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Polyphosphazenes with Immobilized Dyes as Potential Color Filter Materials

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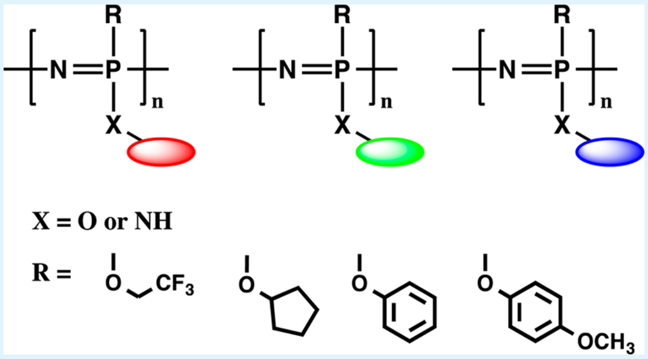
ABSTRACT: Red, green, and blue dye molecules were linked covalently to polyphosphazenes to generate soluble, film-forming materials appropriate for the formation of patterned tricolor filters for possible use in liquid crystalline and other display devices or in camera sensors. The monofunctional dyes (a red 1-[(*E*)-(4-nitrophenyl)diazenyl]-2-naphthol, a green tetraphenylporphyrin [5-(4-hydroxyphenyl)-10,15,20-tetraphenylporphyrin], and a toluidine blue dye) were employed as representative chromophores. The cosubstituents employed included 2,2,2-trifluoroethoxy with and without aryloxy groups or cyclopentanoxy groups. The optical densities were varied by adopting several dye-to-cosubstituent side group ratios. These dyes are models for a wide range of different chromophores that can be linked to polyphosphazene chains.



KEYWORDS: *polymeric dyes, filters, films, liquid-crystal displays, LCD, camera sensors, microcrystallinity, optical density*

INTRODUCTION

Liquid-crystal displays (LCDs) are prevalent and important because they cover the majority of display systems from televisions and computers to smart phones and digital watches. To attain full-color images for LCDs, primary red, green, and blue color filters, as part of the pixel structure, are essential to control the color and the intensity of transmitted light. Similar filters are an essential part of the sensors of digital cameras. Current LCD color filters often contain pigments, such as insoluble copper phthalocyanines, azo dyes, and anthroquinones rather than soluble dyes,[1] with the pigments patterned via a photoresist polymer by multiple printing and etching processes.[2,3] The major problems with these filters arise from pigment aggregates, which lead to serious scattering or even the loss of the original color.[4]

Polymer-linked immobilized dyes provide a promising way to bypass this problem. In contrast to inorganic pigments and insoluble organic molecules, polymer-based color filters have numerous advantages including chemical and physical stability, even morphology, and ease of film casting or lithographic printing. Red, green, and blue dyes with a functional group (−OH or $-NH_2$) can be incorporated as the side chains in polyphosphazenes by using macromolecular substitution processes.[5] It is also possible to vary the dye content of each polymer molecule, thus yielding different color densities as well as satisfying the different mechanical needs of the technological production. For this approach, two crucial requirements are the avoidance of microcrystallinity-based light scattering and the need to maintain the solubility of the polymer despite the poor solubility of many dyes.

The advantages of polyphosphazenes as carriers for dye molecules are that (1) almost any dye molecule with a hydroxyl or amino functional group can be linked to poly(dichlorophosphazene) via nucleophilic substitution.[6] (2) The remaining unreacted chlorine groups along the polymer chain can be replaced by colorless organic subsitituents that control the solubility, morphology, refractive index, or lens-forming character of the polymer. (3) The optical density can be varied by facile changes of the ratio of dye to cosubstituent groups. (4) The polyphosphazene backbone is transparent from the near-infrared part of the spectrum, throughout the visible part, and to the 220 nm region in the ultraviolet part. Thus, the purity of each color is not compromised by the polyphosphazene platform. A challenge in this approach is overcoming the possible steric hindrance limitations arising from the linkage of bulky dye nucleophiles to a macromolecular chain. Previous experience suggests that, although the linkage of two phenoxy or substituted phenoxy substituents to each phosphorus atom is possible,[7,8] the use of polyaromatic or similarly sized nucleophiles may be restricted to the replacement of only one chlorine per phosphorus or fewer due to steric hindrance. Many dye molecules fall into this category. This is not a problem for the assembly of polymers for filter applications because a relatively low loading of each chromophore along the polymer chain will usually be sufficient to yield an appropriate optical density and polymer solubility.

