A Convenient Modular Approach of Functionalizing Aromatic Polyquinolines for Electrooptic Devices

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A versatile and generally applicable synthetic method for making second-order nonlinear optical (NLO) side-chain aromatic polyquinolines has been developed. This approach emphasizes the ease of incorporating NLO chromophores onto the pendent phenyl moieties of parent polyquinolines at the final stage via a mild Mitsunobu reaction, which provides the synthesis of NLO polyquinolines with a broad variation of polymer backbones and great flexibility in the selection of chromophores. The synthesized NLO side-chain polyquinolines possess high glass transition temperature (T_g > 200 °C), good processability, and excellent thermal stability. The promising results of electrooptic (EO) activity (up to 35 pm/V at 830 nm and 22 pm/V at 1300 nm), optical loss (1.5−2.5 dB/cm), and long-term stability of the poling-induced polar order (r_{33} values retained >90% of their original values at 85 °C for more than 1000 h) have demonstrated the advantages of this design approach. The excellent combination of these properties in the resulting polymers have also provided a great promise in the development of EO devices.

Introduction

Organic polymeric second-order nonlinear optical (NLO) materials have been attracting considerable attention due to their potential applications in telecommunications, optical signal processing, computing, and data storage.[1,2] It is most remarkable that the improvements in high glass transition temperature (T_g) polymer systems such as polyimides[3−8] and cross-linkable polymer systems[9,10] have resulted in several prototype EO modulators and switches based on the second-order NLO polymers.[11] However, to develop practical devices suitable for commercial semiconductor processes, the greatest challenge is to achieve excellent tradeoffs in all the properties of the NLO polymers (i.e., EO coefficients, thermal, chemical, and photochemical stability, temporal dipole alignment stability, optical loss, dielectric constant, and mechanical properties). It is well-known that the second-order NLO properties originate typically from noncentrosymmetric alignment of NLO chromophores, either doped as a guest/host system or

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covalently bonded as side chain of poled polymers. To obtain device-quality materials, two stringent issues must be addressed: (1) design and synthesis of second-order NLO chromophores with a good combination of optical, chemical, and thermal properties; (2) incorporation of a proper percentage of efficient NLO chromophores in polymeric matrices in a manner that desired bulk properties, such as processability, thermal stability, poling efficiency, linear and nonlinear optical properties, and temporal stability of EO response, can be simultaneously achieved.

In the context of design and synthesis of efficient NLO chromophores, it has been shown that very large nonlinearities can be achieved by combining heterocyclic conjugating units such as thiophene or thiazole with tricyanovinyl electron acceptors[12,13] or by employing extended polyene π-bridge systems with strong heterocyclic electron acceptors.[14,15] However, the former chromophores are not chemically stable due to the reactive α-CN in the tricyanovinyl electron acceptor which is sensitive to basic conditions,[16] and the latter ones are not thermally stable due to the isomerizable alkenic bond in the conjugated polyene moiety.[17] Most recently, we have developed three efficient approaches to gain a good balance of molecular nonlinearity and thermal and chemical stability, which are novel NLO chromophores using a thiophene π-electron conjugated bridge connected with 2-phenyl-1,1,4,4-tetracyanobutadien-3-yl (Ph−TCBD) electron acceptor,[18] configuration-locked polyene chromophores,[19] and chromone-type chromophores.[20] If their enhanced properties could be efficiently translated into optimized polymer matrices, the new poled polymers derived from these chromophores would provide a great promise in the development of practical devices.

Concurrent with these developments, we have explored utilizing polyquinolines as a new optical polymer system for second-order NLO applications. Polyquinolines, which were first developed by Stille et al.[21] during the 1970s in response to the increasing demand for thermally stable materials, represent a class of high-performance polymers with a unique combination of many desirable properties including very high T_g (250−400 °C) and outstanding thermal oxidative stability (>450 °C), low dielectric constant (2.5−3.0), low moisture absorption (0.10−0.15%), low optical loss, good dimensional stability over a wide temperature range, excellent processability, and compatibility with plasma or reactive ion etching. Their mechanical properties, electrical properties, linear optical, and third-order nonlinear optical properties were well established by Stille[21] and Jenekhe.[22] Our previous studies of their electrooptic properties have shown very promising results for both guest/host[23,24] and side-chain polyquinoline systems.[25,26] However, the general applicability of those synthetic methodologies to make NLO side-chain polyquinolines is limited by the stringent acidic polymerization conditions employed in the synthesis of those polymers, in which many chromophores cannot survive. To alleviate this problem, we have developed a versatile approach for the synthesis of NLO side-chain aromatic polyquinolines.[27] This was accomplished through a modular approach by preparing a hydroxy-containing polyquinoline, followed by the covalent bonding of chromophores onto the pendent phenyl moieties of the polyquinoline via a very mild Mitsunobu reaction[28] (Scheme 1). This methodology allowed us to synthesize NLO side-chain aromatic polyquinolines with a broad variety of polymer backbones and flexibility in selecting NLO chromophores. In addition, by locating the hydroxyl group on the pendent phenyl side group instead of on the polyquinoline backbone, a higher efficiency of chromophore attachment could be achieved. It is also noteworthy that a phenyl spacer between the polymer backbone and the NLO chromophores facilitated the process for high electric field poling of the NLO polyquinolines compared to the case of polyquinolines with chromophores directly attached on the polymer backbone. In this paper, we report the detailed studies of synthesis and characterization of the polyquinolines attached with a series of novel NLO chromophores.

Results and Discussion

Synthesis and Characterization of Polyquinolines. Previously, there were two principal routes for attaching NLO chromomphores onto the polymer backbones to obtain NLO side-chain polyquinolines. One approach involved the synthesis of polyquinoline precursor polymers and then tricyanovinylation of these polyquinolines in solution to activate the side-chain NLO chromophores.[25] However, this approach was limited to the synthesis of side-chain NLO polyquinolines with only tricyanovinyl-containing chromophores. The other approach to NLO side-chain polyquinolines involved the synthesis of a NLO chromophore-containing bis(ketomethylene) monomer and a polymerization between the bis(ketomethylene) monomer and a bis(*o*-amino ketone) monomer.[26] Many chromophores, includ-

