ar), 5.32 (s, 2 H, CH_2Ar), 4.09 (t, J = 6.4 Hz, 2 H, CH_2OAr), 4.02 (t, J = 6.5 Hz, 2 H, CH_2OAr), 3.57 (s, 2 H, CH_2CN), 3.41 (t, J = 6.4 Hz, 4 H, CH_2OMe), 3.36 (s, 6 H, OCH_3), 1.84–1.45 (m, 16 H, CH_2's). ^{13}C NMR ($CDCl_3$): δ 189.2 (CHO), 162.0 (CO_2), 156.0, 150.4, 131.1 (Ar C), 124.9 (Ar C), 113.9 (CN), 113.0 (Ar CH), 109.2 (Ar CH), 72.6 (CH_2OAr), 69.2 (CH_2OMe), 68.6 (CH_2OMe), 63.4 (CH_2O_2C), 58.5 (OCH_3), 49.4 (CH_2CN), 29.5, 29.1, 25.8, 25.7, 24.8, 24.7 (CH_2's). IR (CH_2Cl_2): ester $\nu_{C=O}$ 1756, aldehyde $\nu_{C=O}$ 1681 cm^{-1}. UV–vis (CH_2Cl_2): λ_{max} = 356 nm ($\epsilon = 5.4 \times 10^3$). Anal. Calcd for $C_{25}H_{37}NO_7$: C, 64.77; H, 8.04. Found: C, 64.79; H, 8.11.

Preparation of 5b. A CH_2Cl_2 (10-mL) solution of **4b** (0.65 g, 1.9 mmol) was treated with $NCCH_2COOH$ (0.2 g, 2.2 mmol) and DCC (0.5 g, 2.2 mmol). The mixture was allowed to react at ambient temperature with stirring for 4 h. Ether (50 mL) was added, and the reaction mixture was filtered through Celite. The solvents were removed under reduced pressure, and the product was precipitated from EtOAc/hexanes (1/2, v/v) to afford **5b** as an oil (0.16 g, 85%). ^{1}H NMR ($CDCl_3$): δ 10.53 (s, 1 H, CHO), 7.48–7.37 (m, 10 H, Ar), 7.17 (s, 2 H, Ar), 5.35 (s, 2 H, CH_2OAr), 5.22 (s, 2 H, CH_2OAr), 5.12 (s, 2 H, CH_2O_2C), 3.46 (s, 2 H, CH_2CN). ^{13}C NMR ($CDCl_3$): δ 189.7 (CHO), 163.0 (CO_2), 156.4 (Ar C) 151.1, 137.0 (Ar C's), 129.5, 129.4, 129.3, 129.0, 128.2, 128.0 (Ar

CH's), 126.0 (Ar C), 115.3 (CN), 110.7 (Ar CH), 72.0 (CH_2OAr), 71.4 (CH_2OAr), 65.0 (CH_2O_2C), 64.1 (CH_2CN). IR (CH_2Cl_2): ester $\nu_{C=O}$ 1754, aldehyde $\nu_{C=O}$ 1675 cm^{-1}. UV-vis (CH_2Cl_2): λ_{max} 302 nm ($\epsilon = 4.71 \times 10^3$).

Preparation of 6a. A THF (30-mL) solution of **4a** (1.00 g, 2.5 mmol) was treated with $NCCH_2CO_2Et$ (0.34 g, 3.0 mmol) and K_2CO_3 (1.05 g, 7.6 mmol) and then heated at reflux for 10 h. The mixture was diluted with water (100 mL) and extracted with ether (2 × 150 mL). The organic layers were combined, washed with brine, and then dried over K_2CO_3. The solvents were removed under reduced pressure, and the crude product was precipitated from EtOAc/hexanes (1/2, v/v) to afford **6a** as a pure red viscous oil (0.85 g, 69%). ^{1}H NMR ($CDCl_3$): δ 8.76 (s, 1 H, =CH), 7.85 (s, 1 H, Ar), 7.04 (s, 1 H, Ar), 4.72 (s, 2 H, CH_2OH), 4.36 (q, J = 7.2 Hz, 2 H, CH_2CH_3), 4.03 (t, J = 6.3 Hz, 4 H, CH_2OAr), 3.38 (t, J = 6.3, 4 H, CH_2OMe), 3.34 (s, 6 H, OCH_3), 1.80–1.36 (m, 16 H, CH_2's). ^{13}C NMR ($CDCl_3$): δ 162.8 (CO_2), 153.7 (=CH), 149.4, 138.4, 118.9 (Ar C's), 116.2 (CN), 111.5, 109.6 (Ar CH's), 100.0 (=C(CN)), 72.5 (CH_2OAr), 69.0 (CH_2OMe), 68.2 (CH_2OMe), 62.1 (CH_2Ar), 60.1 (CH_2CH_3), 58.2 (OCH_3), 29.2, 29.1, 28.8, 25.7, 25.6, 25.5 (CH_2's), 13.9 (CH_2CH_3). IR (CH_2Cl_2): ester $\nu_{C=O}$ 1735 cm^{-1}. Anal. Calcd for $C_{27}H_{41}NO_7$: C, 65.96; H, 8.41. Found: C, 65.67; H, 8.72.