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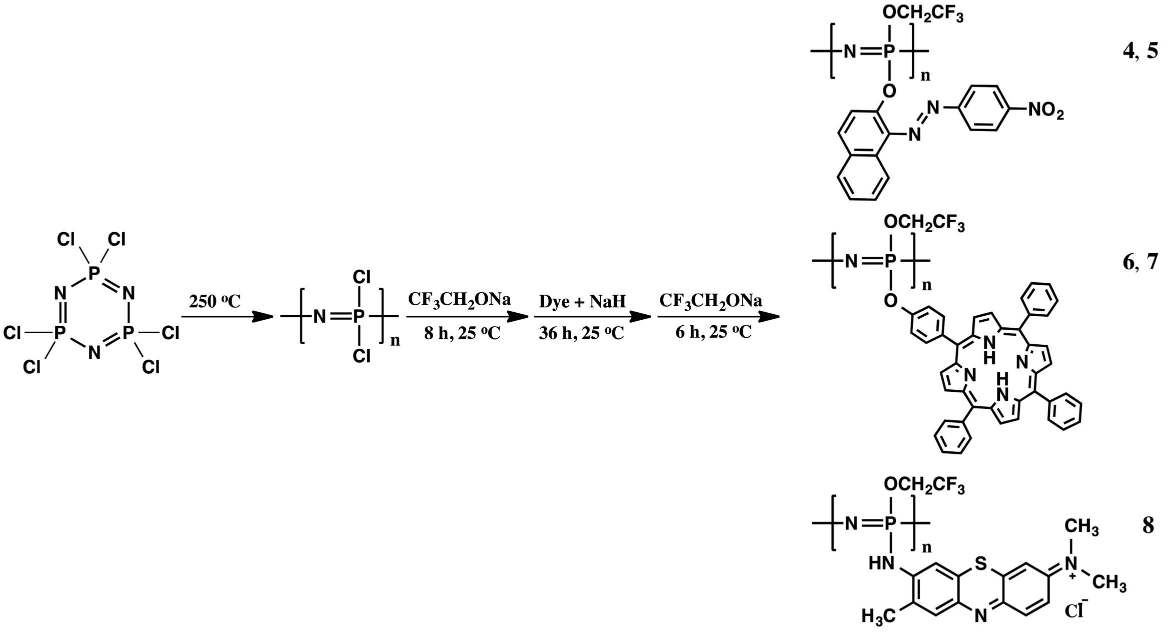
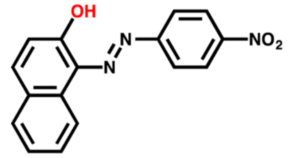
Scheme 1. Synthesis Route for Polyphosphazenes with Dyes and OCH_2CF_3 as Cosubstituents[a]



[a] Note that the ratio between the two side chains is simplified as 1:1 in the scheme for the convenience of drawing the structure.

Chart 1. Red, Green, and Blue Dyes Used for the Synthesis of Polyphosphazene-Based Color Filters[a]



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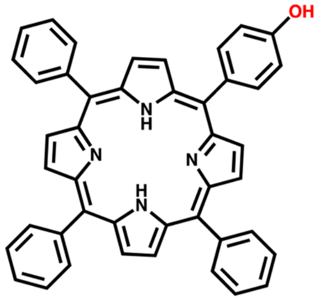

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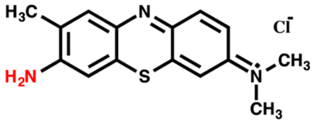

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[a] The linker units for the polymer chains are the highlighted hydroxyl or amino groups.