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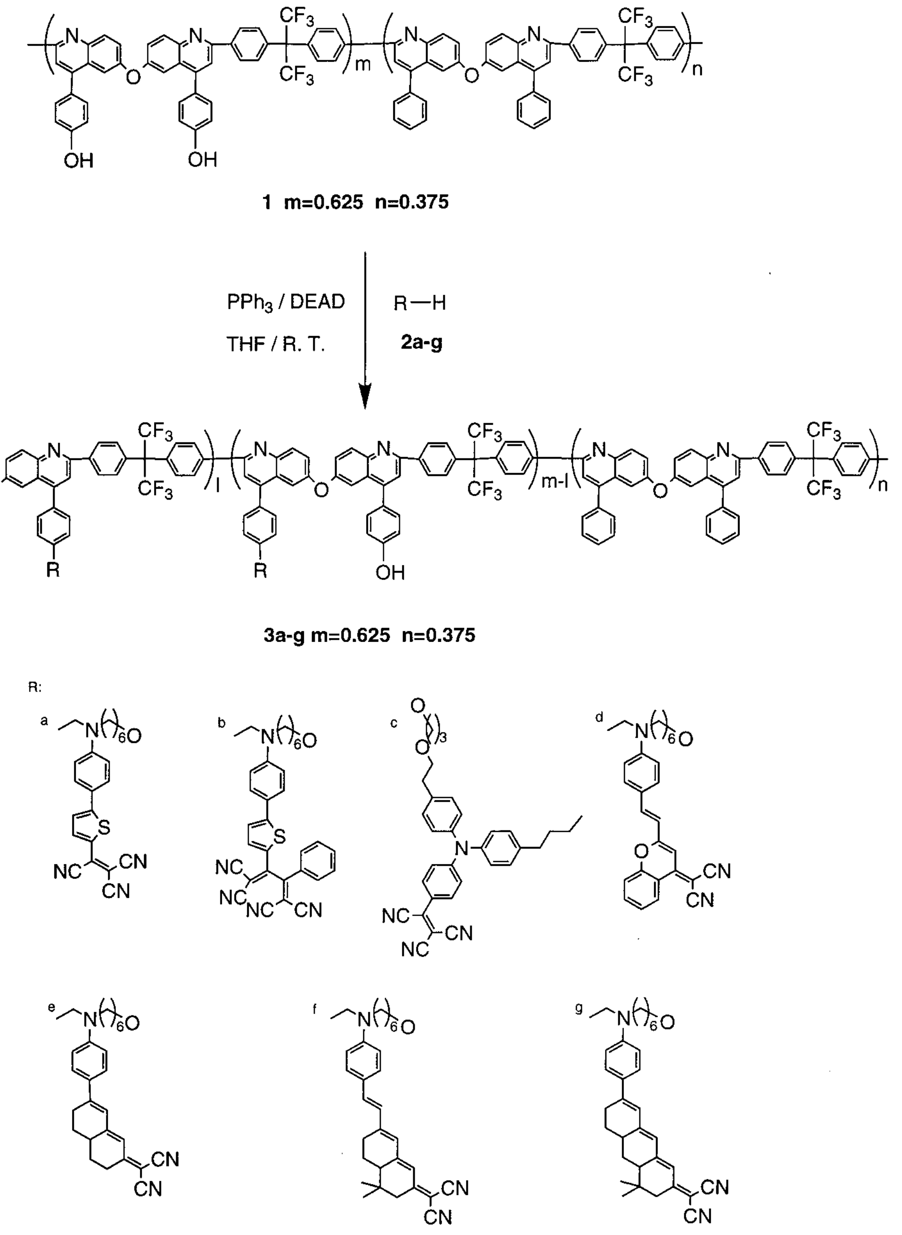
Scheme 1. Synthesis of NLO Side-Chain Aromatic Polyquinolines



ing 4-(dicyanomethylene)-2-methyl-6-(*p*-(dimethylamino)-styryl)-4*H*-pyran (DCM) type chromophores, could not survive the relatively harsh chemical conditions of the acid-catalyzed polymer-forming process. Accordingly, the general applicability of this methodology was severely limited. Our present strategy for the synthesis of NLO side-chain aromatic polyquinolines was to covalently bond the chromophore onto the pendent phenyl moieties of a preformed polyquinoline, by which the harsh acidic polymerization processes previously employed were avoided so as to preserve the NLO chromophores (Scheme 1).

The synthetic procedures of bis(*o*-amino ketone) monomer **10** were well established by Stille.[29] Scheme 2 outlined the approach for the synthesis of methoxy-containing bis(*o*-amino ketone) monomer **7**, which was a modified procedure from the literature.[22b,29] The reaction of 4,4′-dinitrodiphenyl ether **4** with *p*-methoxyphenylacetonitrile **5** in THF/methanol in the presence of base yielded a methoxy-containing bis(benzisoxazole) **6** that could be converted to the methoxy-containing bis(*o*-amino ketone) monomer **7** by the palladium-catalyzed hydrogenation. 2,2-Di(4-acetylphenyl)hexafluoropropane monomer **9** was obtained by reacting 2,2-di(4-carboxyphenyl)hexafluoropropane **8** with methyllithium in THF followed by hydrolysis with 2 N HCl (Scheme 2).

The synthesis of hydroxy-containing polyquinolines was achieved through a two-step process (Scheme 3): (1) the polymerization of either single or both bis(*o*-amino ketone) monomers with a bis(ketomethylene) monomer, yielding the methoxy-containing polyquinoline homopolymer or copolymer; (2) the hydrolysis of the methoxy-containing polyquinoline. The DPP/*m*-cresol was adapted as the optimized medium for the polymerization although other solvent mixtures, such as P_2O_5/*m*-cresol and polyphosphoric acid (PPA)/*m*-cresol, were also suitable for polymerization. Demethylation of the resulting methoxy-containing polyquinolines was

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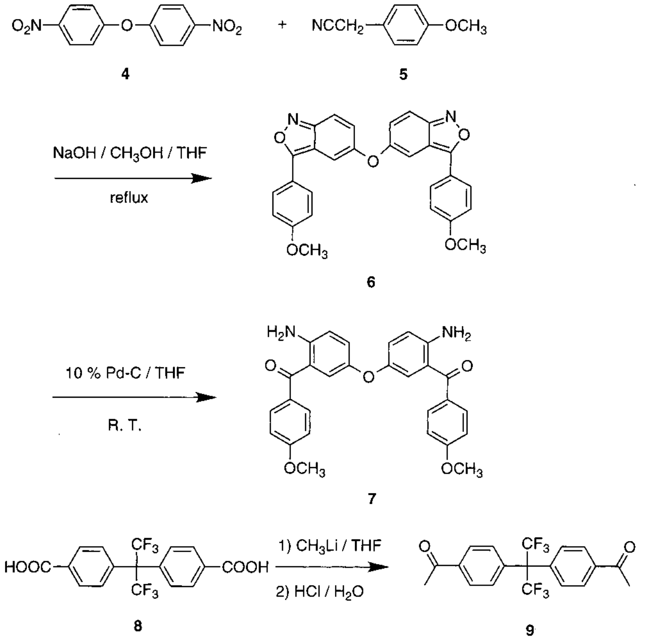
Scheme 2. Synthesis of Methoxy-Containing Bis(*o*-amino ketone) and Hexafluoroisopropylidene-Containing Bis(ketomethylene) Monomers



