

Synthesis and Characterization of Photorefractive Polymers Containing Transition Metal Complexes as Photosensitizer

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Abstract: This paper reports detailed synthesis and characterization of a hybridized polymer system which combines the ionic transition metal complexes and a conjugated polymer backbone bearing NLO chromophores to manifest a large photorefractive (PR) effect. In this system, the conjugated polymer backbone was chosen to play the dual role of a transporting channel for the charge carriers and a macroligand to chelate with the transition metal complex. Ru(II)–tri(bispyridyl) complexes were chosen as the photocharge generator by utilizing their metal-to-ligand charge transfer properties. The Heck coupling reaction was applied to synthesize these multifunctional polymers. A large net optical gain ($>200 \text{ cm}^{-1}$) at a zero electric field was observed on poled samples. The synthetic approach is versatile and was extended to the synthesis of PR polymers containing Os complexes. The resulting polymer showed photorefractivity at a wavelength in the near IR region (780 nm). This approach also offers the opportunity to fine-tune the electronic properties of polymers through modification of the polymer structures. Model reactions were studied to elucidate the structural defects caused by the side reactions in the Heck reaction. The effects of these defects on the PR performance of these polymers were evaluated. It was demonstrated that eliminating these defects could enhance the photorefractive response time.

Organic photorefractive (PR) materials have recently attracted attention not only due to their potential for practical applications, such as in optical signal processing and information storage, but also due to the fundamental challenge in identifying the basic principles of the preparation or synthesis of these materials.¹ The photorefractive effect involves the modulation of the index of refraction of a material by a space charge field via the electro-optic effect.² This space charge field arises from the redistribution of charges in a photoconductor when it is illuminated with a nonuniform light intensity pattern. Since the change of the refractive index is proportional to the magnitude of the space charge field, the generation of a large space charge field is crucial for a high PR performance. The formation of a space charge field involves three processes: the generation of free charge carriers, their transport, and eventually trapping by a trapping center. Therefore, in order to build up a large space charge field, the optimization of these three processes is essential.

The photorefractive effect was discovered in a ferroelectric inorganic crystal (LiNbO_3) 30 years ago.² Since then, numerous crystals such as BaTiO_3 , $\text{Bi}_{12}\text{SiO}_{20}$ (BSO), $\text{Sr}_x\text{Ba}_{1-x}\text{NbO}_3$, etc. have been demonstrated to possess photorefractivity.^{3,4} In the majority of these oxygen-octahedral ferroelectrics with a

pronounced photorefractive effect, $\text{Fe}^{2+}/\text{Fe}^{3+}$ impurities play the most important role as electron donor and trapping centers. It is believed that the photoinduced interconversion of $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$ and the efficient band transporting of the free charge carriers are responsible for the buildup of space charge fields.

Unlike their inorganic counterparts, organic PR materials lack such mechanisms for the formation of the photoinduced space charge field.^{1a} The photogeneration of the charge carriers is accomplished through exciton dissociation. Free charge carriers are transported away through a hopping mechanism along a series of transporting molecules. Because of the low dielectric constant and numerous channels for the relaxation of excited states to ground states, the quantum yield for the charge generation in organic materials is usually low. To address these problems, we recently designed a new photorefractive polymer system which contains multivalent transition metal complexes (Ru^{2+} or Os^{2+} complexes) and conjugated polymer backbones.

In this system, the conjugated polymer backbone was chosen to play the dual role as the transporting channel for the charge carriers and the macroligand to chelate with the transition metal complex. It is well-known that doped conjugated polymer systems have high electrical conductivities, and charge transporting in the polaron or bipolaron states which reside in the forbidden gap could be also very efficient.^{5,6} Therefore, a conjugated backbone could provide an efficient charge transporting pathway and could facilitate the formation of the space charge field.

Ru(II)–tri(bispyridyl) complexes were chosen as a photocharge generator. $\text{Ru}(\text{bpy})_3^{2+}$, and its derivatives are known to exhibit interesting metal-to-ligand charge transfer (MLCT) processes, and their photochemistry, photophysics, electrochemistry, and electron/energy transfer properties have been exten-

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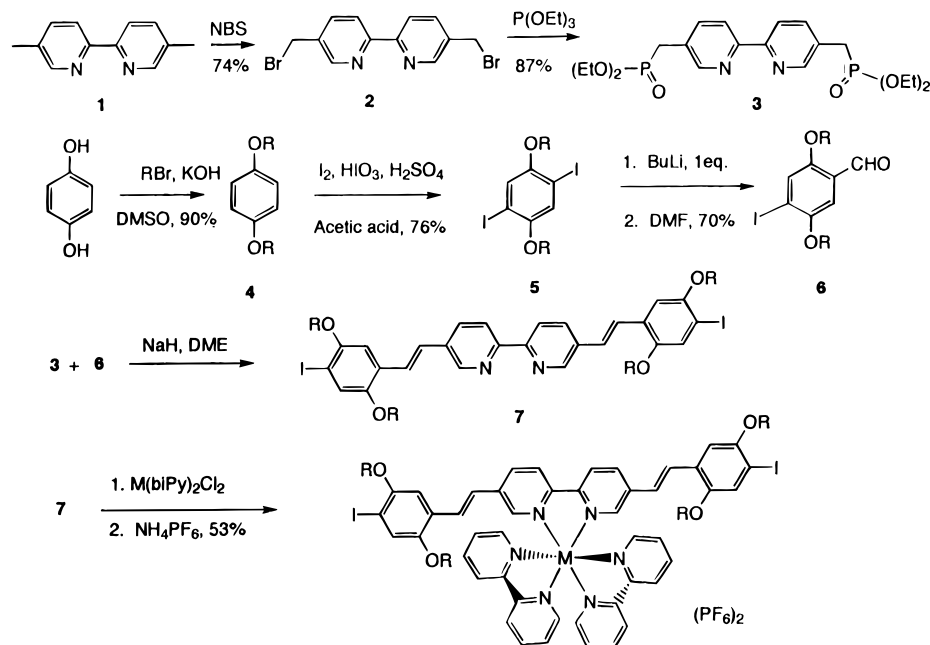
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Scheme 1. Synthesis of Monomers **A** and **B** Containing Transition Metal Complexes

Monomer **A**: $M = \text{Ru}$.
 Monomer **B**: $M = \text{Os}$.

sively studied.⁷ They have also been extensively studied as light-harvesting materials, materials which can reduce water into hydrogen when coupled with other components.⁸ To utilize their interesting charge transfer properties in the synthesis of PR polymers, Ru(II) complexes were designed to chelate with the conjugated polymer backbone. Upon excitation in the region of the MLCT transition of the Ru complex, electrons would be injected into the polymer backbone (equivalent to n-doping of PPV), transported away through either intrachain migration or interchain hopping and eventually trapped by the trapping centers which could be impurities or structural defects. We envision that the combination of the efficient MLCT process of the ruthenium complexes and the efficient charge transporting process of the conjugated backbone will lead to a higher charge separation efficiency and therefore to a better PR performance in this new PR polymer system than our previous ones.^{1f} Experimental results confirmed that the incorporation of the Ru complex into the PR polymers dramatically enhanced the PR performances of the resulting polymers. This approach is versatile and has been extended to synthesize PR polymers containing Os complexes, which have shown photorefractivity at a wavelength in the near IR region. This paper reports the detailed synthetic effort and the physical studies of this new PR polymer system.

Results and Discussion

Since the targeted polymer is a multifunctional polymer which contains conjugated systems, NLO chromophores, and ionic transition metal complexes, a reaction which can tolerate all of these functionalities and possesses a high yield should be utilized for the polymerization. From our previous studies and the work of other groups,⁹ the Heck coupling reaction is found to be versatile in synthesizing conjugated polymers. Its mild reaction

condition and tolerance for a variety of functional groups are especially useful for synthesizing such functional polymers. We have previously demonstrated that the Heck coupling reaction can be utilized to synthesize conjugated polymers containing ionic transition metal complexes, and the resulting polymer exhibits enhanced photoconductivity.¹⁰ That work is the basis for the design of our new PR polymers.

Synthesis of the Monomers and Polymers. To utilize the Heck reaction, Ru complexes bearing diiodofunctional groups were synthesized according to Scheme 1. 5,5'-Dimethyl-2,2'-bipyridine was synthesized by the Raney nickel catalyzed self-coupling of 3-picoline.¹¹ Compound **6**, a crucial compound in this approach, was synthesized by reacting compound **5** with 1 equiv of butyllithium and subsequently quenching with DMF. The reaction of compound **3** with compound **6** under the Horner–Wittig–Emmons (HWE) reaction condition yielded compound **7**. The final ruthenium (or osmium) complex (monomers **A** or **B**), soluble in common organic solvents, was prepared after refluxing compound **7** with Ru(bipy)₂Cl₂ (or Os(bipy)₂Cl₂) and was easily purified by recrystallization from THF/hexane.

Monomer **C** was synthesized by using the approach outlined in Scheme 2. This monomer contains an alkoxy substituent which was introduced to increase the solubility of the resulting conjugated polymers: the polymer without this substituent was insoluble in common organic solvents due to the strong interchain π – π interactions.¹²

The polymerization was carried out according to Scheme 3 where Pd(OAc)₂/P(*o*-tolyl)₃/NEt₃ (0.04:0.2:2.5 mol ratio relative to divinyl benzene) was applied as the catalytic system.