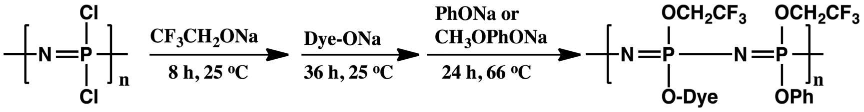
The synthesis protocol for most polyphosphazenes is illustrated in Scheme 1. Poly(dichlorophosphazene), prepared by the thermal ring-opening polymerization of hexachlorocyclotriphosphazene at 250 °C in a sealed system,[9] is used as a platform for nucleophilic chlorine replacement with the use of alkoxides,[10] aryloxides,[8] cyclic aliphatic groups,[11] amines,[12] and with various combinations of these.[5]

In this paper, the synthesis and characterization of polyphosphazenes with red, green, and blue dyes as side chains is illustrated. The dyes 1-[(*E*)-(4-nitrophenyl)diazenyl]-2-naphthol (**1**), 5-(4-hydroxyphenyl)-10,15,20-tetraphenylporphyrin (**2**), and toluidine blue (**3**) generate red, green, and blue polymers, respectively (Chart 1). The electronic absorptions of films cast from the polymers were recorded for selected polymers to evaluate the potential of these polymers as color filters.

■ EXPERIMENTAL SECTION

Reagents and Equipment. All synthesis reactions were carried out under a dry argon atmosphere using standard Schlenk line techniques. Tetrahydrofuran (THF) was dried using a solvent purification system in which the solvents pass through columns of molecular sieves under a dry argon atmosphere.[13] 2,2,2-Trifluoroethanol (Aldrich) and cyclopentanol (VWR) were distilled over sodium metal. Phenol and 4-methoxyphenol were purified by sublimation under vacuum. Acetone (EMD), methanol (EMD), and sodium hydride (60% dispersion in mineral oil, Aldrich) were used as received. Compound **1** was obtained from Fisher Scientific. Compound **2** was synthesized following literature procedures,[14] and compound **3** was obtained from Acros Organics. Compounds **1**, **2**, and **3** were dried under high-vacuum conditions for 24 h to remove residual water. ^{31}P and ^{1}H NMR spectra were obtained with use of a Bruker 360 WM instrument operated at 145 and 360 MHz, respectively. ^{31}P NMR spectra were proton-decoupled. ^{1}H shifts are reported in ppm relative to tetramethylsilane at 0 ppm. ^{31}P shifts are reported in ppm relative to 85% H_3PO_4 at 0 ppm. Glass transition temperatures were measured with a TA Instruments Q10 differential scanning calorimetry apparatus at a heating rate of 10 °C/min and a sample size of approximately 10 mg. Gel permeation chromatograms were obtained using a Hewlett-Packard HP 1100 gel permeation chromatograph equipped with two Phenomenex Phenogel linear 10 columns and a Hewlett-Packard 1047A refractive index detector. The samples were eluted at 1.0 mL/min in THF, and the elution times were calibrated with polystyrene standards. Thermal decomposition traces were obtained using a PerkinElmer TGA 7 thermogravimetric analyzer, and heating occurred at a rate of 20 °C/min from 50 to 800

Scheme 2. Synthesis Route for $[NP(OTFE)_x(O-Dye)_y]_n$[a]



[a]Note that the ratio between the two side chains is simplified as 1:1 in the illustration for the convenience of drawing the scheme. O−Dye represents dye linked to the backbone phosphorous atoms through an oxygen atom.

°C under a nitrogen atmosphere and a flow rate of 50 mL/min. Electronic absorption spectra were recorded on a double-beam spectrophotometer (Cary 500, Varian).