Preparation of 7. A DMF (50-mL) solution of 3,5-bis(methoxy)-4-hydroxybenzaldehyde (5.00 g, 27.5 mmol) was treated with iodohexanol (9.4 g, 41 mmol) and K_2CO_3 (11.4 g, 82.5 mmol). The reaction mixture was allowed to react at 80 °C with stirring for 6 h. The mixture was diluted with water (150 mL) and extracted with ether (3 × 200 mL). The organic layers were combined, washed with brine, and dried over anhydrous $MgSO_4$. The solvents were removed under reduced pressure, and the pure product was oiled out from EtOAc/hexanes (1/2, v/v) to afford pure **7** as a colorless viscous oil (7.60 g, 99%). ^{1}H NMR ($CDCl_3$): δ 9.89 (s, 1 H, CHO), 7.15 (s, 2 H, Ar), 4.10 (t, J = 6.6 Hz, 2 H, CH_2OAr), 3.94 (s, 6 H, OCH_3), 3.68 (t, J = 6.5 Hz, 2 H, CH_2OH), 1.83–1.45 (m, 8 H, CH_2's). ^{13}C NMR ($CDCl_3$): δ 190.9 (CHO), 153.5 (Ar C), 142.6 (Ar C), 131.2 (Ar C), 106.4 (Ar CH), 73.1 (CH_2OAr), 62.1 (CH_2OH), 55.8 (OCH_3), 32.3, 29.7, 25.2, 25.1 (CH_2's). IR (CH_2Cl_2): $\nu_{C=O}$ 1693 cm^{-1}. Anal. Calcd for $C_{15}H_{22}O_5$: C, 63.81; H, 7.85. Found: C, 63.73; H, 7.89.

Preparation of 8. A CH_2Cl_2 (10-mL) solution of **7** (2.02 g, 7.16 mmol) was treated with $NCCH_2COOH$ (0.61 g, 7.16 mmol) and DCC (1.18 g, 7.16 mmol). The mixture was allowed to react at ambient temperature with stirring for 4 h. Ether (25 mL) was added, and the reaction mixture was filtered through Celite. The solvents were removed under reduced pressure, and the crude product was oiled out from EtOAc/hexanes (1/2, v/v) to afford pure **8** as a reddish orange viscous liquid (2.49 g, 99%). ^{1}H NMR ($CDCl_3$): δ 9.89 (s, 1 H, CHO), 7.15 (s, 2 H, Ar), 4.25 (t, J - 6.7 Hz, 2 H, CH_2OAr), 4.09 (t, J = 6.5 Hz, 2 H, CH_2O_2C), 3.94 (s, 6 H, CH_3), 3.48 (s, 2 H, CH_2CN), 1.79–1.62 (m, 8 H, CH_2's). ^{13}C NMR ($CDCl_3$): δ 191.1 (CHO), 162.9 (CO_2), 153.9 (Ar C), 142.6 (Ar C), 131.6 (Ar C), 113.0 (CN), 106.8 (Ar CH), 73.4 (CH_2OAr), 67.0 (CH_2O), 66.0 (CH_2CN), 56.3 (OCH_3), 30.0, 28.3, 25.5, 24.7 (CH_2's). IR (CH_2Cl_2): ester $\nu_{C=O}$ 1750, aldehyde $\nu_{C=O}$ 1693 cm^{-1}. UV–vis (CH_2Cl_2): λ_{max} 290 nm ($\epsilon = 7.61 \times 10^{-3}$).