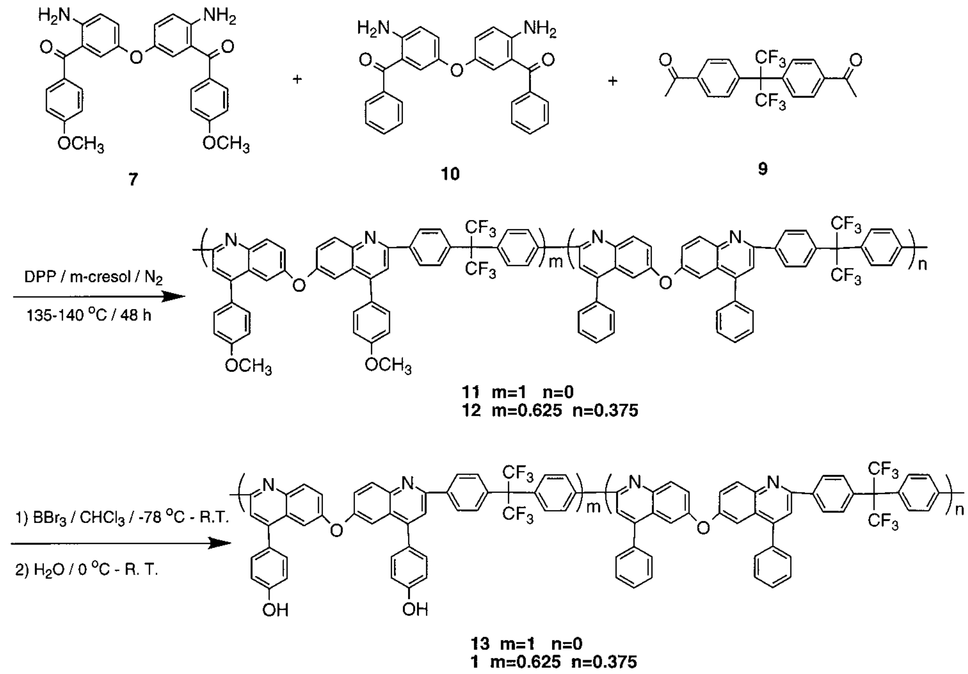
achieved in quantitative yield by reacting with BBr_3 followed by water. Controllable content of the pendent phenol group could be achieved by adjusting ratios between **7** and **10** in the polymerization to fine-tune the content of side-chain phenol group in the preformed polymers and the physical properties of the final NLO polymers. For example, copolymer **1**, which was utilized as the precursor for postcondensation with functional chromophores, had a higher thermal stability and a better reactivity than homopolymer **13**.

Although the polyquinolines prepolymers with hydroxy group directly attached to the backbone were originally designed for chromophore attachment, this was not a very effective method due to steric hindrance between adjacent aromatic rings and intramolecular hydrogen bonding between the −OH and the nitrogen atom on the quinoline moiety (Scheme 4). Therefore, pendent phenol groups were introduced onto polyquinoline backbone to alleviate this problem. The covalent bonding of the chromophore onto the backbone of the polymer could be effected easily via very mild Mitsunobu condensation[28] between the hydroxy group on the chromophores and the pendent phenol group on the precursor copolyquinolines (Scheme 1). The high efficiency of chromophore attachment allowed us to adjust the loading level of the side-chain chomophores and fine-tune the electrooptic and the thermal properties of the final NLO polymers. The chromophore loading levels of these polyquinolines were controlled to be in the range 20−30 wt % in order to prevent potential chromophore aggregation which may lead to the increase of optical loss in the polymers due to light scattering. Moreover, the very mild conditions of the condensation provided us great flexibility in choosing chromophores. A great variety of chromophores with a hydroxy group, such as tricyanovinyl and phenyltetracyanobutadienyl electron acceptor containing chromophores, polyene conjugated π-bridge containing chromophores, and chromone-type chromophores, could be incorporated easily onto the pendent phenyl groups of the polyquinoline. In addition, the residual phenol groups on the NLO side-chain polyquinolines could be further cross-linked with polyepoxide in order to improve the mechanical properties, solvent resistance, and thermal alignment stability of the materials.[2b]

All of the polymers were characterized by ^{1}H NMR spectroscopy to determine the degree of functionalization. The methoxy-containing copolyquinoline **12** has two sets of strong resonance peaks at 8.63 ppm (doublet) and 7.66 ppm (doublet), which correspond to the chemical shifts of the two sets of benzene ring protons in the hexafluoroisopropylidenediphenyl moiety. The chemical shift at 7.15 ppm (doublet) is attributed to pendent phenyl protons that are ortho to the methoxy group. The three sets of resonance peaks at 8.57 ppm (doublet), 7.76−8.20 ppm (multiple), and 7.40−7.56 ppm (multiple) are assigned to be the aromatic protons of the quinoline moieties and the other pendent phenyl protons. The peak appearing at 3.70 ppm (singlet) corresponds to the aliphatic protons of methoxy group on the pendent phenyl ring. After demethylation, the peaks for methoxy protons in polymer **12** disappeared while polymer **1** exhibited a peak at 12.08 ppm due to the hydroxy group, indicating the complete deprotection of methoxy-containing copolyquinoline **12**. Copolyquinoline **1** has six similar sets of resonance peaks at 8.63 ppm (doublet), 8.57 ppm (doublet), 7.76−8.20 ppm (mutiple), 7.66 ppm (doublet), 7.38−7.56 ppm (multiple), and 7.34 ppm (doublet) due to all of the aromatic protons except that the last set of resonance peaks is ascribed to the pendent phenyl protons ortho to the hydroxy group, which is shifted to a lower magnetic field at 7.34 ppm (doublet). In the identification of NLO polymers, for example, the ^{1}H NMR data of polymer **3a** were consistent with the partially functionalized NLO chromophore **2a** side-chain aromatic polyquinoline. (The ratios of functionalization of NLO chromophore relative to phenol group on the polymer were 67 mol % and 29 wt %.) The chemical shifts that are assigned to the protons on the polymer backbone (at 8.59, 8.53, 7.72−8.18, 7.62, 7.36−7.54, and 7.31 ppm) are similar to that of the parent polyquinoline **1**, which suggests that the NLO side-chain chromophore has little effect on the polymer backbone protons owing to the existence of a long alkyl spacer between the chromophore and the backbone. The chemical shift of the intact OH protons was observed at 12.04 ppm. The degree of functionalization (67%) was determined on the basis of the total integrated peak area at 8.59 and 8.53 ppm and the area at 3.97 ppm that corresponds to the oxymethylene ($-OCH_2-$) protons of the alkyl spacer between the polymer backbone and the NLO side-chain chromophore. The chromophore densities of the other NLO side-chain polyquinolines were determined by a similar method and are listed in Table 1.

