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Functional Aromatic Polyethers: Polymers with Tunable Chromogenic and Fluorogenic Properties

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ABSTRACT: This paper describes the preparation and chemical modification of pyranone-based aromatic polyethers to yield polymers that contain pyrylium rings, which permit the design of high performance materials with “a la carte” chromogenic and fluorescence behavior. These materials can be used for innovative applications such as luminescent converter (LUCO) materials for hybrid light-emitting diodes (LEDs) or the preparation of selective chromogenic and fluorogenic sensing materials for the preparation of sensing devices. The fluorescence emission maxima of polyether films ranged from 514 to 561 nm, allowing the future development of LUCO-LED devices. Moreover, the interaction of polyether films with different amines leads to color changes and variations in the intensity and emission maxima of fluorescence, which permits the development of amine sensing materials.

Introduction

Aromatic polyethers are high-performance engineering materials with excellent thermal stability, good mechanical properties, and superior hydrolysis and oxidation resistance. Moreover, aromatic polyethers are characterized by a high glass transition temperature and/or a high melting temperature. The aromatic backbone contributes to the thermal stability, whereas the ether linkages facilitate the oxidative and thermal stability of these compounds during polymer processing.[1−6] Thus, poly(phenylene oxide), poly(ether sulfone)s and poly(ether ketone)s are commercially important polymers that are often used as matrix materials in composites or as blends with other polymers.

Functionalization of the polymer core can increase the number of potential applications of a material, especially in new and cutting edge fields. For instance, fluorescent chemical moieties can be introduced into aromatic polyethers to form luminescent converters (LUCO). These materials can be used in combination with a primary pumping source for the preparation of LEDs, which have tremendous potential in lighting and backlighting applications.[7−10] Moreover, if the fluorescent moieties are able to selectively interact with an analyte, the fluorescence behavior of the materials could be utilized in chemical fluorescent sensors, which can be used to detect analytes based on the variation of light emitted by hybrid LUCO/LEDs devices. Furthermore, if functionalization gives rise to colored host substructures, interactions with guest analytes may lead to color changes, which is useful in “naked eye” colorimetric sensing materials.[11−14]

Because of the aforementioned applications of functionalized aromatic polyethers, novel aromatic poly and copolyethers with a pyranone core were prepared. The pyranone moiety was chemically modified to yield different pyrylium rings, which are chromogenic and fluorogenic functional groups that are widely used in sensing applications.[11−14] The chemical reactions used to modify the polyethers were initially evaluated in polyether models, and the synthesis and characterization of substituted polyethers are described in this paper. Although the polyether models have a defined molecular weight and greater solubility, it was assumed that each model mimicked the behavior of the corresponding polymer. Thus, polyether models were used to study the chromogenic and fluorogenic behavior of the polymers in solution.[15,16]

Experimental Section

A description of the materials and the synthetic and characterization details of the monomer, polyether models, amine sensing related molecules, polyethers, and copolyethers can be found in the Supporting Information.

Measurements and Instrumentation. ^{1}H and ^{13}C NMR spectra were obtained with a Varian Inova 400 spectrometer operating at 399.92 and 100.57 MHz, respectively, using deuterated chloroform ($CDCl_3$) or deuterated dimethyl sulfoxide (DMSO-d_6) as solvents. Low-resolution electron impact (EI-LR) mass spectra were obtained at 70 eV using an Agilent 6890N mass spectrometer. High-resolution mass spectrometry (HRMS) was conducted on a Micromass AutoSpect Waters mass spectrometer. Infrared spectra (FT-IR) were obtained with a Nicolet Impact spectrometer, and elemental analyses were performed with a LECO CHNS-932 microanalyzer. Inherent viscosities were measured with an Ubbelohde viscometer at 25 ± 0.1 °C, and 0.5 g/dL of NMP was used as the solvent. Differential scanning calorimetry (DSC) data were obtained using a Perkin−Elmer Pyris I analyzer with 10 mg of sample under a nitrogen atmosphere at a scan rate of 20 °C/min. Thermogravimetric analysis (TGA) data were obtained from 5 mg of sample under a flow of nitrogen or oxygen using a TA Instruments Q50 TGA analyzer at a scan rate of 10 °C/min.