General Synthesis Procedure for Polyphosphazenes with Dyes and OCH_2CF_3 as Cosubstituents. The synthesis procedure is illustrated in Scheme 1. Poly(dichlorophosphazene) (1.16 g, 10 mmol) was dissolved in THF (100 mL) in a 500 mL Schlenk flask (the main reactor). Trifluoroethanol (0.73 mL, 10 mmol) was added dropwise to a THF suspension (30 mL) of NaH (0.4 g 60% oil dispersion, 10 mmol) in a second Schlenk flask, and the mixture was stirred for 0.5 h until it became a clear solution. This solution was then added slowly to the main Schlenk flask, and the mixture was stirred for 8 h at 25 °C. In a third Schlenk flask, a THF (20 mL) suspension of dye (**1**, **2**, or **3**) was added dropwise to a THF (30 mL) suspension of NaH (60% oil dispersion) in equi-molar amounts. The mixture was stirred for 4 h at 25 °C and then added slowly to the contents of the main Schlenk reactor, and the mixture was stirred for 36 h at 25 °C. Trifluoroethanol (0.91 mL, 12.5 mmol) was then added dropwise to the suspension of NaH (0.5 g 60% oil dispersion, 12.5 mmol) in THF (30 mL) in another Schlenk flask, and the mixture was stirred for 0.5 h until it became a clear solution. This solution was then added slowly to the main reaction flask to complete the replacement of chlorine atoms. The mixture was then stirred for 6 h before the reaction was terminated. The suspension was concentrated by evaporation and was poured into water sequentially three times before dialysis versus acetone/methanol (4:1) for 1 week. The amount of the sodium salt of the dye was in excess of the target amount to compensate for the subsequent displacement of some dye by subsequent $CF_3CH_2O^-$ attack.[15]

In the following molecular formulas of polymers **4**−**8**, OPR represents the deprotonated compound **1** as the side chain, OTPP represents the deprotonated compound **2** as the side chain, NTB represents the deprotonated compound **3** as the side chain, and OTFE represents the deprotonated CF_3CH_2OH as the side chain.

$[NP(OPR)_{0.0019}(OTFE)_{1.998}]_n$ ***(4)***. Collected as a red fibrous solid. Yield 69%. ^1H NMR (acetone-d_6, 360 MHz): 6.86 to 8.86 (m, 10 H), 4.57 (s, 1040 H). ^{31}P NMR (acetone-d_6, 360 MHz): −6.17 (s, flank at bottom right). M_w 447 K. PDI 1.8.

$[NP(OPR)_{0.08}(OTFE)_{1.92}]_n$ ***(5)***. Collected as a red fibrous solid. Yield 71%. ^1H NMR (acetone-d_6, 360 MHz): 6.86 to 8.86 (m, 10 H), 4.57 (s, 48 H). ^{31}P NMR (acetone-d_6, 360 MHz): −6.17 (s, flank at bottom right). M_w 610 K. PDI 1.9.

$[NP(OTPP)_{0.0013}(OTFE)_{1.999}]_n$ ***(6)***. Collected as a green fibrous solid. Yield 61%; ^1H NMR (acetone-d_6, 360 MHz): 8.89 (br, 8 H), 8.30 (br, 8 H), 7.88 (m, 9 H), 6.71 (br, 2 H), 4.26 to 4.57 (m, 1512 H). ^{31}P NMR (acetone-d_6, 360 MHz): −6.28 to −5.59 (m, 1 P), −9.50 to −7.67 (m, 19 P). M_w 278 K. PDI 2.4.

$[NP(OTPP)_{0.0028}(OTFE)_{1.997}]_n$ ***(7)***. Collected as a green fibrous solid. Yield 58%. ^1H NMR (acetone-d_6, 360 MHz): 8.89 (br, 8 H), 8.30 (br, 8 H), 7.88 (m, 9 H), 6.71 (br, 2 H), 4.26 to 4.57 (m, 710 H). ^{31}P NMR (acetone-d_6, 360 MHz): −6.30 to −5.62 (m, 2 P), −9.50 to −7.67 (m, 27 P). M_w 353 K. PDI 1.6.