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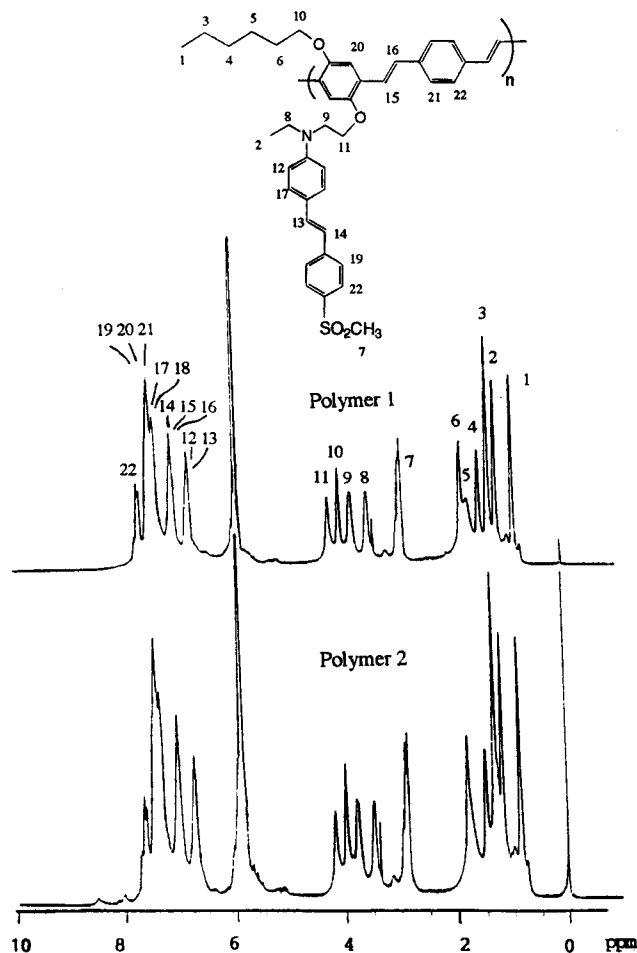
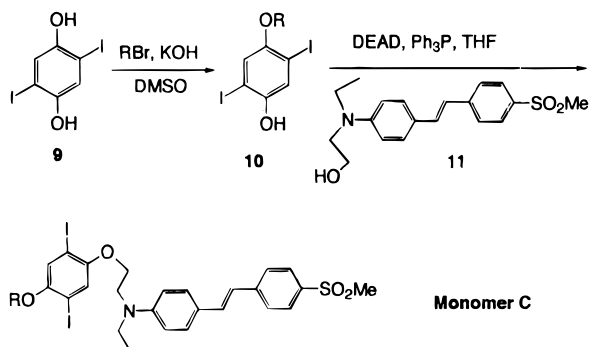


Figure 1. ^1H NMR spectra of polymers 1 and 2.

Scheme 2. Synthesis of Monomer C



Polymers soluble in tetrachloroethane, DMF, and NMP were obtained in excellent yields.

Structural Characterization. Polymers 1 and 2 are insoluble in THF and chloroform but soluble in tetrachloroethane (TCE), DMF, NMP, etc. Their intrinsic viscosities were measured to be 0.46 and 0.53 dL/g, respectively, in NMP at 30 °C, indicating that reasonably high molecular weights were obtained. High optical-quality films with thicknesses over 30 μm were cast from their TCE solutions.

The ^1H NMR spectra of polymers 1 and 2 in tetrachloroethane- d_4 are shown in Figure 1. These two polymers exhibit very similar ^1H NMR spectra. As assigned in Figure 1, the major peaks correspond to the protons of the chromophore and the divinyl benzene moieties. However, the chemical shifts due to the protons of the bipyrindyl ligand at 8.0 and 8.5 ppm are still noticeable for polymer 2, indicating the incorporation of

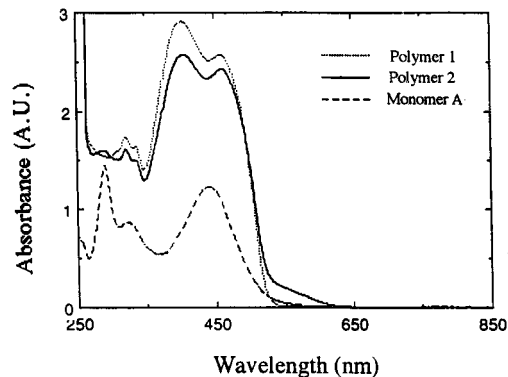


Figure 2. UV/vis spectra of monomer A and polymers 1 and 2.

the ruthenium complex into the polymer. Elemental analyses also support the incorporation of the ruthenium complex.

The UV/vis spectra of the polymers are shown in Figure 2. Both polymers 1 and 2 exhibit two major peaks: one at 390 nm which is due to the absorption of the NLO chromophore, the other at 460 nm which is attributed to the absorption of the conjugated backbone. However, for polymer 2, there is also an absorption tail extending beyond 600 nm, which can be assigned to the metal-to-ligand charge transfer absorption of the ruthenium complexes. This is further evidence of the incorporation of the ruthenium complex into the polymer. It also indicates that the introduction of the ruthenium complex extends the photosensitivity of the polymer to the region of longer wavelengths. By using a diode laser (i.e., 690 nm), we can photoexcite the polymer mainly through the MLCT process, while the absorptions due to the NLO chromophore and the conjugate backbone are minimized. It can be noted that a small peak at 290 nm, due to the ligand-centered transition of the two bipyrindyl ligands in the ruthenium complexes, exists for polymer 2 while polymer 1 does not have this absorption.

DSC studies showed that polymers 1 and 2 have a similar glass transition temperature at ca. 130 °C. The main chain melting temperature for polymers 1 and 2 was observed at 215 °C, overlapping with the cross-linking temperature of the conjugated polymer backbone.¹³ TGA analysis showed that polymer 1 was stable up to 350 °C, while polymer 2 showed a small weight loss starting at 270 °C, caused by the loss of the bipyrindyl ligands in the ruthenium complexes.

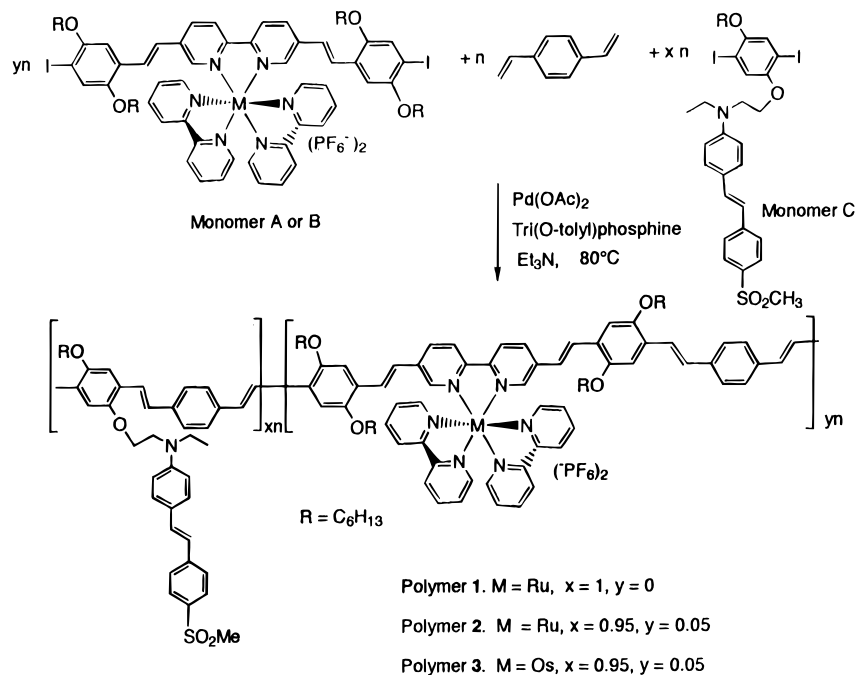
Physical Characterization. The second-order nonlinearity of the poled polymers was demonstrated by the second harmonic generation (SHG) measurements. After corona poling, a SHG coefficient, d_{33} , of 70 pm/V for polymer 2 was obtained at 1064 nm. The poled polymer films also exhibited reasonable thermal and temporal stabilities in their optical nonlinearity. It was found that the SHG signal of polymer 2 was stable up to 80 °C. When the poled polymer film was kept at 60 °C, the SHG signal stabilized at a value of 80% after an initial drop. This stability of the nonlinearity allowed us to perform the photorefractive experiments without applying an external electric field.

To further demonstrate the electro-optic effect, the EO coefficient of polymer 2 was measured using a reflection method.¹⁴ An E-O coefficient of 7 pm/V was obtained at 690 nm, which is relatively high compared with other photorefractive polymers.^{1a} This large nonlinearity arises from the large NLO chromophore concentration in the polymers (~50 wt %).

The photoconductivity of the polymers, another necessary condition for PR effect, was also measured at a wavelength of

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Scheme 3. Synthesis of Polymers **1**, **2**, and **3**

690 nm. As expected, polymer **2** exhibited large photoconductivity. A photoconductivity of 3×10^{-10} s/cm (laser intensity 6.17 mW/cm²) and a photocharge generation efficiency of 0.2% were obtained under an external electric field of 950 kv/cm. This is a significant improvement compared to our previous polymers.¹⁵

To study the PR effect, an effective technique is the two beam coupling experiment which is regarded as the standard experiment to confirm the PR response. We performed the two beam coupling experiment at 690 nm (diode laser, s-polarized). The normal of the sample was rotated 35° with respect to the bisector of the writing beams to obtain a nonzero projection of the EO coefficient. The dynamics of the grating formation in poled polymer **2** at a zero external electric field is shown in Figure 3. The transmitted beam intensities were measured with lock-in amplifiers (the time constant of the lock-in amplifiers was set at 10 ms), and the data were collected by a computer. At the time of 20 s, the two laser beams were overlapped at a pristine spot inside the polymer film. Notice that the intensity of one beam, as a function of time, kept increasing while that of the other decreasing. The gain and loss was calculated (the ratio of the two incident beam intensities was 1.12) according to the equation:

$$\Gamma = \frac{1}{L} \ln \left(\frac{1 + \alpha}{1 - \beta a} \right)$$

where α is the ratio of the intensity modulation ($\Delta I/I_s$) and β is the intensity ratio of the two incident laser beams (I_s/I_q). It was found that polymer **2** exhibited an optical gain higher than 300 cm⁻¹. At the time of 700 s, the pump beam b was blocked, and the transmitted intensity of the other beam returned to the initial value. When the sample was rotated 180° along its axis, the gain and the loss beams were switched due to the reversal of the dipole orientation. This is a clear indication that the grating is indeed of a photorefractive nature, although the process is rather slow. The deep trap centers might be responsible for the slow response time.

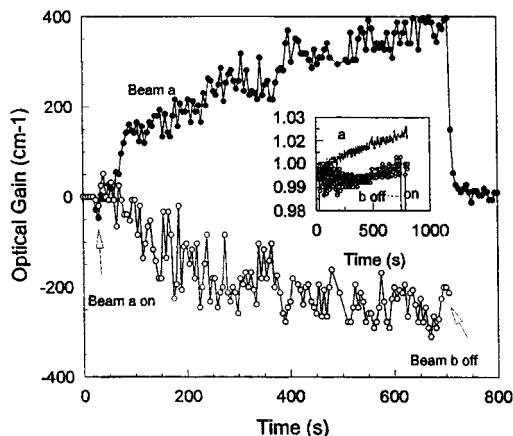


Figure 3. Grating formation dynamics of polymer **2** and polymer **1** (inset) in 2BC experiments.