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Scheme 1. Monomer Synthesis

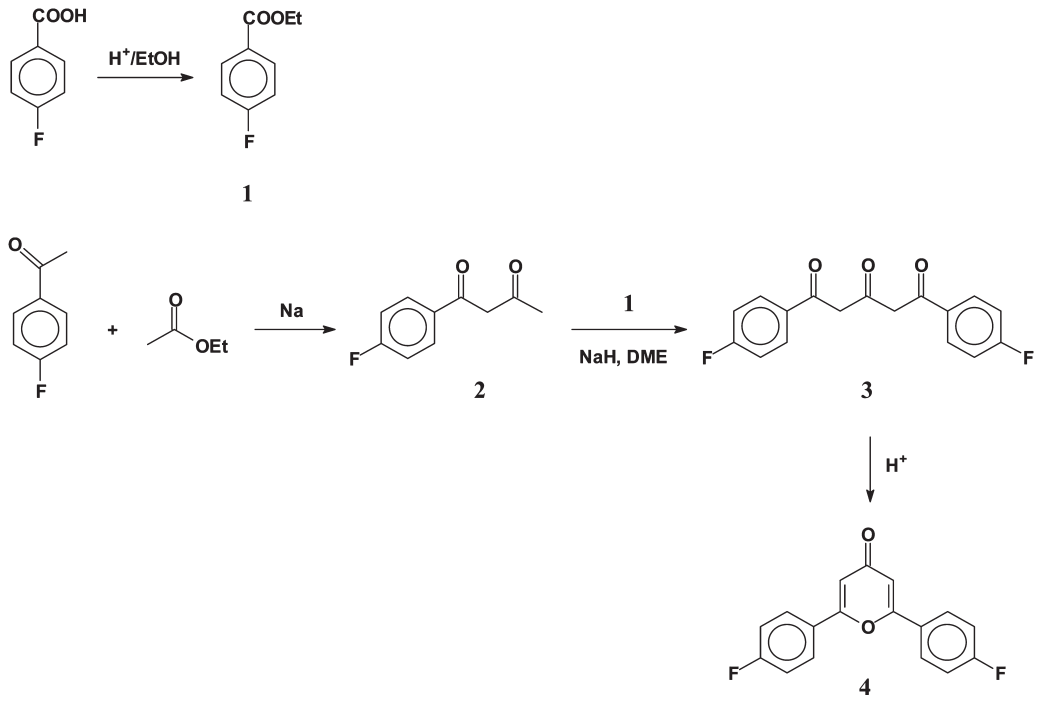
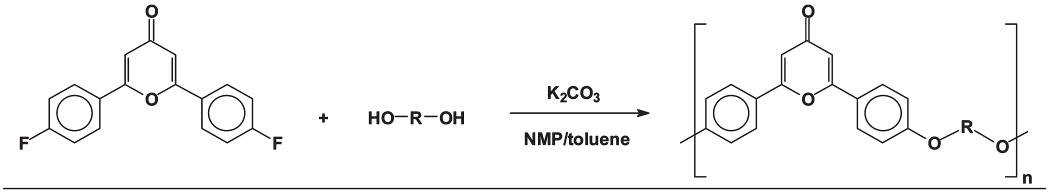
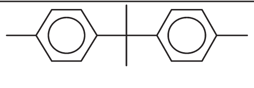
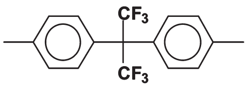
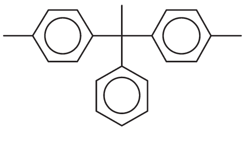
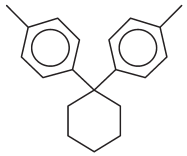


Table 1. Synthesis of Aromatic Polyethers



R	Polymer code	R	Polymer code
	I		III
	II		IV

UV/vis and fluorescence spectra were recorded on a Varian Cary3-Bio UV−vis spectrophotometer and a Varian Cary Eclipse fluorometer, respectively.

Polymer solubility was determined by mixing 10 mg of sample with 1 mL of solvent, and the resultant solution was stirred for 24 h at room temperature. To prepare polymer films, a solution of the polymer was cast from DMA, and the solvent was evaporated. In most cases, a polymer concentration of 10% by weight was employed, and the solvent was removed by heating the sample at 100 °C for 4 h in an air-circulating oven and at 120 °C for 4 h under vacuum (1 mmHg).