$[NP(NTB)_{0.0062}(OTFE)_{1.99}]_n$ ***(8)***. Collected as a blue solid. Yield 27%. ^1H NMR (DMSO-d_6, 360 MHz): 7.17 to 7.97 (m, 5 H), 4.26 to 4.57 (m, 645 H), 3.31 (s, 6 H), 2.26 (s, 3H). ^{31}P NMR (acetone-d_6, 360 MHz): −6.27 to −5.59 (m, 2 P), −9.50 to −7.67 (m, 77 P). M_w 298 K. PDI 2.1.

General Synthesis Procedure for Polyphosphazenes with Immobilized Dyes, $CF_3CH_2O^-$, and C_6H_5O (or $CH_3OC_6H_4O^-$) as Cosubstituents. The procedure is illustrated in Scheme 2. It differs from the above protocol in the sequence of reactions, which is (a) the replacement of chlorine atoms by trifluoroethoxide and (b) the introduction of the dye, followed by (c) the replacement of the remaining chlorine by aryloxides. Thus, poly(dichlorophosphazene) (1.16 g, 10 mmol) in THF (100 mL) was treated dropwise with sodium trifluoroethoxide (2−19 mmol) in THF (30 mL), and the mixture was stirred for 8 h at 25 °C. A THF (50 mL) suspension of the sodium salt of the dye (**1** or **2**) was added, and the contents were stirred for 36 h at 25 °C. Finally, a THF (30 mL) solution of sodium phenoxide or 4-methoxyphenol (1−19 mmol) was added, and the mixture was stirred at reflux for 24 h. The suspension was then concentrated and poured into water sequentially three times before being subjected to dialysis versus acetone/methanol (4:1) for 1 week. The amount of the sodium salt of the dye was in excess of the target amount to compensate for the displacement of some dye by $C_6H_5O^-$ or $CH_3OC_6H_4O^-$.[15]

In the following molecular formula of polymers **9**−**11**, OPR represents the deprotonated compound **1** as the side chain, OTPP represents the deprotonated compound **2** as the side chain, OPh represents the deprotonated C_6H_5OH as the side chain, $OPhOCH_3$ represents the deprotonated $CH_3OC_6H_4OH$ as the side chain, and OTFE represents the deprotonated $HOCH_2CF_3$ as the side chain.

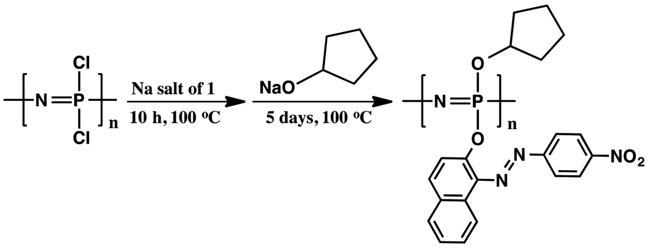
$[NP(OPR)_{0.0028}(OPhOCH_3)_{0.070}(OTFE)_{1.93}]_n$ ***(9)***. Collected as a red solid. Yield 48%. ^1H NMR (acetone-d_6, 360 MHz): 6.93 to 7.10 (m, 110 H), 4.57 to 4.59 (m, 1380 H), 3.79 to 3.80 (m, 75 H). ^{31}P NMR (acetone-d_6, 360 MHz): −5.83 (br, 1 P), −8.43 to −7.67 (m, 32 P), −10.82 (br, 3 P). M_w 157 K. PDI 2.0.