By utilizing a grating-translation technique, the phase of index grating can be studied.¹⁶ This experiment can furnish further evidence for the photorefractive effect. After forming the grating by intersecting the two laser beams inside of the polymer film for a few minutes, the sample was translated along the direction parallel to the grating wave vector. The transmitted intensities of the two beams exhibit an oscillating pattern which reflects the spacing and phase of grating. It was found that a 90° phase shift of the index grating over the intensity distribution exists for polymer **2**. This result verified the photorefractive nature of the grating. Since polymer **2** exhibits an absorption coefficient of 102 cm⁻¹, a large net optical gain is obtained in this polymer at a zero external electric field.

Polymer **1**, without Ru complexes, did not show clear photorefractivity. As shown in the inset of Figure 3, blocking beam **b** had no effect on the transmitted intensity of beam **a**, which implies that there was no asymmetric energy exchange between the two beams.

Synthesis of Near-IR Sensitive PR polymers. The synthetic approach described above is versatile and can be applied to

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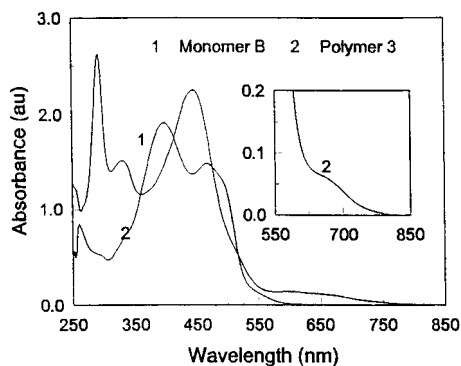


Figure 4. UV/vis spectra of monomer **B** and polymer **3**.

synthesize other metal-containing polymers, such as polymers containing Os complexes. The advantage of utilizing the Os complex as a photosensitizer is that the Os complex has a spin-allowed ¹MLCT transition at 450 nm and an extremely broad (over 200 nm bandwidth) spin-forbidden ³MLCT transitions at around 640 nm (e.g., see Figure 4, the UV/vis spectrum for monomer **B**).⁷ The broad absorption which extends beyond 750 nm is very useful for the design of IR sensitive materials. If we polymerize the Os complex into the conjugated PPV polymer system, the resulting polymer could show photorefractivity at wavelengths in the near-IR regions (for example at 780 nm).

The Os complex (monomer **B**) was synthesized by reacting the ligand (compound **7** in Scheme 1) with Os(II)(bpy)₂Cl₂, which was prepared according to a literature procedure.¹⁷ The resulting Os complex is a black, shiny powder, soluble in common organic solvents such as chloroform, THF, methylene chloride, etc.

For the purpose of comparison, a polymer with the same molar composition (5 mol % Os complex) as polymer **2** was synthesized (polymer **3**), using the Heck reaction with similar conditions. Polymer **3** is a dark powder which is soluble in NMP, DMF, etc. The incorporation of the Os complex into the polymer backbone can be clearly seen from its UV/vis spectrum. As shown in Figure 4, there is an absorption tail extending to 600 nm, which can be assigned to the spin allowed transition of the Os complex. The inset of Figure 4 is the UV/vis spectra of the concentrated solution of polymer **3**. It clearly shows that polymer **3** has an absorption tail extending to near 800 nm.

This polymer has a glass transition temperature of 110 °C and a cross-linking temperature of 175 °C. TGA analysis showed two weight losses, one at around 240 °C and the other at 310 °C. The first weight loss (6%) is due to the decomposition of the Os complex, supported by the studies on the complex, while the second one is caused by the decomposition of the backbone.^{9d}

In order to study the PR effect of polymer **3**, we performed the two beam coupling experiment at 780 nm (30 mW, s-polarized) on a corona poled polymer film with a thickness of 5.09 μm. The sample was tilted 30° and the angle between the two incident laser beams was θ (= 46.4°), which gave a grating spacing ($\Lambda = \lambda/4\pi\sin(\theta/2)$) of 0.24 μm (the polymer has a refractive index of 1.7486 at 780 nm). The results are shown in Figure 5 where the data were taken under zero external field after overlapping the two laser beams inside the sample for four to five minutes. The asymmetric energy exchange was

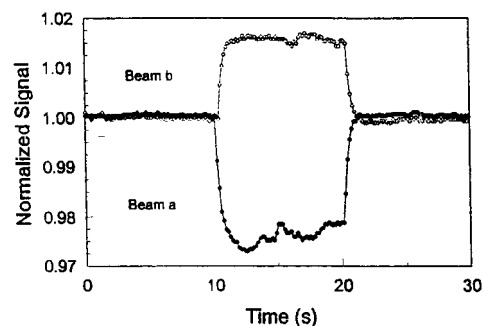
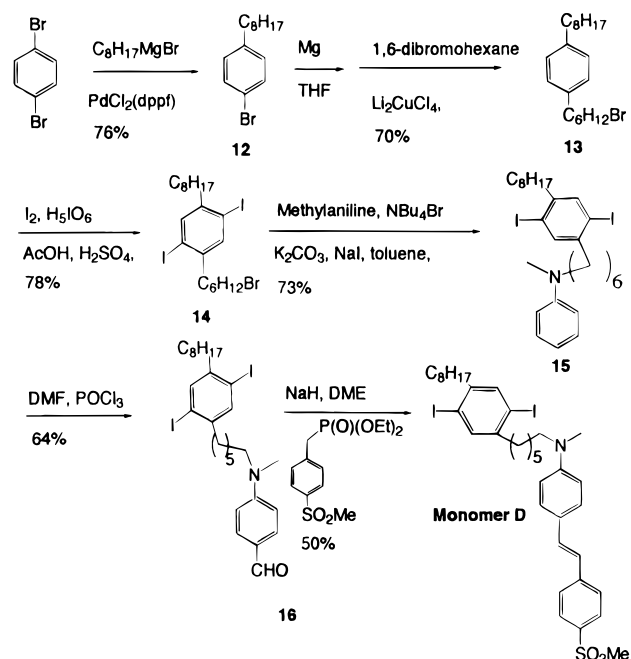


Figure 5. Asymmetric energy exchange in the 2BC experiment for polymer **3** at zero external field (laser wavelength; 780 nm).

Scheme 4. Synthesis of Monomer **D**

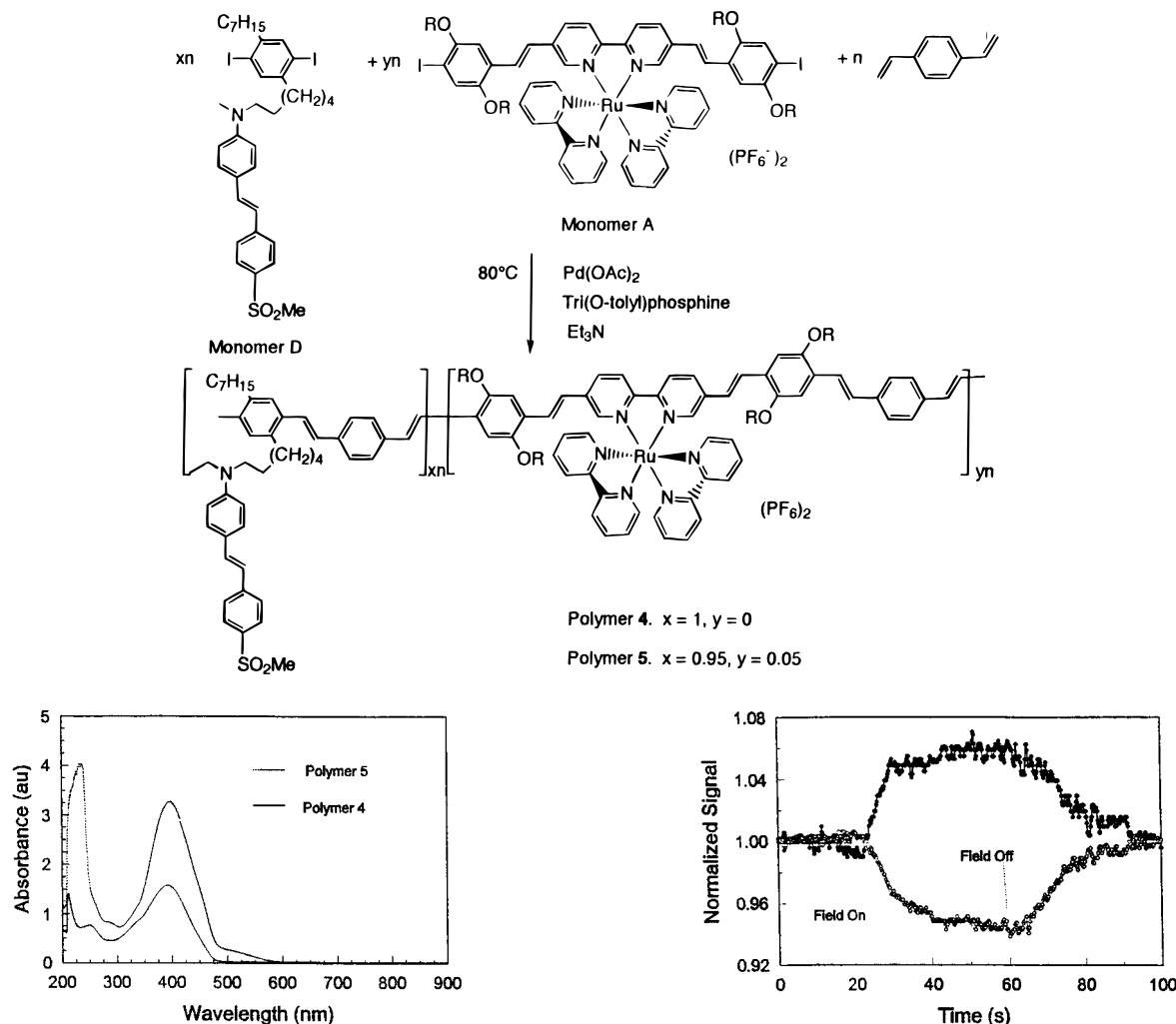


clearly observed and the corresponding optical gain was calculated to be 80 cm⁻¹. Although net optical gain was not obtained in this case (α was measured to be 186 cm⁻¹ at 780 nm), the observation of such a photorefractive response at near-IR region is still very interesting. Net optical gain may be possible for polymers with lower Os complex concentrations.