Preparation of 9. A THF (30-mL) solution of 4-hydroxy-3,5-bis(methoxy)benzaldehyde (5.00 g, 27.4 mmol) was treated with $NCCH_2CO_2Et$ (6.21 g, 54.9 mmol) and K_2CO_3 (15 g, 108.0 mmol). The reaction mixture was heated at reflux for 12 h. The mixture was diluted with water (200 mL) and extracted with CH_2Cl_2 (2 × 200 mL). The organic layers were combined, washed with brine, and dried over anhydrous $MgSO_4$. The solvents were removed under reduced pressure, and the crude product was recrystallized from EtOAc/hexanes (1/2, v/v) to afford pure **9** as a yellow crystalline solid (6.1 g, 81%, mp 208–210 °C). ^{1}H NMR ($CDCl_3$): δ 8.15 (s, 1 H, =CH), 7.38 (s, 2 H, Ar), 6.13 (s, 1 H, OH), 4.42 (q, J = 7.1 Hz, 2 H, CH_2CH_3), 3.99 (s, 6 H, OCH_3), 1.42 (t, J = 7.1 Hz, 3 H, CH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 163.1 (CO_2), 154.9 (=CH), 147.1, 140.1, 123.1 (Ar C's), 116.4 (CN), 108.5 (Ar CH), 99.5 (=C(CN)), 62.5 (CH_2CH_3), 56.5 (OCH_3), 14.2 (CH_3).

Preparation of 10. A THF (30-mL) solution of **7** (2.00 g, 7.1 mmol) was treated with $NCCH_2CO_2Et$ (0.96 g, 8.5 mmol) and DMAP (0.8 g, 6.5 mmol). The reaction mixture was allowed to react at ambient temperature with stirring for 2 h. The mixture was diluted with water (100 mL) and extracted with CH_2Cl_2 (3 × 200 mL). The organic layers were combined, washed with brine, and dried over anhydrous $MgSO_4$. The solvents were removed under reduced pressure, and the crude product was purified by passing through an alumina column using a mixture of $MeOH/CH_2Cl_2$ (1/20, v/v) as eluant to afford pure **10** as a reddish orange oil (2.38 g, 89%). ^{1}H NMR ($CDCl_3$): δ 8.15 (s, 1 H, =CH), 7.30 (s, 2 H, Ar), 4.39 (q, J = 6.8 Hz, 2 H, CH_2CH_3), 4.11 (t, J = 6.7 Hz, 2 H, CH_2OAr), 3.91 (s, 6 H, OCH_3), 3.67 (t, J = 6.7 Hz, 2 H, CH_2OH), 1.79–1.45 (m, 8 H, CH_2's), 1.41 (t, J = 7.1 Hz, 3 H, CH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 162.7 (CO_2), 154.8 (=CH), 153.5, 142.2, 126.4 (Ar C's), 116.0 (CN), 108.6 (Ar CH), 101.0 (=C(CN)), 73.5 (CH_2OAr), 62.8 (CH_2OH), 62.6 (CH_2CH_3), 56.2 (OCH_3), 32.6, 30.0, 25.5 (CH_2's), 14.1 (CH_3). Anal. Calcd for $C_{20}H_{27}NO_6$: C, 63.65; H, 7.20. Found: C, 63.51; H, 7.22.

Preparation of 11. A THF solution (30-mL) of **7** (5.62 g, 19.9 mmol) was treated with $NCCH_2CO_2CH_2CH_2OH$ (8.66 g, 67.4 mmol) and DMAP (0.30 g, 2.0 mmol) and allowed to react with stirring at ambient temperature for 10 h. The mixture was treated with 1 N HCl (5 mL), washed with brine (5 mL), and extracted with CH_2Cl_2 (2 × 200 mL). The solvents were removed under reduced pressure to afford pure **11** as an orange oil (6.08 g, 80%). ^{1}H NMR ($CDCl_3$): δ 8.18 (s, 1 H, =CH), 7.30 (s, 2 H, Ar), 4.45 (t, J = 7 Hz, 2 H, CH_2), 4.10 (t, J = 7 Hz, 2 H, CH_2), 3.97 (m, 2 H, CH_2), 3.91 (s, 6 H, OMe), 3.70 (t, J = 6.5 Hz, 2 H, CH_2OH), 1.79–1.62 (m, 8 H, CH_2=s). ^{13}C NMR ($CDCl_3$): δ 163.0 (CO_2), 155.5 (Ar C), 153.5 (=CH), 142.4 (Ar C), 126.2 (Ar C), 116.0 (CN), 108.7 (Ar CH), 100.3 (=C(CN)), 73.6 (CH_2OAr), 68.0 (CH_2O_2C), 62.8 (CH_2OH), 60.7 (CH_2OH), 56.2 (OCH_3), 32.6, 30.0, 25.8 (CH_2's). IR (CH_2Cl_2): ν_{OH} = 3615, $\nu_{C=O}$ = 1724 cm^{-1}. UV-vis (CH_2Cl_2): λ_{max} = 356 nm ($\epsilon = 8.4 \times 10^3$).