Water sorption experiments were conducted gravimetrically at room temperature. Two hundred milligrams of the powdered sample was dried at 120 °C for 24 h over phosphorus pentoxide, and the sample was placed in a closed box containing a saturated aqueous solution of $NaNO_2$ at 20 °C, which provided a relative humidity of 65%. The samples were weighed periodically over a period of 8 days until they equilibrated with their surroundings and presented no further changes in weight.

Dense membranes or films of homopolyethers were prepared by casting the polymers from a solution of NMP (7% w/v). Copolyether films were prepared by casting a mixture of the corresponding copolymer and the homopolymer derived from the homopolymerizaton of 2,6-difluorobenzonitrile and 4,4′-(1-phenylethylidene)bisphenol in NMP. Each film contained 0.04 equiv of pyrylium residue per bisphenol subunit.

Results and Discussion

This paper describes the synthesis, characterization, and properties of aromatic poly and copolyethers that contain a pyranone moiety in the polymer chain, which was incorporated as a subgroup in one of the monomers used in the preparation of the polymers. Copolymers containing the pyranone ring were chemically modified to obtain polymers with tuned chromogenic and photoluminescent properties. Moreover, the selective reaction of modified pyrylium copolymers with amines produced chemosensing materials: due to their chromogenic and photoluminescence behavior, these polymers respond upon interacting with certain amines.

Model compounds were used to determine the optimal reaction conditions for transformation of the pyranone subgroup into synthpyrylium substituted rings. Moreover, upon modification, the models were used as representatives of pyrylium-based copolymers, and characterization data of the models were helpful in order to characterize the copolymers. The models also permitted the chemical characterization of the species obtained upon selective reaction of a variety of amines with the pyrylium substructure of the copolyethers.

Monomer and Polymer Synthesis. The monomer (**4**) was prepared in a straightforward manner from simple, commercially available materials, as shown in Scheme 1. The difluoro monomer (**4**) was easily purified by recrystallization from ethanol, yielding a high purity condensation monomer.

The difluoro monomer (**4**) was condensed with four commercially available diphenols following a standard procedure for the preparation of aromatic polyethers, yielding four new aromatic pyranone-based polyethers. The structure of the polymer and the polymerization conditions are shown in Table 1, and the elemental analyses and viscosities of the polymers are provided in Table 2. As an example, Figure 1 shows the characterization data of polyether **II**. The spectra of monomer **4** and model **5** were used to assign the peaks in the ^{1}H and ^{13}C NMR of polyether **II**.

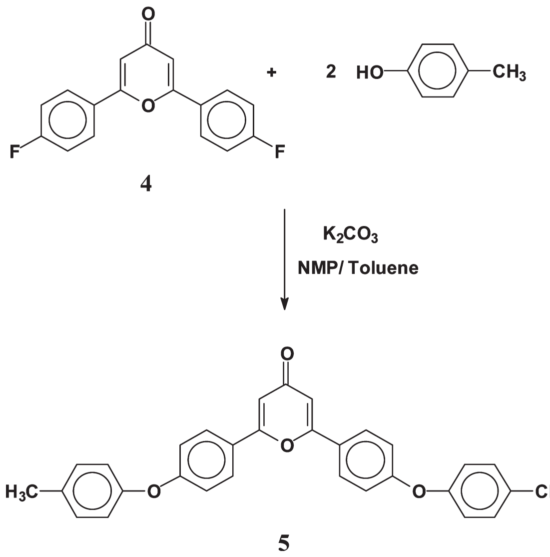
Table 2. Inherent Viscosities and Elemental Analyses of the Polyethers

		elemental analysis			
		theoretical		found	
polymer	η_{inh} (dL g^{-1})	C (%)	H (%)	C (%)	H (%)
I	0.23	81.16	5.32	81.37	5.28
II	0.44	82.97	5.08	83.03	5.00
III	0.40	66.10	3.29	66.66	3.62
IV	0.24	81.85	5.69	82.68	5.56

Synthesis and Characterization of the Models. The synthesis of polyether model **5** was conducted according to a synthetic procedure similar to the one used in the preparation of the polymers (Scheme 2). Difluoro monomer **4** was reacted with two equivalents of 4-hydroxytoluene, providing model **5** in good yield and high purity. A phenol with a methyl group in the *para* position was used to simplify the analysis of the NMR spectra.