PR Polymers Based on Alkyl-Substituted PPV. As mentioned earlier, the alkoxy-substituted PPV has a π - π^* transition maximum at 450 nm, overlapping partially with the MLCT transition of the Ru complex. Absorptions at the working laser wavelength (690 nm in the case of polymers containing Ru complex) by the conjugated components will reduce the quantum efficiency for the charge generation and should be minimized. It is known that the π - π^* transition of alkyl-substituted PPVs occurs at shorter wavelengths. By changing the alkoxy substitutes in polymer **2** to alkyls, we should be able to decrease the absorption of the PPV backbones significantly. For this purpose, a new chromophore (monomer **D**) was synthesized as shown in Scheme 4. The polymer structures are shown in Scheme 5. Two polymers were synthesized: polymer **4** without a Ru complex and polymer **5** with 5 mol % Ru complexes.

Unlike polymers **1** and **2**, polymers **4** and **5** are soluble in chloroform and THF. Their molecular weights were measured by GPC (polystyrene as standard) to be 21 kdalton (Mn, PD = 2.8) and 18 kdalton (Mn, PD = 2.25), respectively. The incorporation of the Ru complex into the polymer backbone

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Scheme 5. Synthesis of Polymers **4** and **5****Figure 6.** UV/vis spectra of polymers **4** and **5**.

was again proved by the 1H NMR spectra typical chemical shifts at 8.0 and 8.5 ppm due to the bipyridyl ligand protons and at 4.0 ppm due to the $-OCH_2-$ protons were observed for polymer **5**.

The UV/vis spectra of the polymers are shown in Figure 6. The absorption due to the PPV backbone overlaps with that of the chromophores, both systems having a maximum at around 380 nm. Again, polymer **5**, unlike polymer **4**, has an absorption tail extending beyond 600 nm. Since both the chromophores and the PPV backbones essentially have no absorption beyond 500 nm, a much smaller absorption coefficient (21.5 cm^{-1}) was obtained for polymer **5**.

Polymers **4** and **5** have a relatively low glass transition temperature of $75^\circ C$. Consequently their SHG stability is not as good as polymers **1** and **2**. However, we were able to prepare thick films sandwiched between two ITO coated glasses. Two beam coupling experiments were carried out by applying external fields across the sandwiched sample. As shown in Figure 7, when an electric field (1000 V over $75\ \mu m$ thick film) was applied at 20 s, the transmitted intensity of one beam increased, while that of the other beam decreased with a response time of 10 s. Energy exchange of more than 5% between the two beams was observed, giving an optical gain of 16 cm^{-1} . When the field was turned off at 60 s, the intensities of the two beams returned to their original values gradually during a period of 20 s. Considering the small field applied (less than $15\text{ V}/\mu m$), one would expect higher optical gain values

Figure 7. Two beam coupling results for a thick film made from polymer **5**.

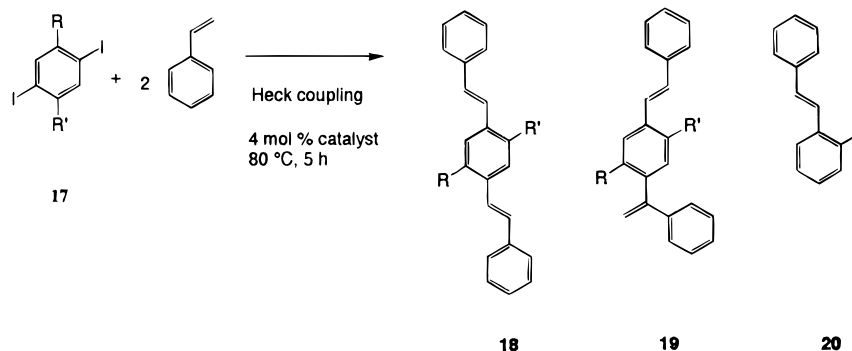
if higher electric fields could be applied. Further studies are in progress.

Study of the Structural Defects in the Heck Reaction and Their Effects on the Photorefractivity. It was found that the 1H NMR spectra of all of our polymers synthesized by the Heck reaction exhibited small peaks which could not be removed by any purification process. For example, as shown in Figure 1, small peaks at 0.82, 1.02, and 5.30 ppm exist. It is known that the Heck reaction involves many side reactions which clearly introduces defects into the conjugated backbone.¹⁸ These defects may play the role of deep trapping centers and thus exert a profound effect on the PR performance of the polymers. To identify the structural defects in the conjugated polymers synthesized by the Heck reaction, we carried out model reactions involving similar monomers and styrene as shown in Scheme 6.

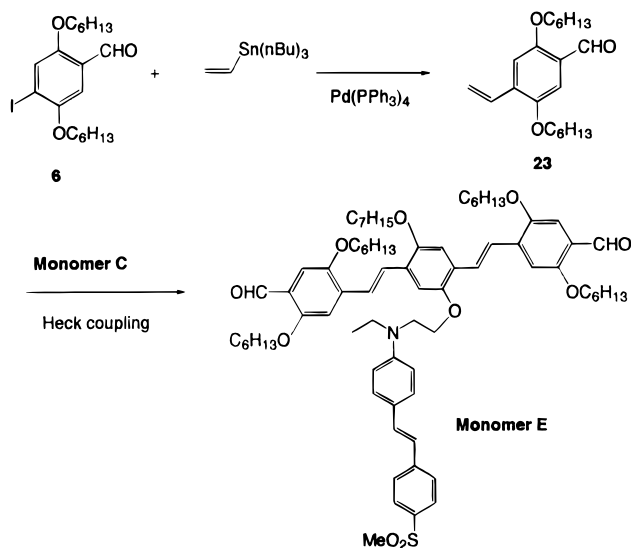
Three diiodo compounds were used to run the model reactions. After completion of the reactions, the mixtures were poured into aqueous solution (5% HCl) and extracted with ethyl ether. The 1H NMR spectra of the mixtures were collected. Based on the spectra, the relative yields of the products were calculated. The results are shown in Table 1.

Within 5 h, the coupling reactions were completed for all three model reactions. No proton peaks corresponding to the

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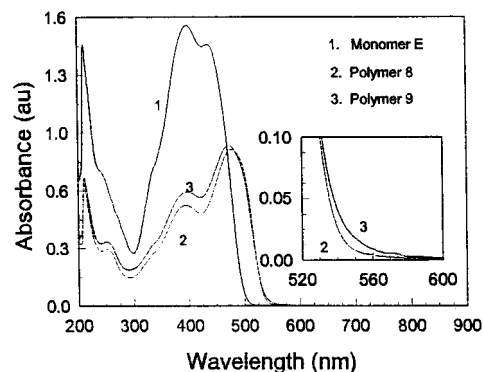
Scheme 6. Model Reactions via the Heck Coupling**Table 1.** Yields of the Products in the Model Reaction

Entries	R	R'	18	19	20
a	OC ₆ H ₁₃	OC ₆ H ₁₃	85	14	1
b	C ₆ H ₁₃	C ₆ H ₁₃	92	8	...
c	OC ₇ H ₁₅		90	10	...

Scheme 7. Synthesis of Monomer E

diiodo-starting material were observed in the ¹H NMR of the reaction mixtures. It was found that a significant amount of the α -substituted product **19** was obtained in all three cases. The small peaks mentioned above in the ¹H NMR spectra of polymers (polymers **1** and **2**) correspond well to the α -substituted structural moieties. These α -substituted units break the conjugation and therefore form structural defects. However, the defect densities in the polymers are much smaller than those observed in the model reactions, as indicated by the integrations of ¹H NMR spectra. The exact reason is not clear.

To study the effects of these defects on the polymer properties, we synthesized the ruthenium complex-containing PR polymers via the Horner–Wadsworth–Emmons (HWE) reaction, by which the α -coupling structures can be avoided. It is known that tetraethyl xylenebisphosphonate reacts with benzaldehyde resulting in only *trans*-products.¹⁹ In addition, the phosphorus product is a phosphate ester and hence soluble in water, making it easy to separate it from the olefin product. We found that the HWE reaction gave all-*trans* linear conjugated polymers.²⁰

**Figure 8.** UV/vis spectra of polymers **6** and **7**.

As shown in Scheme 7, we utilized the Heck reaction to synthesize monomer **E** from monomer **C**. Considering the uncertainty of the Ru complex under the harsh reaction condition of the HWE reaction (a strong base was used), we chose to synthesize the conjugate polymer first and then coordinate with the ruthenium complex. This approach, of course, lacks the certainty regarding the yield of the coordination of the ruthenium complexes.

As shown in Scheme 8, polymer **6** was synthesized as a red powder. THF was found to be the best solvent for the polymerization, and the polymer precipitated out of the reaction mixture in several hours. The final coordination step was carried out in THF. The resulting polymer **7** displayed much better solubility in THF, chloroform, etc. than polymer **6**.

The ¹H NMR spectrum of polymer **7** showed that a linear conjugated polymer was obtained. The side peaks corresponding to the α -adducts were not observed. However, the incorporation of the Ru complex is not evident in the ¹H NMR spectrum. But the UV/vis spectra do provide some structural information. As shown in Figure 8, polymer **7** showed a backbone absorption maximum at 474 nm, slightly blue-shifted compared to polymer **6** (477 nm), and an absorption tail extending near 600 nm. These results imply that some coordination of the ruthenium complex indeed occurred. More evidence of the coordination comes from the elemental analysis: 0.09% ruthenium was found in the polymer, which accounts for 12% of the dipyrindyl site. This low coordination ratio could be due to the poor solubility of polymer **6**.

Preliminary two beam coupling studies gave encouraging results. As shown in Figure 9, a response time of less than 150 s and an optical gain of 99 cm⁻¹ were obtained. The photorefractive response time is faster than that of our previous PR polymers made by the Heck reaction (over 500 s), although such a comparison should be considered with caution. The smaller optical gain could be due to the incomplete coordination of the ruthenium complexes.