$[NP(OPR)_{0.0096}(OPh)_{1.84}(OTFE)_{0.15}]_n$ ***(10)***. Collected as a red solid. Yield 55%. ^1H NMR (acetone-d_6, 360 MHz): 8.54 (br, 1H), 7.51 to 8.05 (m, 23 H), 6.98 (s, 954 H), 3.85 (s, 32 H). ^{31}P NMR (acetone-d_6, 360 MHz): −16.77 (br, 1 P), −19.53 (br, 5 P). M_w 115 K. PDI 2.2.

$[NP(OTPP)_{0.01}(OPh)_{0.87}(OTFE)_{1.12}]_n$ ***(11)***. Collected as a green solid. Yield 41%. ^1H NMR (acetone-d_6, 360 MHz): 8.54 (br, 1 H), 7.51 to 8.05 (m, 23 H), 6.95 (s, 435 H), 3.86 (s, 226 H). ^{31}P NMR (acetone-d_6, 360 MHz): −16.75 (br, 4 P), −19.55 (br, 3 P). M_w 195 K. PDI 2.1.

*Synthesis Procedure for Polyphosphazenes with Compound 1 and Cyclopentanoxy Groups as Cosubstituents ($[NP(OPR)_{0.011}(OC_5H_9)_{1.99}]_n$ **(12)**).* The synthesis procedure is illustrated in Scheme 3. It followed a similar protocol to the examples described above but with the following changes. Specifically, the dye was introduced first. Poly(dichlorophosphazene) (0.58 g, 5 mmol) in dioxane (150 mL) was allowed to react with the sodium salt of dye **1** (0.25 mmol), followed by the sodium salt of cyclopentanol (80 mmol)

Scheme 3. Synthesis Route for $[NP(OPR)_x(OC_5H_9)_y]_n$[a]



[a]Note that the ratio between the two side chains is simplified as 1:1 in the illustration for the convenience of drawing the scheme. OPR represents the deprotonated compound **1** as the side chain, and OC_5H_9 represents the deprotonated cyclopentanol as the side chain.

in dioxane for 5 days at 100 °C. Dioxane was removed by distillation, and the resultant solid was redissolved in chloroform. The chloroform solution of the polymer was washed with water sequentially three times before dialysis versus acetone/methanol (4:1) for 1 week. The amount of the sodium salt of the dye was in excess of the target loading to compensate for the subsequent displacement of some dye by cyclopenanoxide.[15] A total of 0.29 g of red polymer was collected as the product. Yield 26%. ^{1}H NMR ($CDCl_3$, 360 MHz): 6.88 to 7.89 (m, 10 H), 4.85 (s, 181 H), 1.46 to 1.79 (m, 1448 H). ^{31}P NMR ($CDCl_3$, 360 MHz): −10.74 (s, flank at bottom right). M_w 333 K. PDI 1.6.

Film Casting. For method I (solution evaporation), 100 mg of polymer was dissolved in 10 mL of THF, and the solution was poured into a tray (3 cm × 3 cm × 2 cm) with a Teflon inner wall. The solvent was allowed to evaporate slowly for 3 days. For method II (spin-coating), 2−3 drops of a saturated polymer solution in THF was carefully spin-cast on 1 cm × 2.5 cm glass plates.

■ RESULTS AND DISCUSSION

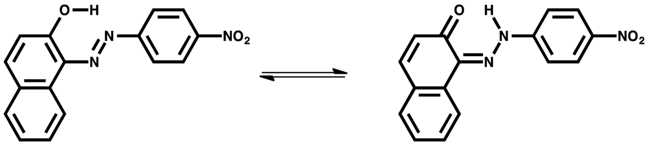
Challenges. Suitable dyes that bear a single functional group as the linker unit are rare. Most commercial organic dyes are decorated with multiple sulfate, carboxyl, hydroxyl, or amino groups. Such species will cross-link poly(dichlorophosphazene) before the chlorine replacement reaction is complete. However, dye molecules are highly conjugated structures with relatively large dimensions and a high tendency for stacking. Many have poor solubility in the organic solvents that are needed for reactions with poly(dichlorophosphazene). Moreover, impurities in dyes are common because they are introduced during the synthesis or extraction process and are difficult to remove.