The bulky hexafluoroisopropylidene moiety and the flexible ether linkage in the polymer backbone help to reduce the intermolecular packing and enhance the solubility of polyquinolines. The precursor polyquinolines **11**, **12**, **13**, **1**, and the NLO side-chain polyquinolines **3a**−**3h** were all soluble in polar solvents, such as cyclopentanone, *N*,*N*-dimethylacetamide, and THF. The

Scheme 3. Synthesis of Hydroxy-Containing Homopolyquinolines and Copolyquinolines



Scheme 4. Intramolecular Hydrogen Bonding between the Hydroxy Group on the Polymer Backbone and the Nitrogen Atom on the Quinoline Moiety

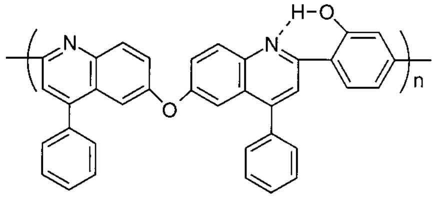


Table 1. Linear and Nonlinear Optical Properties of NLO Side-Chain Polyquinolines

polymers	chromophore density (w/w%)	T_g (°C)	λ_{max} (nm)	r_{33} (pm/V)[a]	n[b]	loss (dB/cm)[b]
3a	29	222	640	22	1.667	2.5
3b	27	230	604	20	1.641	2.2
3c	23	220	538	19	1.661	1.9
3d	22	218	529	20	1.658	2.3
3e	27	250	535	17	1.654	2.1
3f	24	230	556	35	1.655	1.5
3g	20	237	548	15	1.649	6.7

[a] Measured at 1300 nm for polymers **3a**, **3b** and at 830 nm for polymers **3c**–**3g** after poling. [b] Measured at 1300 nm for polymers **3a**, **3b** and at 830 nm for polymers **3c**–**3g** before poling.

molecular weights of the polymers were thus determined by gel permeation chromatography (GPC). Parent hydroxy copolymer **1**, for example, has a weight-average molecular weight (relative to polystyrene standards) M_w of 23 000 and a polydispersity of 3.93. The M_w's of NLO side-chain polyquinolines **3a**–**3h** are between 20 000 and 51 000 with polydispersities of 1.61–5.71. The M_w and M_n values of these side-chain NLO polyquinolines are not absolute and are only good for comparison purposes among the same series of polymers because of the vast difference between chain structure of these polymers and polystyrene.

Thermal Stability. Thermal properties of the polymers were examined by DSC and TGA measurements.

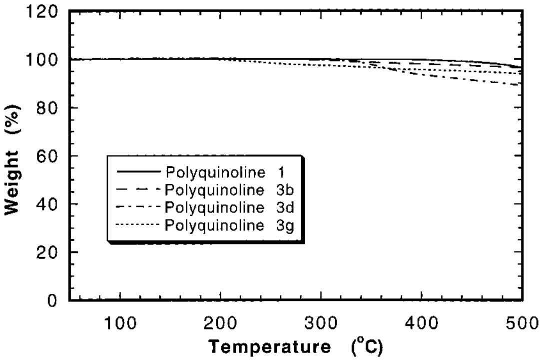


Figure 1. TGA traces of side-chain polyquinolines **3b**, **3d**, and **3g** and the parent hydroxy polyquinoline **1** with the heating rate of 20 °C/min under nitrogen atmosphere.

All of the resulting NLO side-chain polyquinolines have high glass transition temperatures (T_g > 200 °C) (Table 1) and excellent thermal stabilities. The T_g's of these polymers varied from 218 to 250 °C, depending on the structure and the density of attached NLO chromophores. Weight losses of <3% up to 300 °C were observed for all the NLO polymers. The parent hydroxy polyquinoline **1** has even better thermal stability (<3% weight loss up to 400 °C) (Figure 1), which suggests that the thermal properties of the NLO polyquinolines can be further improved if more thermally stable NLO chromophores are chosen.

Since thermal stability of the NLO polymers is also related to the stability of NLO chromophores in the environment of the polymers upon heating, thin film samples of the NLO polymers were heated on a hot stage isothermally between 175 and 275 °C (N_2) at an interval of 25 °C for 20 min, respectively. The π–π* charge-transfer absorption band of the chromophores was used to monitor the decomposition temperature. Less than 5% change in the intensity of the absorption due to the chromophore was observed at 225 °C for polymers **3c, 3d, 3f,** and **3g** and at 250 °C for polymers **3c, 3d**, and **3g**, indicating high thermal stability of these

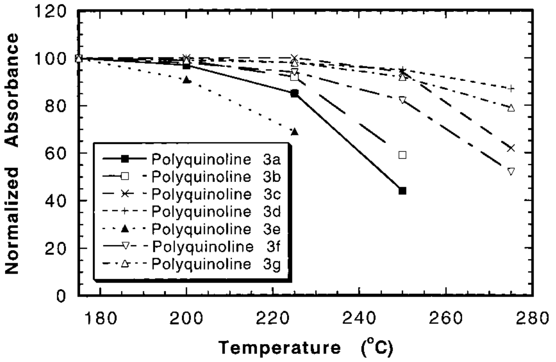


Figure 2. Thermal stability of side-chain polyquinolines **3a**–**3g** with the isothermal heating at 175, 200, 225, 250, and 275 °C for 20 min under nitrogen atmosphere, respectively. Normalized absorbance as a function of baking temperature.

NLO polyquinolines (Figure 2). In particular, polyquinoline **3d** containing a side-chain chromone chromophore was the most stable among all of the synthesized NLO polymers, which had ca. 10% of decomposition after heating at 275 °C for 20 min. It has also been shown from Figure 2 that polymer **3b** with Ph-TCBD-containing chromophore is more thermally stable than polymer **3a**, which has a tricyanovinyl-containing chromophore. Also, the chromophore with a configuration-locked polyene bridge further enhances the thermal stability of polymer **3g** when compared to that of polymer **3f**, which has a less rigid polyene chromophore.