The pyranone moiety of model **5** was transformed into four different pyrylium rings (Scheme 3, model **6** to **9**). The pyrylium ring was chosen due to its fluorescent and chromomeric properties, and its ability to selectively interact with different nucleophiles, which is a defining characteristic of chemosensors. The reaction conditions were optimized to

Scheme 2. Synthesis of the Pyranone Model



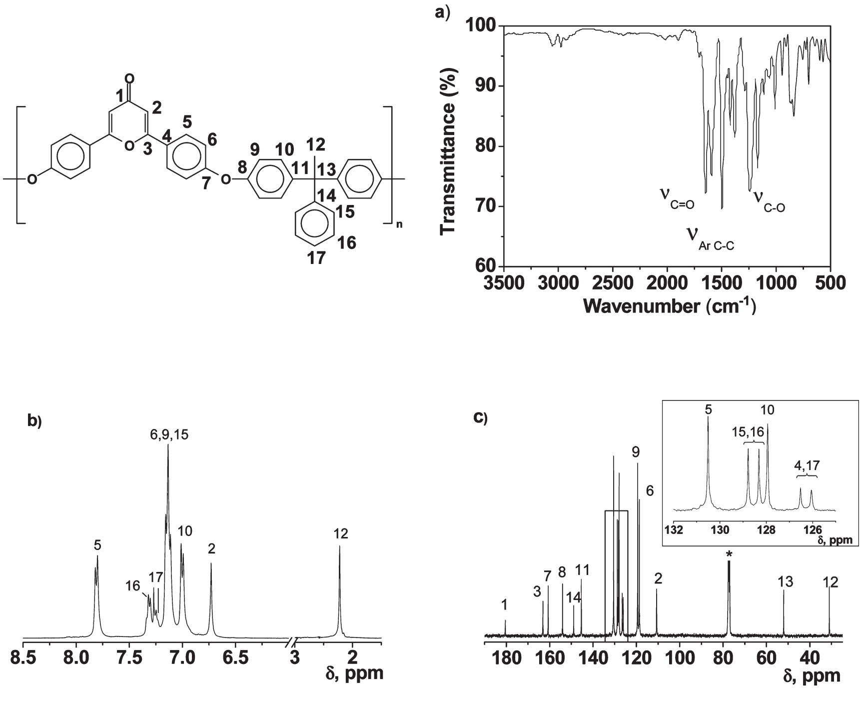


Figure 1. Characterization of polyether **II**: (a) IR-FT, (b) ^{1}H NMR, and (c) ^{13}C NMR (NMR solvent: $CDCl_3$).