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Scheme 8. Synthesis of Polymers 6 and 7 via HWE Reaction

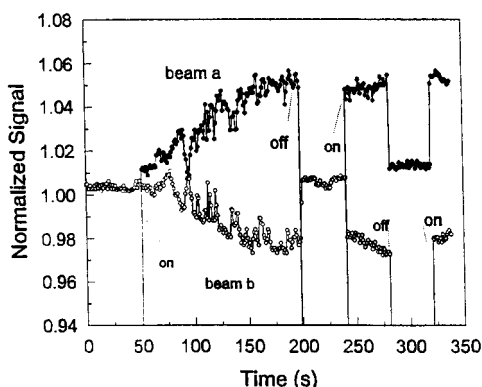
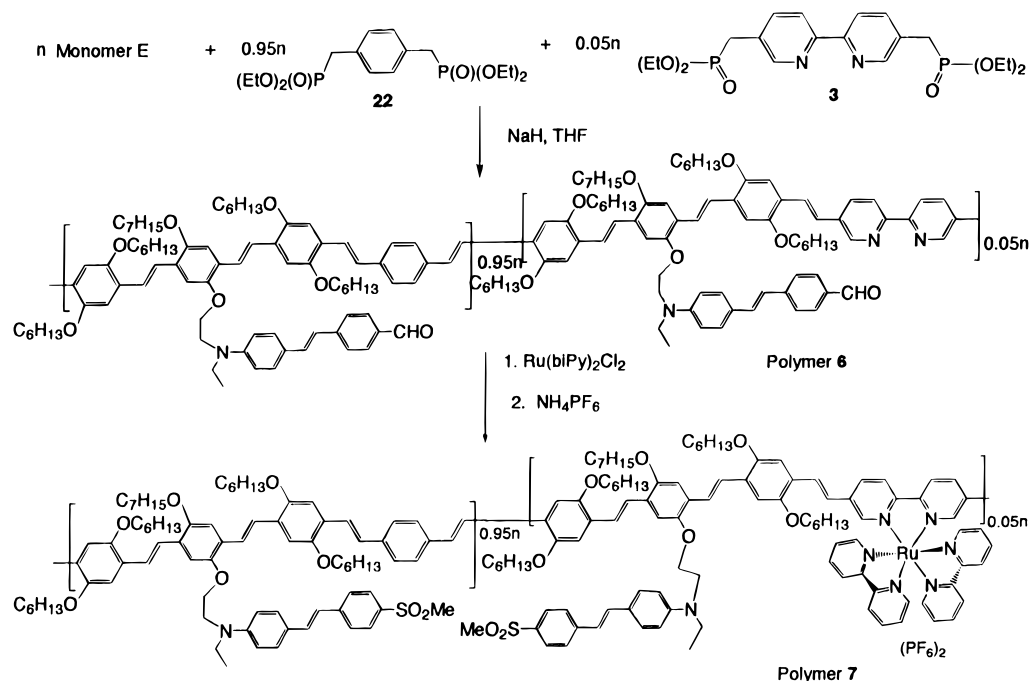


Figure 9. Grating formation dynamics in the 2BC experiment for polymer 7.

Conclusions

We have demonstrated that the hybridized polymers, which combine the ionic transition metal complexes and a conjugated polymer backbone bearing NLO chromophores, exhibited large photorefractivity. In this system, the conjugated polymer backbone was designed to play the dual role of both transporting channel for the charge carriers and the macroligand to chelate with the transition metal complex. The Ru(II)-tri(bispyridyl) complex was selected as the photocharge generator because of its metal-to-ligand charge transfer properties. The Heck coupling reaction was successfully applied to synthesize these multifunctional polymers. A large net optical gain ($> 200 \text{ cm}^{-1}$) at a zero external electric field was observed. The synthetic approach is versatile and was extended to the synthesis of PR polymers containing Os complexes. The resulting polymer showed photorefractivity at a wavelength in the near IR region. This approach also offers the opportunity to fine-tune the electronic properties of polymers through easy modification of the polymer structures. Model reactions were studied to elucidate the structural defects caused by the side reactions of the Heck reaction. The effects of these defects on the PR performance of these polymers were evaluated. It was demonstrated that elimination of these defects could enhance the photorefractive response time. These results indicate that this

approach is promising and warrants further exploration. This work also revealed a dilemma in choosing polymerization approaches. The Heck reaction can unambiguously assure the coordination of the transition metal complex, but it introduces undesired structural defects in the conjugated backbone. While HWE reaction minimizes the structural defects in the conjugated backbone, it cannot guarantee complete coordination. Therefore, a new polymerization method which not only can tolerate transition metal complex but also give defect-free linear conjugate polymer chain is needed.

Experimental Section

THF and ethyl ether were purified by distillation over sodium chips and benzophenone. Styrene was distilled over calcium hydride. The *p*-divinylbenzene was separated from a mixture of *p*-divinylbenzene and *m*-divinylbenzene according to the literature procedure.²¹ All of the other chemicals were purchased from Aldrich Chemical Co. and used as received unless otherwise stated.

Syntheses of Monomers. The following compounds were synthesized according to literature procedures: 5,5'-dimethyl-2,2'-bipyridine **1**,¹¹ compound **2**,²² compound **5**.²³

Compound 3. The mixture of compound **2** (3.00 g, 8.77 mmol) and P(OEt)₃ (4.37 g, 26.3 mmol) was stirred at 125 °C for 4 h. The excess P(OEt)₃ was distilled out, and the residual solid was recrystallized from chloroform/hexane to give 3.50 g of compound **3** (87%, mp 99–100 °C). ¹H NMR (CDCl₃, ppm): δ 1.27 (m, 12 H, -CH₃), 3.16 (d, $J = 21.71$ Hz, 4 H, -CH₂P-), 4.03 (m, 8 H, -OCH₂-), 7.73 (d, $J = 8.16$ Hz, 2 H, aromatic protons), 8.27 (d, 8.07 Hz, 2 H, aromatic protons), 8.50 (s, 2 H, aromatic protons). Anal. Calcd for C₂₀H₃₀N₂O₆P₂: C, 52.63; H, 6.62; N, 6.14. Found: C, 52.44; H, 6.54; N, 6.07.

Compound 6. BuLi (14.33 mL, 2.5 M solution in hexane, 35.82 mmol) in ether (50 mL) was added dropwise into an ether solution containing 2,5-dialkoxy-1,4-diiodobenzene ($R = \text{C}_7\text{H}_{15}$, 20.00 g, 35.82 mmol, 75 mL ether) at 0 °C. After addition of BuLi was completed, DMF (3.93 g, 53.76 mmol) in 15 mL of ether was added dropwise into the solution. The resulting mixture was stirred at room temperature for 2 h and then poured into water (200 mL). The ether layer was washed three times with water and dried over MgSO₄. The ether was

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then removed by vacuum evaporation. The resulting liquid was dissolved in hexane and refrigerated. Compound **6** crystallized out of the solution (10.70 g, 65% yield, mp 51.5–52 °C). ¹H NMR (CDCl₃, ppm): δ 0.89 (t, *J* = 6.56 Hz, 6 H, –CH₃); 1.31 (m, 8H, –CH₂CH₂–CH₃); 1.36 (m, 4H, –CH₂CH₂CH₂CH₃); 1.46 (m, 4 H, –CH₂CH₂CH₂–CH₂CH₃); 1.80 (quartet, *J* = 6.89 Hz, 4H, –OCH₂CH₂–); 3.97 (t, *J* = 5.47 Hz, 2 H, –OCH₂–); 3.99 (t, *J* = 5.65 Hz, 2 H, –OCH₂–); 7.14 (s, 1 H, aromatic proton, ortho to CHO); 7.4 (s, 1 H, aromatic proton, meta to CHO); 10.34 (s, 1H, –CHO). ¹³C NMR (CDCl₃, ppm): 14.2, 22.8, 26.1, 29.2, 29.3, 31.9, 69.6, 70.0, 108.9, 124.6, 125.3, 152.3, 155.9, 189.2. Anal. Calcd for C₂₁H₃₃O₃I: C, 54.79; H, 7.22; I, 27.56. Found: C, 54.86; H, 7.21; I, 27.49.

Compound 7. Sodium hydride (0.24 g, 9.81 mmol) was added to a solution of compound **6** (3.01 g, 6.65 mmol) in DME (20 mL). The resulting suspension was stirred for 5 min. Compound **3** (1.49 g, 3.27 mmol) in DME (10 mL) was then added dropwise at room temperature. The mixture was refluxed overnight. After the solution cooled down to room temperature, water was added. The resulting mixture was stirred for 5 min, and the crude product was separated by filtration. Recrystallization from dichloromethane/methanol gave 2.20 g of pure compound **7** (83%, mp 84–85 °C). ¹H NMR (CDCl₃, ppm): δ 0.9 (m, 12 H, –CH₃); 1.3–1.9 (m, 40H, aliphatic protons); 3.95 (t, *J* = 6.2 Hz, 4 H, –OCH₂–); 4.01 (t, *J* = 6.2 Hz, 4 H, –OCH₂–); 6.99 (s, 2 H, aromatic protons meta to iodo); 7.10 (d, *J* = 16.47, 2 H, vinyl protons); 7.26 (s, 2 H, aromatic protons ortho to iodo); 7.44 (d, *J* = 15.56 Hz, 2 H, vinyl protons); 7.92 (dd, *J* = 8.42 (1.73) Hz, 2 H, 4-pyridine protons); 8.34 (d, *J* = 8.24 Hz, 2 H, 3-pyridine protons); 8.71 (s, 2 H, 2-pyridine protons). ¹³C NMR (CDCl₃, ppm): 14.4, 22.8, 26.3, 29.3, 29.5, 32.0, 69.6, 70.3, 86.9, 110.0, 120.9, 123.7, 125.5, 126.8, 133.4, 148.3, 151.6, 152.3, 154.6. Anal. Calcd for C₅₄H₇₄N₂O₄I₂: C, 60.67; H, 6.98; N, 2.62. Found: C, 60.90; H, 6.93; N, 2.59.

Monomer A. A solution of 0.1500 g of compound **7** (0.14 mmol) in 10 mL of methoxyethanol was heated to 100 °C. *cis*-dichlorobis-(2,2'-bipyridine)ruthenium(II) hydrate (0.0679 g, 0.14 mmol) in ethanol (10 mL) was added. The ethanol was evaporated, and the resulting solution was stirred at 140 °C for 3 h. After cooling to room temperature, the solution was added into a solution of (NH₄)PF₆ (0.2283 g) in water (50 mL). An orange solid was collected by filtration and recrystallized from THF/hexane to give 0.1300 g of the desired product. (53%, mp 234–235 °C). ¹H NMR (CDCl₃, ppm): δ 0.86 (t, *J* = 6.56 Hz, 12 H, –CH₃); 1.28–1.78 (m, 40 H, aliphatic protons); 3.87–4.01 (m, 8H, –OCH₂–); 6.93 (d, *J* = 16.45 Hz, 2 H, vinyl protons); 7.07 (s, 2 H, aromatic protons meta to iodo); 7.20 (s, 2 H, aromatic protons ortho to iodo); 7.38 (d, *J* = 16.44 Hz, 2H, vinyl protons); 7.47 (t, *J* = 6.63 Hz, 2H, aromatic protons on the dipyridine ligand); 7.51 (t, *J* = 6.22 Hz, 2 H, aromatic protons on the dipyridine ligand); 7.67 (s, 2 H, aromatic protons); 7.81 (d, *J* = 5.28 Hz, 4 H, aromatic protons); 7.91 (m, 4 H, aromatic protons); 8.07 (d, *J* = 8.47 Hz, 2 H, aromatic protons); 8.15 (d, *J* = 8.67 Hz, 2 H, aromatic protons); 8.22 (t, 7.82 Hz, 2 H, aromatic protons). Anal. Calcd for C₇₄H₉₀N₆O₄I₂P₂F₁₂Ru: C, 50.14; H, 5.12; N, 4.74; I, 14.32. Found: C, 50.17; H, 5.15; N, 4.73; I, 14.44.