Linear and Nonlinear Optical Properties. The synthesized NLO side-chain aromatic polyquinolines offer good processabilty that optical quality thin films can be easily prepared from their solutions. The results from the UV/vis study of these NLO polymer films are shown in Table 1. All of the polymers exhibit strong absorption maxima in the visible region ascribed to the $\pi-\pi^*$ charge-transfer band of NLO chromophores and show color ranging from red to blue. The Ph–TCBD electron acceptor in polymer **3b** demonstrates a strong blue-shift effect in the absorption behavior compared to the case of tricyanovinyl electron acceptor in polymer **3a**. This is due to the dicyanovinyl group on the Ph–TCBD which is not located on the same plane as the main conjugation path and enhances the electron-withdrawing strength of the acceptor through the inductive effect instead of the resonance effect. Polymer **3g** with a three-ring locked polyene chromophore has λ_{max} at 548 nm, showing a 13 nm red shift due to the extended conjugation length compared to that of polymer **3e**. To minimize the optical loss contributed from absorption, it is important to have the material with its absorption band edge far away from the operating wavelength of the EO devices. Therefore, polymers **3a** and **3b** are suitable for use at 1300 nm; by the same token, polymers **3c**–**3h** are more suitable to be used at 830 nm. Accordingly, the measurement of refractive indices, optical loss, and EO coefficients was carried out at two different wavelengths, and the results are also summarized in Table 1.

The refractive indices and optical loss of these polymer films varied from 1.64 to 1.67 and from 1.5 to 6.7 dB/cm, respectively, depending on the structures of attached NLO chromophores.

The criteria of second-order nonlinear process require that these materials should be noncentrosymmetric. For the amorphous polyquinoline films, the dipole moment of the attached NLO chromophores could be aligned by either contact poling or corona poling. Optical quality thin films (1–2 μm) of the side-chain polyquinolines were prepared by spin-coating of the polymer solutions in cyclopentanone or cyclopentanone/pyridine (10–15% w/w, filtered through a 0.2 μm syringe filter) onto an indium tin oxide (ITO) glass substrate. The films were kept in a vacuum oven at 80 °C overnight and briefly heated on a hot stage at 160–175 °C under nitrogen for 25 min to ensure the removal of residual solvent. A thin layer of gold was vacuum evaporated onto the polyquinoline films to serve as the top electrode for poling. The samples were poled at a temperature above T_g with a dc electric field of 1.0–1.4 MV/cm and then slowly cooled to room temperature, with the poling field subsequently removed. The EO coefficient, r_{33}, was measured with an experimental setup similar to that described by Teng et al.[30] The sizable r_{33} values of 15–35 pm/V for the synthesized NLO side-chain polyquinolines were obtained, owing to both a proper loading level of efficient NLO chromophores in the polymers and a high poling efficiency resulting from the excellent electrical properties of these NLO polymers and the presence of a phenyl spacer between polymer backbone and NLO side-chain chromophore. The combination of high EO coefficient and low optical loss makes these polymers as ideal candidates for device fabrication.

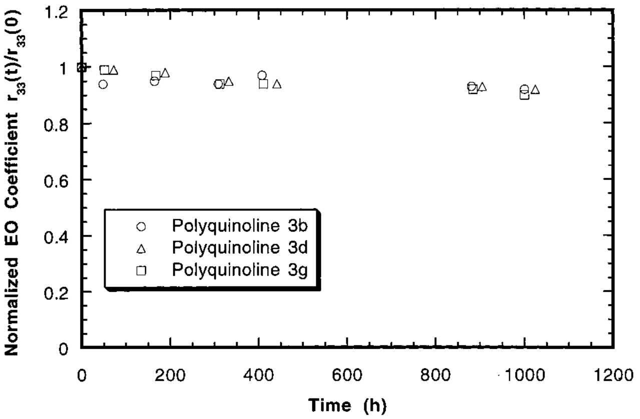


Figure 3. Temporal stability of the poled side-chain polyquinolines **3b**, **3d**, and **3g** at 85 °C in air. Normalized r_{33} as a function of baking time.

The long-term stability of the poling induced polar order is a critical requirement for practical applications. The temporal stability of chromophore dipole orientation after the removal of the external electric field was examined at 85 °C by measuring the change of EO coefficient with time. The r_{33} values retained >90% of the original values at 85 °C for more than 1000 h (Figure 3), indicating the dipole orientations in these NLO polymers are quite stable which can be attributed to high T_g's of these polymers.

Conclusion

A versatile, generally applicable synthetic methodology for NLO side-chain aromatic polyquinolines has been developed. The obvious advantages of this method over others include flexibility in selecting NLO chro-

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(30) Teng, C. C.; Man, H. T. *Appl. Phys. Lett.* **1990,** *56,* 1734.

mophores, ease in controlling the chromophore loading level, and the ability to adjust the polymer backbone structures in order to fine-tune their physical properties. The resulting polyquinolines with NLO side-chain Ph−TCBD electron acceptor containing chromophore, polyene-locked π-bridge containing chromophore, and chromone-type chromophore demonstrate an excellent combination of processability, thermal stability, poling efficiency, EO coefficients, dipole alignment stability, and optical loss. These desirable properties provide great promise in the development of EO devices. Further cross-linking of the poled polymers through the intact OH groups on the polymer with polyepoxide at high temperature may further enhance both their mechanical properties and temporal stability.

Experimental Section

General Procedures. 2,2-Di(4-carboxyphenyl)hexafluoropropane was purchased from Chriskev Co., Inc. Other chemicals were purchased from Aldrich or Lancaster Synthesis Inc. and used as received unless otherwise specified. Tetrahydrofuran (THF) was distilled under nitrogen from sodium benzophenone ketyl. Chloroform was dried with 4 Å molecular sieve.

NMR spectra were obtained on a Varian XL 300 MHz FT NMR spectrometer. UV−vis spectra were recorded on a Perkin-Elmer Lambda 9 UV/vis/NIR spectrophotometer. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed under a nitrogen atmosphere by using the DSC-50 and TGA-50 systems from Shimadzu TA instruments. The molecular weights and polydispersities (relative to polystyrene standards) were determined using a Waters 410 gel permeation chromatograph (GPC) with a refractive index detector and HR-4E columns at room temperature (THF as the eluant).