Preparation of 12. A CH_2Cl_2 (20-mL) solution of **10** (6.43 g, 17.1 mmol) was treated with methacryloyl chloride (1.778 g, 17.1 mmol) and Et_3N (1.73 g, 17.1 mmol). The reaction mixture was allowed to react with stirring at 0 °C for 4 h. The reaction mixture was treated with 1 N HCl (20 mL) and extracted with CH_2Cl_2 (150 mL). The organic layer was then washed with brine and dried over anhydrous $MgSO_4$. The solvents were removed under reduced pressure, and the crude product was purified by passing through an alumina column and eluting with CH_2Cl_2 to afford pure **12** as a yellow oil (5.77 g, 76%). ^{1}H NMR ($CDCl_3$): δ 8.16 (s, 1 H, =CH), 7.31 (s, 2 H, Ar), 6.11 (s, 1 H, =CH_2), 5.57 (s, 1 H, =CH_2), 4.41 (q, J = 7.1 Hz, 2 H, CH_2CH_3), 4.18 (t, J = 6.6 Hz, 2 H, CH_2OAr), 4.12 (t, J = 6.6 Hz, 2 H, CH_2O_2C), 3.92 (s, 6 H, OCH_3), 1.96 (s, 3 H, =C(CH_3)), 1.75–1.73 (m, 8 H, CH_2's), 1.42 (t, J = 7.1 Hz, 3 H, CH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 167.5 (CO_2), 162.7 (CO_2), 154.8 (Ar C), 153.5 (=CH), 142.1 (Ar C), 136.4 (=C(CH_3)), 126.4 (Ar CH), 125.1 (=CH_2), 116.0 (CN), 108.6 (Ar CH), 101.0 (=C(CN)), 73.5 (CH_2OAr), 64.6 (CH_2O_2C), 62.5 (CH_2CH_3), 56.2 (OCH_3), 30.0, 28.5, 25.7, 25.4 (CH_2's), 18.3 (=CCH_3), 14.1 (CH_2CH_3). IR (CH_2Cl_2): $\nu_{C=O}$ 1715 cm^{-1}. UV–vis (CH_2Cl_2): λ_{max} 354 nm ($\epsilon = 17.08 \times 10^4$).

Preparation of 13a. A THF (10-mL) solution of **5a** (0.20 g, 0.4 mmol) was treated with DMAP (0.05 g, 0.43 mmol) and allowed to react at 50 °C with constant stirring for 4 h. The reaction mixture was then treated with 5% HCl (20 mL) and extracted with ether (50 mL). The solvents were removed under reduced pressure, and the polymer was precipitated from THF/hexanes (1/5, v/v) to afford **13a** as an orange solid (0.17 g, 89%). ^{1}H NMR ($CDCl_3$): δ 8.88 (s, 1 H, =CH), 7.93 (s, 1 H, Ar), 7.25 (s, 1 H, Ar), 5.45 (s, 2 H, CH_2Ar), 4.16–4.06 (m, 4 H, CH_2OAr), 3.33–3.31 (m, 4 H, CH_2OMe), 3.28 (s, 6 H, Me), 1.79–1.37 (m, 16 H, CH_2's). ^{13}C NMR ($CDCl_3$): δ 162.4 (CO_2), 154.0 (=CH), 149.9, 135.5, 119.9 (Ar C's), 116.3 (CN), 112.8 (Ar C), 110.3, 108.8 (Ar CH's), 100.0 (=C(CN)), 72.2 (CH_2OAr), 69.4 (CH_2OMe), 68.9 (CH_2OMe), 62.9 (CH_2Ar), 58.5 (OCH_3), 29.5, 29.1, 29.0, 26.0, 25.9, 25.8 (CH_2's). IR (CH_2Cl_2): $\nu_{C=O}$ 1737 cm^{-1}. UV–vis (CH_2Cl_2): λ_{max} 414 nm ($\epsilon = 3.59 \times 10^4$).