Synthesis. Three different series of polymer were synthesized, as shown in Schemes 1−3. Scheme 1 illustrates the use of two different side units: the dye and the colorless, solubilizing cosubstituent groups. Scheme 2 illustrates the use of three different types of side units (the dye, trifluoroethoxy, and the aryloxy cosubstituent groups) as a means to control glass transition temperatures and eliminate long-term microcrystallinity, and Scheme 3 illustrates the use of two different side units (the dye and the cyclopentanoxy groups) that also avoid the possibility of microcrystallite formation. Dyes **1**−**3** were converted to their sodium salts by treatment with sodium hydride in THF. Although amino chromophores can be used together with triethylamine as a hydrochloride scavenger during reactions with poly(dichlorophosphazene),[5,16,17] the conversion of **3** to its sodium salt was also proved to be an efficient method for the synthesis of high-molecular-weight polyphosphazenes. Trifluoroethoxy groups were selected as cosubstituents in the first two series because the sodium salt of trifluoroethanol reacts readily with poly(dichlorophosphazene), and these side groups confer excellent chemical stability on the resultant polymer. Moreover, the trifluoroethoxy group is a THF-solubilizing component that can enhance the solubility of the synthesized polymer in ethers and ketones. However, the use of cyclopentanoxy cosubstituents in place of trifluoroethoxy, as shown in Scheme 3, yields polymers with excellent film-forming properties and no tendency for microcrystallite formation.[11] In Scheme 2, a third substituent (either a phenoxy or a 4-methoxyphenoxy group) was introduced together with trifluoroethoxy groups and the dye to raise the glass transition temperature and disrupt any potential symmetry and microcrystallinity. Increasing the glass transition temperature above room temperature is beneficial for the formation of amorphous films.

In the first two series, as shown in Schemes 1 and 2, a specific ratio (0.2 eq to 1.9 eq per $NPCl_2$ repeating unit) of trifluoroethoxy side chains was introduced in the first step. This maintains the solubility of the polymer in preparation for the introduction of the bulky dye side units, which have a tendency towards poor solubility. In addition, the partial replacement of the labile chlorine atoms by stable trifluoroethoxy units reduces the risk of cross-linking.

Isomerization of 1-[(*E*)-(4-nitrophenyl)diazenyl]-2-naphthol. The compound 1-[(*E*)-(4-nitrophenyl)diazenyl]-2-naphthol undergoes an isomerization process as shown in Scheme 4, the equilibrium of which is determined by the temperature and polarity of the environment.[18,19] However, our previous study revealed that only the azo form is observed in the methyl ether of para red.[6]

Scheme 4. Isomerization of Para Red



Thermal Properties. The thermal properties, including the glass transition temperature (T_g), a mesophase transition temperature (T_1), and the temperature of 10% weight loss (T_{10}) for the presented polymers are summarized in Table 1.

As shown in Table 1, the apparent thermal stabilities of the polymers increase as the percentage of dyes or aryloxy side units is increased. For polymers **4** and **5** (or **6** and **7**), as the percentage of dye molecules linked to the polymer chains increases, the glass transition temperature rises, while the mesophase transition temperature decreases. This indicates that microcrystallinity is efficiently reduced. Meanwhile, by introduction of a third substituent (in this case, phenoxy groups), the microcrystallinity can be further suppressed. In compound **10**, the T_1 transition was not detected, which indicates that the microcrystallinity was completely absent. The DSC traces of polymers **4**, **5**, **9**, and **10** with deprotonated dye **1** as the side chain clearly illustrate the correlation between the percentage of the bulky side chains and the thermal properties, as shown in Figure 1. From polymer **4** to **5**, where the percentage of the bulky side chain increases from 0.1% to 4%, the T_g increases from −58 °C to −47 °C, and the T_1 decreases from 58 to 41 °C. When a third side chain (phenoxy) is introduced, the T_1 signal further decreases (polymer **9**) and is eventually eliminated (polymer **10**). No mesophase transition temperature was detected for polymer **12**, which is consistent with other results that illustrate the amorphous, film-forming ability of polyphosphazenes with cyclopentanoxy side groups.[11]