The cyclopentanone (or cyclopentanone/pyridine) solutions of the NLO polymers (10−15% w/w) were filtered through a 0.2 μm syringe filter and then spin-coated onto microslides or indium tin oxide (ITO) glass substrate. The films were kept in a vacuum oven at 160−175 °C for 25 min to ensure removal of the residual solvent. The refractive indices and optical loss of polymer films on microslides were measured by using a Metricon model 2010 prism coupler. A thin gold plating (∼20 nm) was sputtered on top of the polymer-coated ITO substrate followed by electrode poling. Semiconductor lasers (830, 1300 nm) were used as the light sources. The relevant electrooptic coefficients r_{33} of electrode-poled films were measured by an ellipsometric technique similar to that described by Teng and Man.[30]

5,5′-Oxybis(3-*p*-methoxyphenyl-2,1-benzisoxazole) (6). To a vigorously stirred solution of sodium hydroxide (21.60 g, 0.54 mol) in 120 mL of absolute methanol and 340 mL of tetrahydrofuran (THF) in an ice bath was added dropwise *p*-methoxyphenylacetonitrile (27.4 mL, 29.70 g, 0.20 mol). Then, 4,4′-dinitrodiphenyl ether (13.00 g, 0.05 mol) was slowly added with four equal portions, and the mixture was stirred in an ice bath for 5 min. The resulting dark green slurry was heated at reflux temperature for 20 h. After cooling in an ice bath, the resulting dark precipitate was filtered and washed with cold methanol until the methanol washings were clear to afford a yellow powder (12.60 g, 54%, mp 231−233 °C). ^{1}H NMR (CDCl$_3$, ppm): δ 7.84 (d, J = 8.97 Hz, 4H), 7.66 (d, J = 10.14 Hz, 2H), 7.19−7.24 (m, 4H), 7.02 (d, J = 8.91 Hz, 4H), 3.86 (s, 6H). $C_{28}H_{20}N_2O_5$ (464.46): calcd C, 72.40, H, 4.34, N, 6.03; found C, 72.46, H, 4.35, N, 5.82.

4,4′-Diamino-3,3′-di(*p*-methoxybenzoyl)diphenyl Ether (7). A total of 0.56 g of 10% palladium on powdered charcoal was added to a suspension of **6** (4.00 g, 8.60 mmol) in 35 mL of dry THF and 1.0 mL of triethylamine. The suspension was flushed with hydrogen gas and stirred at room temperature under a hydrogen atmosphere for 27 h. To the reaction mixture was added an additional 0.28 g of 10% palladium on powdered charcoal in 10 mL of THF, and the hydrogenation was continued for another 14 h. The catalyst was removed by filtration, and the solvent was removed by rotatory evaporation under reduced pressure. The resulting oil was purified through a packed silica gel column with hexane/ethyl acetate (1:1) as eluant to afford a yellow crystal (2.80 g, 70%, mp 124−126 °C). ^{1}H NMR (CDCl$_3$, ppm): δ 7.63 (d, J = 8.7 Hz, 4H), 7.07 (d, J = 2.6 Hz, 2H), 6.96 (dd, J = 8.8 Hz, 2.6 Hz, 2H), 6.89 (d, 8.7 Hz, 4H), 6.68 (d, J = 8.8 Hz, 2H), 5.35 (br, 4H), 3.85 (s, 6H). $C_{28}H_{24}N_2O_5$ (468.49): calcd C, 71.78, H, 5.16, N, 5.98; found C, 71.70, H, 5.04, N, 5.84.

2,2-Di(4-acetylphenyl)hexafluoroprapane (9). To a stirred solution of 2,2-di(4-carboxyphenyl)hexafluoroprapane (19.60 g, 50 mmol) in 30 mL of THF was added methyllithium (1.0 M solution in THF/cumene) (250 mL, 250 mmol, 5 equiv) by syringe at 0 °C under nitrogen. After the stirring for 2 h, the reaction mixture was poured into a solution of 2 N HCl (600 mL) at 0 °C. The resulting solution was extracted with methylene chloride. The organic layer was separated, washed with water, and dried over Na_2SO_4. The solvent was then removed by rotatory evaporation under reduced pressure, and the viscous liquid was purified through a packed silica gel column with hexane/methylene chloride (2:3) as eluant. The product was a white solid (10.29 g, 53%, mp 78−80 °C). ^{1}H NMR (CDCl$_3$, ppm): δ 7.49 (d, J = 8.31 Hz, 4H), 7.97 (d, J = 8.31 Hz, 4H), 2.63 (s, 6H). $C_{19}H_{14}F_6O_2$ (388.30): calcd C, 58.77, H, 3.63; found C, 58.54, H, 3.33.

Methoxy-Containing Homopolyquinoline (11). A mixture of **7** (0.9366 g, 2.00 mmol), **9** (0.7764 g, 2.00 mmol), diphenyl phosphate (DPP) (12.51 g, 50.0 mmol), and freshly distilled *m*-cresol (2.40 mL, 23.0 mmol) was placed in a three-necked flask. With the stirring, the reaction mixture was flushed with nitrogen for about 20 min and then heated in an oil bath from room temperature to 135−140 °C in about 30 min. It was maintained at this temperature for 48 h under a nitrogen atmosphere. After cooling, the resulting viscous solution was added dropwise into an agitated solution of 400 mL of methanol containing 10% v/v of triethylamine. The precipitated polymer was redissolved in 30 mL of chloroform and reprecipitated by slow addition to a stirred solution of 400 mL of methanol containing 10% v/v of triethylamine. The polymer was collected by suction filtration and continuously extracted in a Soxhlet extractor for 24 h with a methanol solution containing 10% v/v of triethylamine and then dried at 100 °C under vacuum for 24 h to afford an off-white polymer (1.51 g, 96%). ^{1}H NMR (pyridine-d_5, ppm): δ 8.65 (d, 4H), 8.60 (d, 2H), 8.16 (s, 2H), 7.94 (d, 2H), 7.90 (d, 4H), 7.84 (dd, 2H), 7.65 (d, 4H), 7.16 (d, 4H), 3.71 (s, 6H). Molecular weight: M_w = 25 000, M_n = 8000 with the polydispersity of 3.13. T_g = 261 °C. Thermal stability: <3% weight loss up to 400 °C (20 deg/min, N$_2$).