Compound 9. To a solution of 2,5-dimethoxy-1,4-diiodobenzene (10.00 g, 25.6 mmol) in dichloromethane (50 mL), cooled in dry ice/acetone, was added dropwise BBr₃ (26.50 g, 105.8 mmol) in dichloromethane (15 mL). The resulting solution was stirred at room temperature overnight and then poured into ice water. A white precipitate was collected by filtration and recrystallized from THF/hexane to yield compound **9** (8.1 g, 87%, mp 192–194 °C). ¹H NMR (CDCl₃, ppm): δ 7.10 (s, 2 H, aromatic protons); 9.72 (s, 2 H, –OH).

Compound 10. To a solution of compound **9** (7.00 g, 19.34 mmol) in DMSO (50 mL) was added potassium hydroxide powder (3.25 g, 58.02 mmol). A solution of bromohexane (3.19 g, 19.34 mmol) in DMSO (10 mL) was then added immediately. The resulting mixture was stirred at room temperature overnight and then poured into water. A white solid (mainly dialkoxy side product) was filtered out, and the filtrate was neutralized by hydrochloric acid. The product was collected by filtration and recrystallized further from hexane (refrigeration) to give compound **10** (5.00 g, 56%, mp 48–50 °C). ¹H NMR (CDCl₃, ppm): δ 0.91 (m, 3 H, –CH₃); 1.34–1.80 (m, 8 H, aliphatic protons);

3.88 (t, *J* = 6.16 Hz, 2 H, –OCH₂–); 4.88 (b, 1 H, –OH); 6.97 (s, 1 H, aromatic protons ortho to OH); 7.35 (s, 1 H, aromatic protons meta to OH).

Monomer C. Diethyl azodicarboxylate (DEAD) (1.00 g, 5.7 mmol) in THF (5 mL) was added into a solution of compound **10** (1.70 g, 3.8 mmol), 4-(2-hydroxy ethyl)ethylamino-4'-sulfone stilbene (compound **11**, 1.30 g, 3.8 mmol), and triphenylphosphine (1.50 g, 5.7 mmol) in THF (20 mL). The resulting mixture was stirred overnight and then concentrated to less than 5 mL. The solution was poured into hot methanol and filtered while it was still hot. The resulting yellow solid was purified by chromatography (CH₂Cl₂ as eluent) and then recrystallized from acetone/methanol. The resulting product was a light yellow-colored crystal (2.05 g, 70%, mp 145–147 °C). ¹H NMR (CDCl₃, ppm): δ 0.90 (m, 3H, –CH₃ in alkoxy); 1.23 (t, *J* = 7.01 Hz, 3 H, –CH₃ on chromophore), 1.33–1.79 (m, 8H, aliphatic protons), 3.03 (s, 3H, –SO₂CH₃), 3.56 (m, 2H, NCH₂CH₃), 3.78 (m, 2H, –CH₂CH₂N), 3.90 (m, 2H, –OCH₂– on alkoxy side chain), 4.07 (t, *J* = 5.46 Hz, 2H, –OCH₂CH₂N–), 6.69 (d, *J* = 8.34 Hz, 2H, aromatic protons), 6.86 (d, *J* = 16.33 Hz, 1H, vinyl proton), 7.12 (s, 1H, aromatic protons), 7.13 (d, *J* = 16.56 Hz, 1H, vinyl proton), 7.37 (d, *J* = 8.59 Hz, 2H, aromatic protons), 7.55 (d, *J* = 8.26 Hz, 2H, aromatic protons), 8.01 (d, *J* = 7.91 Hz, 2H, aromatic protons). ¹³C NMR (CDCl₃, ppm): 12.6, 14.4, 22.8, 26.2, 29.2, 29.3, 32.0, 44.9, 46.0, 49.6, 68.1, 70.5, 86.2, 86.5, 112.0, 121.8, 122.7, 122.9, 124.3, 126.5, 127.9, 128.8, 132.9, 137.7, 144.0, 148.0, 152.6, 153.5. Anal. Calcd for C₃₁H₃₇NO₄Si₂: C, 48.13; H, 4.82; N, 1.81. Found: C, 48.22; H, 4.78; N, 1.77.

Monomer B. To a solution of compound **7** (0.20 g, 0.187 mmol) in ethylene glycol (15 mL) was added at 120 °C *cis*-dichlorobis(2,2'-bipyridine)osmium(II) (0.10 g, 0.187 mmol) in 5–10 mL of ethylene glycol. The resulting solution was stirred at 140 °C for 48 h. After cooling to room temperature, the solution was concentrated to 10 mL and then added to a solution of (NH₄)PF₆ (0.25 g) in 80 mL of water. A dark solid was collected by filtration and recrystallized from CH₂Cl₂/MeOH to give 0.2 g of product as a black shining crystal (57%). ¹H NMR (CDCl₃, ppm): δ 0.85 (t, *J* = 6.56 Hz, 12 H, –CH₃); 1.20–1.55 (m, 32 H, aliphatic protons); 1.73 (m, 8H, –CH₂–); 3.86 (t, *J* = 5.33 Hz, 4H, –OCH₂–); 3.97 (t, *J* = 5.6 Hz, 4H, –OCH₂–); 6.90 (d, *J* = 16.40 Hz, 2 H, vinyl protons); 7.04 (s, 2H, aromatic protons meta to iodo); 7.19 (s, 2H, aromatic protons ortho to iodo); 7.31–7.34 (m, 4H, 2 vinyl protons and 2 ArH); 7.37 (t, *J* = 6.82 Hz, 2H, ArH); 7.56 (s, 2H, ArH); 7.66–7.70 (m, 8H, ArH); 7.90 (d, *J* = 8.29 Hz, 2H, ArH); 8.15 (d, *J* = 8.34 Hz, 2H, ArH); 8.21 (t, *J* = 5.70 Hz, 4H, ArH). Anal. Calcd for C₇₄H₉₀N₆O₄I₂P₂F₁₂Os: C, 47.74; H, 4.87; N, 4.51. Found: C, 47.67; H, 4.88; N, 4.53.

Compound 12. Mg (1.89 g, 0.0777 mol) and ether (30 mL) were added to a two-necked flask. Octyl bromide (15.00 g, 0.0777 mol) in 20 mL of ether was then added to the above suspension at such a rate that the reaction mixture maintained self-refluxing. After the addition was complete, the mixture was further refluxed in an oil bath for half an hour. The solution was then transferred to an addition funnel and added dropwise into a mixture containing 1,4-dibromobenzene (19.73 g, 0.0777 mol), PdCl₂(dppf) (0.60 g, 0.7 mmol), and 40 mL of ether. The resulting mixture was refluxed overnight and then poured into water. After removal of the catalyst residue (red precipitate) by filtration, the filtrate was extracted with ethyl ether. The organic layer was washed with water and dried (MgSO₄), and the solvent was evaporated. The resulting liquid was distilled to give 17 g of product, a colorless liquid (76%, bp 91–92 °C/0.8 mmHg). ¹H NMR (CDCl₃, ppm): δ 0.87 (t, *J* = 6.79 Hz, 3H, –CH₃), 1.28 (m, 10 H, alkyl protons), 1.56 (m, 2 H, alkyl protons), 2.53 (t, *J* = 7.31 Hz, 2 H, benzyl protons), 6.89 (d, *J* = 7.63 Hz, 2H, aromatic protons), 7.32 (d, *J* = 7.72 Hz, 2 H, aromatic protons).

Compound 13. To a suspension containing Mg (0.90 g, 37.14 mmol) and a small crystal of iodine and THF (10 mL) was added 1 mL of compound **12** (10.00 g, 37.14 mmol). After stirring for a couple of minutes, the mixture started to reflux. The rest of the compound **12** was then added to the mixture at such a rate as to maintain the refluxing. After the addition was complete, the mixture was refluxed for another half an hour. The resulting Grignard reagent was transferred to an addition funnel and added dropwise into a mixture containing 1,6-dibromohexane (9.06 g, 37.14 mmol), Li₂CuCl₄ (3.71 mL of 0.1 M THF solution, 37.14 mmol), and 20 mL of THF at 5–10 °C. The

resulting mixture was stirred overnight at room temperature and then poured into water. The mixture was extracted with methylene chloride. The organic layer was washed with water, aqueous NaHCO₃ solution, and water again. It was then dried with MgSO₄. After removal of the solvent, the resulting liquid was purified by passing the solution through a short filtration column (hexane as the eluent), and 9.02 g of pure product was obtained as colorless liquid (70%). ¹H NMR (CDCl₃, ppm): δ 0.87 (t, *J* = 6.79 Hz, 3H, -CH₃), 1.24–1.34 (m, 12H, alkyl protons), 1.44 (m, 2H, alkyl protons), 1.59 (m, 4H, alkyl protons), 1.83 (m, 2H, alkyl protons), 2.55 (t, *J* = 7.20 Hz, 4H, benzyl protons), 3.36 (t, *J* = 6.34 Hz, 2H, -CH₂Br), 7.02 (s, 4H, aromatic protons).

Compound 14. A mixture containing compound **13** (9.00 g, 25.47 mmol), iodine (5.19 g, 20.47 mmol), H₅IO₆ (2.332 g, 10.23 mmol), acetic acid (17 mL), 30% sulfuric acid (3 mL), and CCl₄ (8 mL) was stirred at 80 °C for 48 h. It was then poured into aqueous solution of NaHSO₃ and extracted with methylene chloride. The organic layer was washed with water and dried (MgSO₄), and the solvent was evaporated. The resulting liquid was purified by flash chromatography (hexane as the eluent) to give 11.8 g of product (78%). ¹H NMR (CDCl₃, ppm): δ 0.87 (t, *J* = 6.79 Hz, 3H, -CH₃), 1.24–1.34 (m, 12H, alkyl protons), 1.46–1.59 (m, 6H, alkyl protons), 1.83 (m, 2H, alkyl protons), 2.55 (t, *J* = 7.20 Hz, 4H, benzyl protons), 3.36 (t, *J* = 6.34 Hz, 2H, -CH₂Br), 7.52 (s, 2H, aromatic protons).