Electronic Absorption and Transmission. Self-standing or spin-coated films of the polymers were easily fabricated by solvent evaporation from THF solutions. The color filtering abilities of the polymers were monitored via the visible region electronic absorption and transmission spectra of the spin-cast films of selected polymers **5**, **7**, and **8**. The spectra are shown in Figure 2.

Thus, the red polymer **5** absorbs strongly in the blue and green regions, allowing red light transmission; the green polymer **7** absorbs strongly in the blue region and moderately in the red region so that the transmitted light is principally green; the blue polymer **8** absorbs strongly in the green and red

Table 1. Thermal Properties of the Polymers 4−12

	polymer								
	4	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
T_g (°C)	−58	−47	−55	−50	−55	−53	−9	−2	−55
T_1 (°C)	58	41	57	52	48	37	null	null	null
T_{10} (°C)	343	345	361	357	339	361	350	345	null

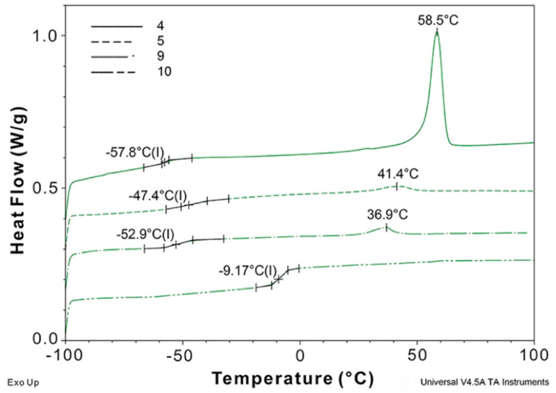


Figure 1. DSC traces of polymers containing the deprotonated compound **1** side chain.

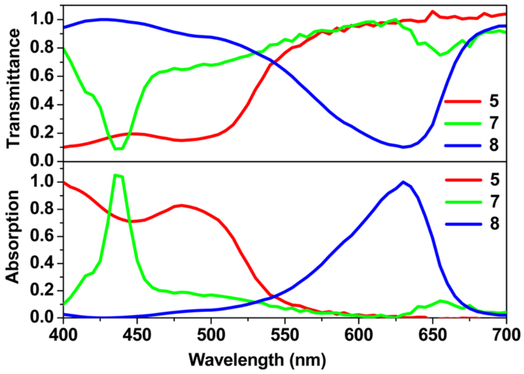


Figure 2. Visible region light absorption (top) and transmission (bottom) spectra for spin-cast films of **5**, **7**, and **8**.

regions with the major transmission in the blue. These results suggest that these polymers are potential candidates as novel soluble and processable color filters. The color filtering abilities of the polymers are limited only by the available dyes. Thus, the choice of alternative dyes with better wavelength selectivity is under investigation in our program.

■ CONCLUSIONS

In this paper, nine polyphosphazenes with immobilized dyes and different cosubstituents were synthesized and characterized. The optical densities of the polymers were tuned by varying the side chain percentages. All of these polymers are good film formers. By incorporating three different side chains, we can tune the T_g values, and any tendency for microcrystallite formation is further reduced. The introduction of cyclopentanoxy groups as cosubstituents with the dye provides an alternative method for avoiding microcrystallite formation and for controlling T_g. The polymers produced in this study are excellent prototypes for the development of stable, printable color filters for LCDs and other applications and allow the use of a variety of different functional dyes for this purpose.

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Notes

The authors declare no competing financial interest.

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