Methoxy-Containing Copolyquinoline (12). It was synthesized with a similar procedure as described for polymer **11** using **7** (0.5854 g, 1.25 mmol), **10** (0.3062 g, 0.75 mmol), and **9** (0.7764 g, 2.00 mmol) as the three monomers. DPP (12.51 g, 50.0 mmol) with *m*-cresol (2.40 mL, 23.0 mmol) was used as the reaction medium. An off-white polymer (1.44 g, 95%) was obtained. ^{1}H NMR (pyridine-d_5, ppm): δ 8.63 (d, 4H), 8.57 (d, 2H), 7.76−8.20 (m, 10H), 7.66 (d, 4H), 7.40−7.56 (m, 2.25H), 7.15 (d, 2.5H), 3.70 (s, 3.75H). Molecular weight: M_w = 23 000, M_n = 5000 with the polydispersity of 4.64. T_g = 264 °C. Thermal stability: <3% weight loss up to 400 °C (20 deg/min, N$_2$).

Hydroxy-Containing Homopolyquinoline (13). To a vigorously stirred solution of **11** (0.59 g, 0.75 mmol of repeat unit, 1.50 mmol of methoxy group) in 200 mL of dried chloroform at −78 °C under an atmosphere of nitrogen was added dropwise boron tribromide (1.00 mL, 10.50 mmol, 7 equiv to the amount of methoxy group). The resulting yellow suspension was stirred for 40 min at −78 °C and 14 h at room temperature. Then, the reaction mixture was hydrolyzed by adding 200 mL of water in an ice bath for 15 min and warmed to room temperature for an additional 30 min. The reaction mixture was filtered and washed well with water. The resulting yellow solid was transferred to a flask with a large amount of water followed by stirring for 5 h at room temperature under an atmosphere of nitrogen. The mixture was filtered, washed well with water and methanol, and then dried at 40 °C under vacuum for 24 h to afford 0.52 g (91%) of slightly yellow polymer. The polymer was redissolved in 5 mL of THF and further purified by reprecipitating into 100 mL of methanol. The polymer was then filtered and dried at 40 °C under vacuum for 24 h to afford an off-white polymer (0.47 g, 82%). ^{1}H NMR (pyridine-d_5, ppm): δ 12.12 (s, 2H), 8.64 (d, 4H), 8.57 (d, 2H), 8.17 (s, 2H), 8.07 (d, 2H), 7.90 (d, 4H), 7.85 (dd, 2H), 7.67 (d, 4H), 7.35 (d, 4H). Molecular weight: $M_w = 18\,000$, $M_n = 7000$ with the polydispersity of 2.54. $T_g = 245$ °C. Thermal stability: <3% weight loss up to 400 °C (20 deg/min, N_2).

Hydroxy-Containing Copolyquinoline (1). It was synthesized with a similar procedure as described for polymer **13** by adding dropwise boron tribromide (1.13 mL, 11.90 mmol, 7 equiv to the amount of methoxy group) to a vigorously stirred solution of **12** (1.04 g, 1.36 mmol of repeat unit, 1.70 mmol of methoxy group) in 270 mL of dried chloroform at −78 °C under an atmosphere of nitrogen. A slightly yellow polymer (0.95 g, 94%) was obtained. The polymer was redissolved in 5 mL of THF and further purified by reprecipitating into 100 mL of methanol. The polymer was then filtered and dried at 40 °C under vacuum for 24 h to afford an off-white polymer (0.84 g, 83%). ^{1}H NMR (pyridine-d_5, ppm): δ 12.08 (s, 1.25H), 8.63 (d, 4H), 8.57 (d, 2H), 7.76−8.20 (m, 10H), 7.66 (d, 4H), 7.38−7.56 (m, 2.25H), 7.34 (d, 2.5H). Molecular weight: $M_w = 23\,000$, $M_n = 6000$ with the polydispersity of 3.93. $T_g = 259$ °C. Thermal stability: <3% weight loss up to 400 °C (20 deg/min, N_2).

Side-Chain Aromatic Copolyquinoline (3a). Hydroxy-containing copolyquinoline **1** (0.238 g, 0.320 mmol of repeat unit, 0.400 mmol of hydroxy group), PPh_3 (0.090 g, 0.342 mmol), and **2a** (0.138 g, 0.342 mmol) were dissolved in 40 mL of dry THF successively. The flask was flushed with dry nitrogen. Diethyl azodicarboxylate (DEAD) (0.054 mL, 0.060 g, 0.342 mmol) was added dropwise to the solution. The reaction mixture was further stirred at room temperature for 48 h and was then added dropwise into 400 mL of methanol. The collected precipitate was redissolved in 5 mL of THF and reprecipitated into 100 mL of methanol. The polymer was further purified by Soxhlet extraction with methanol for 48 h and dried at 40 °C under vacuum to afford the blue side-chain copolyquinoline (0.26 g, 76%). ^{1}H NMR (pyridine-d_5, ppm): δ 12.04 (s, 0.41H), 8.59 (d, 4H), 8.53 (d, 2H), 7.72−8.18 (m, 10H), 7.62 (d, 4H), 7.36−7.54 (m, 5.60H), 7.31 (d, 2.5H), 6.72 (d, 1.68H), 3.97 (br, 1.68H), 3.65 (br, 1.68H), 3.10−3.46 (m, 1.68H), 0.50−2.24 (m, 9.21H). Molecular weight: $M_w = 32\,000$, $M_n = 7000$ with the polydispersity of 4.46. $T_g = 222$ °C. Thermal stability: <1% weight loss up to 300 °C (20 deg/min, N_2).

Side-Chain Aromatic Copolyquinoline (3b). It was prepared with a similar procedure as described for polymer **3a** using hydroxy-containing copolyquinoline **1** (0.253 g, 0.340 mmol of repeat unit, 0.425 mmol of hydroxy group), PPh_3 (0.072 g, 0.274 mmol), **2b** (0.146 g, 0.274 mmol), DEAD (0.043 mL, 0.048 g, 0.274 mmol), and THF (40 mL) as the starting materials and the solvent. A blue side-chain copolyquinoline (0.26 g, 74%) was obtained. ^{1}H NMR (pyridine-d_5, ppm): δ 12.02 (s, 0.70H), 8.59 (d, 4H), 8.52 (d, 2H), 7.72−8.16 (m, 10H), 7.62 (d, 4H), 7.35−7.54 (m, 7.20H), 7.31 (d, 2.5H), 6.71 (d, 1.1H), 3.96 (br, 1.1H), 3.65 (br, 1.1H), 3.21−3.38 (m, 1.1H), 1.00−2.30 (m, 6.05H). Molecular weight: $M_w = 33\,000$, $M_n = 6000$ with the polydispersity of 4.71. $T_g = 230$ °C. Thermal stability: <1% weight loss up to 300 °C (20 deg/min, N_2).