Compound 15. A solution of compound **14** (4.00 g, 6.71 mmol), *N*-methyl aniline (1.078 g, 10.07 mmol), potassium carbonate (1.85 g, 13.42 mmol), tetrabutylammonium bromide (0.11 g, 0.34 mmol), and sodium iodide (2.02 mg, 0.013 mmol) in toluene (5 mL) was stirred under reflux overnight. Diethyl ether (25 mL) and water (25 mL) were then added. The organic layer was separated and dried over magnesium sulfate. After removal of the solvent, the residual liquid was purified by chromatography (methylene chloride as eluent) to give 3.1 g of product as colorless liquid (73%). ¹H NMR (CDCl₃, ppm): δ 0.87 (t, *J* = 6.79 Hz, 3H, -CH₃), 1.26–1.37 (m, 14H, alkyl protons), 1.51–1.58 (m, 6H, alkyl protons), 2.56 (t, *J* = 6.50 Hz, 4H, benzyl protons), 2.90 (s, 3H, -NCH₃), 3.28 (t, *J* = 7.15 Hz, 2H, -CH₂N), 6.40 (t, *J* = 7.95 Hz, 3H, aromatic protons), 7.17 (d, *J* = 7.08 Hz, 2H, aromatic protons), 7.52 (s, 2H, aromatic protons).

Compound 16. Phosphorus oxychloride (1.21 g, 7.919 mmol) was added dropwise to DMF (5 mL, 64.6 mmol) at 0 °C. The solution was stirred at 0 °C for 1 h and then at 25 °C for another 1 h. Compound **15** (5.00 g, 7.919 mmol) in 5 mL of DMF was then added dropwise to the mixture. The resulting solution was stirred at 80 °C overnight. After being cooled to room temperature, the solution was poured into cold water and neutralized with NaAc. The mixture was extracted with methylene chloride. The organic layer was washed with water and then dried. After removal of the solvent, hexane was added to the liquid residue. The product crystallized and was collected by filtration as white solid (3.34 g, 64%, mp: 70–71 °C). ¹H NMR (CDCl₃, ppm): δ 0.88 (t, *J* = 6.48 Hz, 3H, -CH₃), 1.27–1.64 (m, 20H, alkyl protons), 2.55–2.59 (m, 4H, benzyl protons), 3.02 (s, 3H, -NCH₃), 3.38 (t, *J* = 7.36 Hz, 2H, -CH₂N), 6.63 (d, *J* = 8.61 Hz, 2H, aromatic protons), 7.52 (s, 2H, aromatic protons), 7.66 (d, *J* = 8.61 Hz, 2H, aromatic protons), 9.65 (s, 1H, aldehyde proton).

Monomer D. Sodium hydride (0.40 g, 16.51 mmol) was added to a solution of compound **16** (7.26 g, 11.01 mmol) in 1,2-dimethoxyethane (DME) (10 mL). The suspension was stirred for 5 min and diethyl 4-(methylsulfonyl)benzyl phosphate (3.37 g, 11.01 mmol) in 5 mL of DME was then added dropwise. The resulting solution was stirred at 80 °C overnight and then poured into water. The mixture was extracted with methylene chloride. The organic layer was washed with water and dried. After removal of the solvent, the resulting mixture was purified by chromatography (hexane:ethyl acetate = 2:1 as eluent) and recrystallization from ether to give 1.8 g of product as greenish yellow solid (50%, mp: 94–95 °C). ¹H NMR (CDCl₃, ppm): δ 0.87 (t, *J* = 6.48 Hz, 3H, -CH₃), 1.23–1.60 (m, 20H, alkyl protons), 2.57–2.58 (m, 4H, benzyl protons), 2.96 (s, 3H, -SO₂CH₃), 3.03 (s, 3H, -NCH₃), 3.33 (t, *J* = 6.60 Hz, 2H, -CH₂N), 6.62 (d, *J* = 8.15 Hz, 2H, aromatic protons), 6.84 (d, *J* = 16.13 Hz, 1H, vinyl proton), 7.11 (d, *J* = 16.20 Hz, 1H, vinyl proton), 7.36 (d, *J* = 8.39 Hz, 2H, aromatic protons), 7.53–7.55 (m, 4H, aromatic protons), 7.80 (d, *J* = 7.97 Hz, 2H, aromatic protons). Anal. Calcd for C₃₆H₄₇SNiO₂: C, 53.27; H, 5.84; N, 1.73. Found: C, 53.21; H, 5.86; N, 1.67.

Polymerization via the Heck Coupling Reaction. A typical polymerization was exemplified by the synthesis of polymer **2**. Triethylamine (0.19 mL, 1.36 mmol) was added to a solution of monomer **A** (0.0458 g, 0.0258 mmol), monomer **C** (0.4000 g, 0.517 mmol), *p*-divinylbenzene (0.0707 g, 0.543 mmol), Pd(OAc)₂ (4.9 mg, 0.0217 mmol), and tri-*o*-tolylphosphine (32.9 mg, 0.108 mmol) in 5–10 mL of DMF. The resulting mixture was stirred at 80 °C overnight in a nitrogen atmosphere and was then poured into methanol. The precipitated polymer was collected by filtration, redissolved in tetrahydrofuran and reprecipitated in methanol. The polymer was further purified by extraction in a Soxhlet extractor with methanol for 24 h and dried under a vacuum at 50 °C for 2 days.

Polymer 1. ¹H NMR (CDCl₂-CDCl₂, ppm): δ 0.88 (broad, 3H, -CH₃ in alkoxy chain), 1.21 (b, 3H, -CH₃ in chromophore), 1.38, 1.49, 1.71, 1.80 (four broad peaks, each has 2H, methylene protons), 2.87 (m, 3H, -SO₂Me), 3.48 (b, 2H, -NCH₂CH₃), 3.79 (b, 2H, -NCH₂-CH₂O-), 4.00 (b, 2H, -OCH₂- in alkoxy chain), 4.20 (b, 2H, -OCH₂CH₂N-), 6.75 (b, 4H, aromatic protons), 7.02 (b, 5H, vinyl protons), 7.38 (b, 5H, four aromatic and one vinyl protons), 7.46 (b, 4H, aromatic protons), 7.69 (m, 2H, aromatic protons). Anal. Calcd for C₄₁H₄₅NO₄S: C, 76.04; H, 6.96; S 4.94. Found: C, 74.38; H, 7.00; S, 5.09

Polymer 2. ¹H NMR spectra of polymer **2** is very similar to that of polymer **1** except for some small peaks due to the ruthenium complex (8.00, 8.5 ppm). Anal. Calcd for C_{43.15}H_{47.65}N_{1.25}O₄S_{0.95}P_{0.1}F_{0.6}Ru_{0.05}: C, 74.28; H, 6.83; N, 2.49; Ru, 0.69. Found: C, 73.36; H, 6.98; N, 2.67; Ru, 0.55.

Polymer 3. ¹H NMR spectra of polymer **5** is very similar to that of polymer **3** except for some small peaks due to the osmium complex (4.0, 8.00, 8.5 ppm). Anal. Calcd for C_{47.9}H_{57.15}N_{1.25}O_{2.1}S_{0.95}P_{0.1}F_{0.6}Os_{0.05}: C, 74.02; H, 6.98; N, 2.38. Found: C, 71.48; H, 6.73; N, 2.36.

Polymer 4. ¹H NMR (CDCl₃, ppm): δ 0.87 (broad, 3H, -CH₃ in alkyl chain), 1.19–1.16 (b, 20H, aliphatic protons), 2.74 (b, 4H, benzyl protons), 2.92 (b, 3H, -SO₂Me), 2.99 (b, 3H, -NCH₃), 3.31 (b, 2H, -NCH₂-), 6.59 (b, 2H, aromatic protons), 6.99 (m, 1H, vinyl protons), 7.02 (b, 2H, aromatic protons), 7.07 (d, *J* = 16.85 Hz, 1H, vinyl proton), 7.32 (b, 2H, aromatic protons), 7.40 (b, 4H, vinyl protons), 7.49 (b, 6H, aromatic protons), 7.77 (m, 2H, aromatic protons). Anal. Calcd for C₄₆H₅₅SNiO₂: C, 80.54; H, 8.08; N, 2.04. Found: C, 80.50; H, 8.02; N, 2.08.

Polymer 5. ¹H NMR spectra of polymer **5** is very similar to that of polymer **4** except for some small peaks due to the ruthenium complex (4.0, 8.0, 8.5 ppm). Anal. Calcd for C_{47.9}H_{57.15}N_{1.25}O_{2.1}S_{0.95}P_{0.1}F_{0.6}Ru_{0.05}: C, 78.38; H, 7.85; N, 2.38, Ru, 0.67 Found: C, 76.48; H, 7.72; N, 2.41, Ru, 0.50

Compound 21. Compound **21** was synthesized from compound **5** by an approach similar to that used in the synthesis of compound **6** (2 equiv of butyllithium was used) mp 74–75 °C. ¹H NMR (CDCl₃, ppm): 0.90 (t, *J* = 6.50 Hz, 6H, -CH₃), 1.33 (m, 8H, methylene protons), 1.46 (m, 4H, methylene protons), 1.79–1.84 (m, 4H, methylene protons), 4.05 (t, *J* = 6.16 Hz, 4H, -OCH₂-), 7.37 (s, 2H, aromatic protons), 10.44 (s, 2H, aldehyde protons). Anal. Calcd for C₂₀H₃₀O₄: C, 71.82; H, 9.04; O, 19.14. Found: C, 71.69; H, 9.11.

Compound 23. A mixture of compound **6** (0.60 g, 1.388 mmol), vinyl tributyltin (0.44 g, 1.388 mmol), and Pd(PPh₃)₄ (0.032 g, 0.0278 mmol) in DMF (8 mL) was stirred at 100 °C for 4 h. After cooling to room temperature, the mixture was filtered, and the filtrate was poured into water. After extraction with ethyl ether, the organic layer was collected and dried over MgSO₄. Then, after removal of the solvent, the crude product was purified by chromatography (hexane:ethyl acetate = 20:1 as eluent) to give the product (0.24 g, 52%). ¹H NMR (CDCl₃, ppm): 0.86–0.93 (m, 6H, -CH₃), 1.26–1.46 (m, 12H, methylene protons), 1.75–1.83 (m, 4H, methylene protons), 3.95 (t, *J* = 6.51 Hz, 2H, -OCH₂-), 4.04 (t, *J* = 6.38 Hz, 2H, -OCH₂-), 5.38 (d, *J* = 11.30 Hz, 1H, vinyl proton), 5.80 (d, *J* = 17.71 Hz, 1H, vinyl proton), 7.01 (m, 2H, one vinyl and one aromatic protons), 7.24 (s, 1H, aromatic proton), 10.36 (s, 1H, -CHO).