Preparation of 13b. Polymer **13b** was prepared in a 62% isolated yield similar to the procedure outlined for **13a**. Spectroscopic and analytical data: ^{1}H NMR ($CDCl_3$): δ 7.47–7.36 (m, 10 H, Ar), 7.03 (s, 1 H, =CH), 6.94 (s, 2 H, Ar), 6.92 (s, 1 H, Ar), 5.08 (s, 2 H, CH_2OAr), 5.05 (s, 2 H, CH_2OAr), 3.42 (s, 2 H, CH_2). ^{13}C NMR ($CDCl_3$): δ 162.7 (CO_2), 152.8 (=CH), 150.9, 136.9 (Ar C's), 133.0, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 124.1 (Ar CH's), 116.9 (Ar C), 115.7 (CN), 114.0, 113.3, 113.0, 112.9 (Ar CH's), 70.7 (CH_2OAr), 70.5 (CH_2OAr), 63.9 (CH_2). IR (CH_2Cl_2): $\nu_{C=O}$ 1750 cm^{-1}. UV–vis (CH_2Cl_2): λ_{max} 410 nm ($\epsilon = 1.10 \times 10^3$).

Preparation of 14. A THF (15-mL) solution of **9** (1.0 g, 2.87 mmol) was treated with DMAP (0.70 g, 5.73 mmol) and allowed to react at ambient temperature with constant stirring for 4 h. The reaction mixture was treated with 5% HCl (40 mL) and extracted with ether (50 mL). The solvents were removed under reduced pressure, and the polymer was precipitated from $CHCl_3$/hexanes (1/5, v/v) to afford **14** as a red solid (0.81 g, 86%). ^1H NMR ($CDCl_3$): δ 8.15 (s, 1 H, =CH), 7.31 (s, 2 H, Ar), 4.34 (t, J = 6.6 Hz, 2 H, CH_2OAr), 4.12 (t, J = 6.5 Hz, 2 H, CH_2O_2C), 3.92 (s, 6 H, OCH_3), 1.84–1.54 (m, 8 H, CH_2's). ^{13}C NMR ($CDCl_3$): δ 162.9 (CO_2), 154.9 (=CH), 153.5, 142.2, 126.4 (Ar C's), 116.0 (CN), 108.7 (Ar CH), 101.0 (=*C*(CN)), 73.5 (CH_2OAr), 66.5 (CH_2-OMe), 56.3 (OCH_3), 30.0, 28.5, 25.5, 25.4 (CH_2's). IR (CH_2Cl_2): $\nu_{C=O}$ 1721 cm^{-1}. UV–vis (CH_2Cl_2): λ_{max} 354 nm ($\epsilon = 1.72 \times 10^4$). Anal. Calcd for [$C_{36}H_{44}N_2O_5$]: C, 63.52; H, 6.51. Found: C, 64.07; H, 6.73.

Preparation of 15. A dioxane solution (10-mL) of monomer **10** (0.77 g, 2.0 mmol) and 1,6-diisocyanatohexane (0.34 g, 2.0 mmol) was heated at reflux for 12 h. The reaction mixture was then poured into MeOH to precipitate the polymer. The polymer was further purified by dissolving in dioxane and precipitating in methanol to afford **15** as a bright yellow solid (0.70 g, 61%). ^1H NMR ($CDCl_3$): δ 8.18 (s, 1 H, =CH), 7.32 (s, 2 H, Ar), 4.52–4.39 (m, 4 H, CH_2's), 4.13–4.06 (m, 2 H, CH_2's), 3.92 (s, 6 H, OMe), 3.18 (m, 4 H, CH_2's), 2.20–1.34 (m, 12 H, CH_2's). ^{13}C NMR ($CDCl_3$): δ 162.7 (CO_2), 156.9 (CONH), 155.4 (=CH), 153.5, 142.3, 126.4 (Ar C's), 115.8 (CN), 108.7 (Ar CH), 73.6 (CH_2OAr), 64.7 (CH_2O_2C), 62.0 (CH_2O), 56.3 (OCH_3), 45.4 (CH_2NH), 39.9, 30.1, 29.9, 28.9, 26.3, 26.2, 25.4 (CH_2's). IR (CH_2Cl_2): $\nu_{C=O}$ 1723 cm^{-1}. UV–vis (CH_2Cl_2): λ_{max} = 356 nm ($\epsilon = 6.95 \times 10^3$).

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