Side-Chain Aromatic Copolyquinoline (3c). It was prepared with a similar procedure as described for polymer **3a** using hydroxy-containing copolyquinoline **1** (0.238 g, 0.320 mmol of repeat unit, 0.400 mmol of hydroxy group), PPh_3 (0.067 g, 0.255 mmol), **2c** (0.129 g, 0.255 mmol), DEAD (0.040 mL, 0.044 g, 0.255 mmol), and THF (40 mL) as the starting materials and the solvent. A red side-chain copolyquinoline (0.30 g, 97%) was obtained. ^{1}H NMR (pyridine-d_5, ppm): δ 12.04 (s, 0.79H), 8.59 (d, 4H), 8.52 (d, 2H), 7.70−8.18 (m, 10H), 7.62 (d, 4H), 7.36−7.54 (m, 5.03H), 7.30 (d, 2.5H), 6.92−7.14 (m, 1.85H), 6.78 (d, 0.93H), 4.06 (br, 0.93H), 3.62 (m, 0.93H), 3.35 (m, 0.93H), 0.76−3.00 (m, 6.01H). Molecular weight: $M_w = 43\,000$, $M_n = 8000$ with the polydispersity of 5.27. $T_g = 220$ °C. Thermal stability: <1% weight loss up to 300 °C (20 deg/min, N_2).

Side-Chain Aromatic Copolyquinoline (3d). It was prepared with a similar procedure as described for polymer **3a** using hydroxy-containing copolyquinoline **1** (0.206 g, 0.277 mmol of repeat unit, 0.346 mmol of hydroxy group), PPh_3 (0.072 g, 0.273 mmol), **2d** (0.120 g, 0.273 mmol), DEAD (0.043 mL, 0.048 g, 0.273 mmol), and THF (20 mL) as the starting materials and the solvent. A red side-chain copolyquinoline (0.20 g, 77%) was obtained. ^{1}H NMR (pyridine-d_5, ppm): δ 12.00 (s, 0.75H), 8.89 (d, 0.50H), 8.55 (d, 4H), 8.48 (d, 2H), 7.68−8.16 (m, 10H), 7.58 (d, 4H), 7.32−7.48 (m, 4.25H), 7.24 (d, 2.5H), 6.70−6.90 (m, 2.00H), 3.90 (br, 1.00H, 3.10−3.36 (m, 2.00H), 0.90−1.78 (m, 5.50H). Molecular weight: $M_w = 51\,000$, $M_n = 9000$ with the polydispersity of 5.49. $T_g = 218$ °C. Thermal stability: <1% weight loss up to 300 °C (20 deg/min, N_2).

Side-Chain Aromatic Copolyquinoline (3e). It was prepared with a similar procedure as described for polymer **3a** using hydroxy-containing copolyquinoline **1** (0.236 g, 0.317 mmol of repeat unit, 0.396 mmol of hydroxy group), PPh_3 (0.125 g, 0.475 mmol), **2e** (0.197 g, 0.475 mmol), DEAD (0.075 mL, 0.083 g, 0.475 mmol), and THF (20 mL) as the starting materials and the solvent. A red side-chain copolyquinoline (0.29 g, 91%) was obtained. ^{1}H NMR (pyridine-d_5, ppm): δ 12.10 (s, 0.54H), 8.64 (d, 4H), 8.58 (d, 2H), 7.75−8.22 (m, 10H), 7.67 (d, 4H), 7.40−7.58 (m, 3.68H), 7.35 (d, 2.5H), 6.80−6.98 (br, 2.85H), 4.01 (br, 1.43H), 3.71 (br, 1.43H), 3.34 (br, 1.43H), 0.96−2.94 (m, 14.25H). Molecular weight: $M_w = 26\,000$, $M_n = 8000$ with the polydispersity of 3.38. $T_g = 250$ °C. Thermal stability: <3% weight loss up to 300 °C (20 deg/min, N_2).

Side-Chain Aromatic Copolyquinoline (3f). It was prepared with a similar procedure as described for polymer **3a** using hydroxy-containing copolyquinoline **1** (0.250 g, 0.336 mmol of repeat unit, 0.420 mmol of hydroxy group), PPh_3 (0.086 g, 0.328 mmol), **2f** (0.145 g, 0.328 mmol), DEAD (0.052 mL, 0.057 g, 0.328 mmol), and THF (20 mL) as the starting materials and the solvent. A red side-chain copolyquinoline (0.24 g, 73%) was obtained. ^{1}H NMR (pyridine-d_5, ppm): δ 12.02 (s, 0.74H), 8.59 (d, 4H), 8.53 (d, 2H), 7.70−8.16 (m, 10H), 7.62 (d, 4H), 7.35−7.52 (m, 3.28H), 7.30 (d, 2.5H), 7.05 (s, 0.51H), 6.96 (s, 0.51H), 6.92 (s, 0.51H), 6.80 (br, 1.03H), 6.52 (s, 0.51H), 3.94 (br, 1.03H), 3.65 (br, 1.03H), 3.28 (br, 1.03H), 0.96−2.70 (m, 12.30H). Molecular weight: $M_w = 36\,000$, $M_n = 7000$ with the polydispersity of 5.24. $T_g = 230$ °C. Thermal stability: <2% weight loss up to 300 °C (20 deg/min, N_2).

Side-Chain Aromatic Copolyquinoline (3g). It was prepared with a similar procedure as described for polymer **3a** using hydroxy-containing copolyquinoline **1** (0.240 g, 0.322 mmol of repeat unit, 0.403 mmol of hydroxy group), PPh_3 (0.068 g, 0.260 mmol), **2g** (0.129 g, 0.260 mmol), DEAD (0.041 mL, 0.045 g, 0.260 mmol), and THF (20 mL) as the starting materials and the solvent. A red side-chain copolyquinoline (0.24 g, 86%) was obtained. ^{1}H NMR (pyridine-d_5, ppm): δ 12.02 (s, 1.0H), 8.58 (d, 4H), 8.52 (d, 2H), 8.10 (d, 2H), 7.73−8.18 (m, 10H), 7.35−7.52 (m, 3.03H), 7.30 (d, 2.5H), 7.12 (br, 0.39H), 7.05 (br, 0.39H), 6.92 (br, 0.39H), 6.82 (br, 0.78H), 3.94 (br, 0.78H), 3.64 (br, 0.78H), 3.32 (br, 0.78H), 0.62−2.96 (m, 10.08H). Molecular weight: $M_w = 20\,000$, $M_n = 12\,000$ with the polydispersity of 1.61. $T_g = 237$ °C. Thermal stability: <3% weight loss up to 300 °C (20 deg/min, N_2).

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