Monomer E. The typical Heck reaction conditions as for polymerization were applied. The product was purified by chromatography (H:EA=10:1 as eluent) and recrystallized from methylene chloride/methanol. Yield: 38%, mp 123–124 °C. ¹H NMR (CDCl₃, ppm): δ 0.87–0.91 (m, 15H, -CH₃ in alkoxy); 1.23 (t, *J* = 7.08 Hz, 3H, -CH₃

on chromophore), 1.27–1.38 (m, 22H, aliphatic protons), 1.47–1.55 (m, 10H, aliphatic protons), 1.80–1.87 (m, 10H, aliphatic protons), 3.04 (s, 3H, $-\text{SO}_2\text{CH}_3$), 3.51 (t, $J = 7.04$ Hz, 2H, NCH_2CH_3), 3.81 (t, $J = 5.60$ Hz, 2H, $-\text{CH}_2\text{CH}_2\text{N}$), 3.97–4.08 (m, 10H, $-\text{OCH}_2-$ on alkoxy side chain), 4.22 (t, $J = 5.81$ Hz, 2H, $-\text{OCH}_2\text{CH}_2\text{N}-$), 6.70 (d, $J = 8.57$ Hz, 2H, aromatic protons), 6.74 (d, $J = 16.39$ Hz, 1H, vinyl proton), 7.02 (d, $J = 16.23$, 1H, vinyl proton), 7.08 (d, $J = 6.56$ Hz, 2H, aromatic protons), 7.10 (d, $J = 15.50$ Hz, 2H, vinyl protons), 7.25 (s, 1H, aromatic proton), 7.28 (s, 2H, aromatic protons), 7.30 (s, 1H, aromatic proton), 7.39 (d, $J = 16.45$ Hz, 1H, vinyl proton), 7.44 (s, 1H, aromatic proton), 7.46 (s, 1H, aromatic proton), 7.49 (d, $J = 8.06$ Hz, 2H, aromatic protons), 7.52 (d, $J = 16.56$ Hz, 1H, vinyl proton), 7.80 (d, $J = 8.15$ Hz, 2H, aromatic protons), 10.33 and 10.34 (s, 2H, $-\text{CHO}$). Anal. Calcd for $\text{C}_{74}\text{H}_{101}\text{NO}_{10}\text{S}$: C, 74.27; H, 8.51; N, 1.17. Found: C, 74.29; H, 8.47; N, 1.21.

Model Reaction. The reaction conditions were similar to the above. The reaction mixture was poured into 5% hydrochloric acid solution and extracted with ethyl ether. The organic layer was washed with water and dried over MgSO_4 , and then the solvent was removed. After collecting the ^1H NMR, the residue was separated by chromatography (hexane:ethyl acetate = 6:1 as the eluent) to give compounds **18**, **19**, and **20**. The relative yield was calculated based on the ^1H NMR spectrum. The characterizations of the products were exemplified by entry a (2,5-dihexoxyl-1,4-diiodobenzene as the reactant) as below.

Compound 18. Purified yield, 78%. ^1H NMR (CDCl_3 , ppm): 0.92 (t, $J = 6.58$ Hz, 6H, $-\text{CH}_3$), 1.37 (m, 8H, methylene protons), 1.53 (m, 4H, methylene protons), 1.85 (m, 4H, methylene protons), 4.02 (t, $J = 6.21$ Hz, 4H, $-\text{OCH}_2-$), 7.07 (s, 2H, aromatic protons), 7.08 (d, $J = 15.98$, 2H, vinyl protons), 7.30 (t, $J = 7.40$, 6H, aromatic protons), 7.42 (d, $J = 16.51$, 2H, vinyl protons), 7.47 (d, $J = 7.38$, 4H, aromatic protons). ^{13}C NMR (CDCl_3 , ppm): 14.0, 22.6, 25.9, 29.4, 31.6, 69.4, 110.5, 123.4, 126.4, 126.7, 127.3, 128.6, 137.9, 151.0. Anal. Calcd for $\text{C}_{34}\text{H}_{42}\text{O}_2$: C, 84.60; H, 8.77. Found: C, 84.72; H, 8.76.

Compound 19. Purified yield, 11.7%. ^1H NMR (CDCl_3 , ppm): 0.82 (m, 3H, $-\text{CH}_3$), 0.92 (m, 3H, $-\text{CH}_3$), 1.02 (m, 2H, methylene protons), 1.10 (m, 2H, methylene protons), 1.18 (m, 2H, methylene protons), 1.33 (m, 6H, methylene protons), 1.52 (m, 2H, methylene protons), 1.81 (m, 2H, methylene protons), 3.73 (t, $J = 6.11$ Hz, 2H, $-\text{OCH}_2-$), 3.96 (t, $J = 6.03$ Hz, 2H, $-\text{OCH}_2-$), 5.30 (s, 1H, vinyl proton), 5.60 (s, 1H, vinyl proton), 6.81 (s, 1H, aromatic proton), 7.04 (s, 1H, aromatic proton), 7.07 (d, $J = 16.30$, 1H, vinyl proton), 7.18–7.31 (m, 8H, aromatic protons), 7.42–7.48 (m, 3H, two aromatic protons + one vinyl proton). ^{13}C NMR (CDCl_3 , ppm): δ , 13.99, 22.41, 22.58, 25.29, 25.88, 29.06, 29.39, 31.48, 31.56, 68.96, 69.35, 110.49, 115.27, 115.97, 123.47, 126.40, 126.56, 126.74, 127.16, 127.26, 127.88, 128.51, 128.66, 131.57, 137.88, 141.47, 147.52, 150.63, 150.72. Mass spectra $m^+/e = 482.3$ (required 482.32).

Polymerization via the HWE Reaction. Typical polymerization procedures were exemplified by the synthesis of polymer **6**: Monomer **E** (0.5680 g, 0.475 mmol) was dissolved in THF (5 mL), and NaH (0.0340 g, 1.42 mmol) was then added. A solution of compound **22** (0.1710 g, 0.451 mmol) and compound **3** (0.0110 g, 0.024 mmol) in THF (5 mL) was added into the above solution while stirring. The resulting mixture was refluxed for 4 h, and the red polymer began to precipitate out. The reaction was stopped, and the mixture was poured into methanol. The polymer was collected by filtration and purified by extraction in a Soxhlet extractor with methanol for 24 h. It was then dried under a vacuum at 50 °C for 2 days (0.55 g, 91%).

Polymer 6. A similar ^1H NMR spectrum as polymer **7** was obtained. Since the solubility of polymer **7** is much better than that of polymer **6** in CDCl_3 , ^1H NMR data of polymer **7** was presented.

Polymer 7. ^1H NMR (CDCl_3 , ppm): δ 0.89 (b, 15H, $-\text{CH}_3$ in alkoxy); 1.25 (b 3H, $-\text{CH}_3$ on chromophore), 1.35 (m, 22H, methylene

protons), 1.55 (b, 10H, methylene protons), 1.87 (m, 10H, methylene protons), 3.04 (b, 3H, $-\text{SO}_2\text{CH}_3$), 3.55 (b, 2H, NCH_2CH_3), 3.80 (b, 2H, $-\text{CH}_2\text{CH}_2\text{N}$), 4.10 (b, 10H, $-\text{OCH}_2-$ on alkoxy side chain), 4.22 (b, 2H, $-\text{OCH}_2\text{CH}_2\text{N}-$), five broad peaks at 6.70, 7.15, 7.31, 7.48, 7.70 were observed which could not be unambiguously assigned. Anal. Calcd for C, 74.02; H, 6.89; Ru, 0.72. Found: C, 75.33; H, 8.24; Ru, 0.09.

Characterization. The ^1H NMR spectra were collected on a Varian 500-MHz FT NMR spectrometer. The FTIR spectra were recorded on a Nicolet 20 SXB FTIR spectrometer. A Shimadzu UV-2401PC UV/vis spectrometer was used to record the UV/vis spectra. Thermal analyses were performed by using the DSC-10 and TGA-50 systems from TA Instruments under a nitrogen atmosphere. The melting points were obtained with open capillary tubes on a Mel-Tem apparatus without corrections. Elemental analyses were performed by Atlantic Microlab, Inc., except for the ruthenium analyses, which were done by Galbraith Laboratories, Inc.. Molecular weights were measured with a Waters RI GPC system using polystyrene as the standard and THF as the eluent.

The photoconductivity was studied by measuring the voltage across a 1 M Ω resistor resulting from a photocurrent running through the sample. A Diode laser (690 nm) with an intensity of 20 mW was used as the light source.²⁴

Second-order NLO properties of poled polymeric films were characterized by second harmonic generation measurements. A mode-lock Nd:YAG laser (Continuum-PY 61 C-10, 10-Hz repetition rate) was used as the light source. The second harmonic of the fundamental wave (1064 nm) generated by the polymer sample was detected by a photomultiplier tube (PMT), then amplified, and averaged in a boxcar integrator. To measure the temperature dependence of the second order nonlinearity, a polymer film was mounted to a heating stage. The transmitted SHG signal was monitored while the sample was heated.

The linear electrooptic coefficient, r_{33} , of the poled polymer films was measured at 690 nm using a reflection method.¹⁴ A Soleil-Babinet compensator was used to bias the DC intensity at its half maximum intensity. The phase retardation between the p and s waves was modulated by an external oscillating field. The amplitude of the modulation intensity was collected using a lock-in amplifier, which was then used to calculate the r_{33} value.

Two-beam coupling experiments were performed using a diode laser (690 nm, 25 mW, Laser Power Technology, 690–300 or 780 nm, 30 mW) as the light source. The laser beam (s-polarized) was split into two beams, which were intersected in the polymer film at a geometry reported before.²⁵ The transmitted intensities of the two beams were monitored by lock-in amplifiers and collected by a computer.

To measure the phase shift of the refractive index grating over the intensity interference pattern, a motor driven piezoelectric translator was used to move the sample along the grating vector. The transmitted intensity of the two beams was collected in the same way as in the two beam coupling experiment.

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