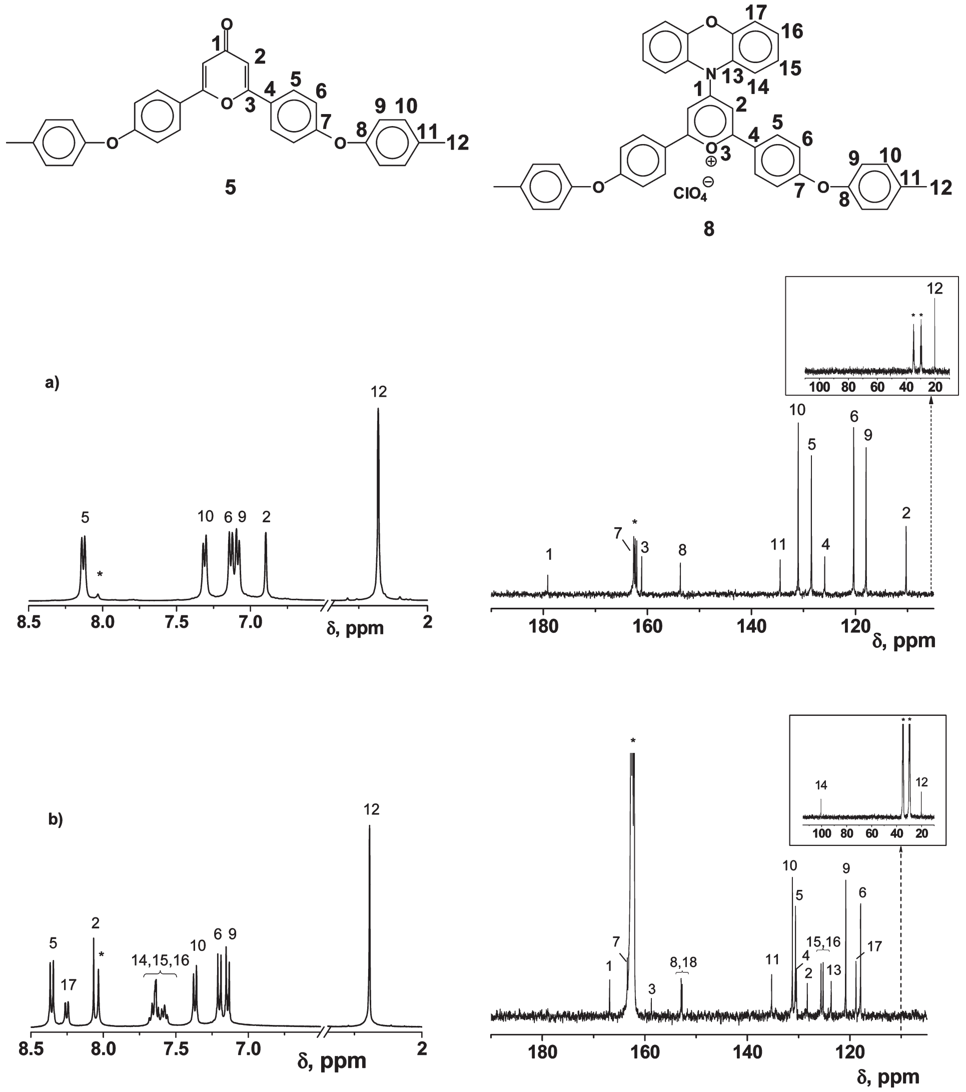
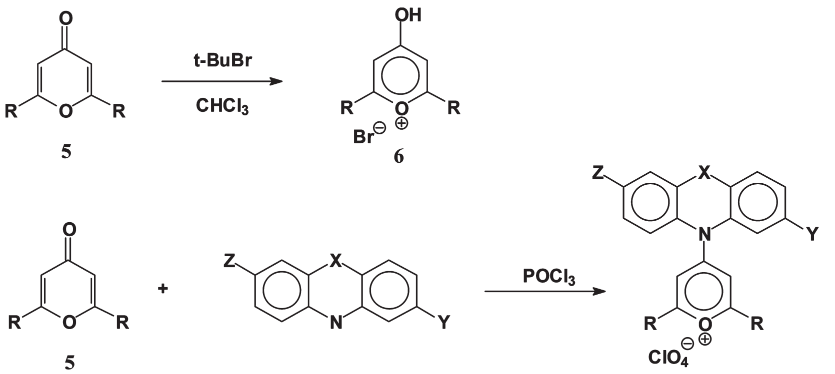


Figure 2. ^{1}H NMR and ^{13}C NMR: (a) model **5**; (b) model **8** (NMR solvent: $CDCl_3$).

Scheme 3. Synthesis of the Pyrylium Model



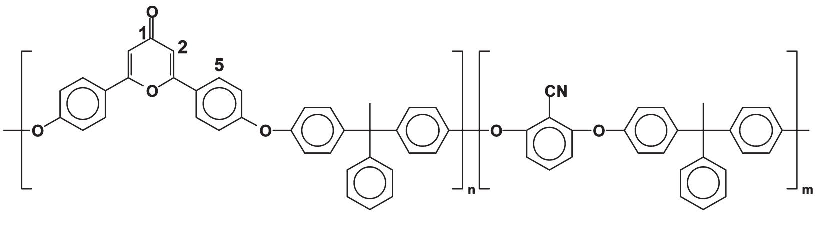
7: X = S; Y, Z = H

8: X = O; Y, Z = H

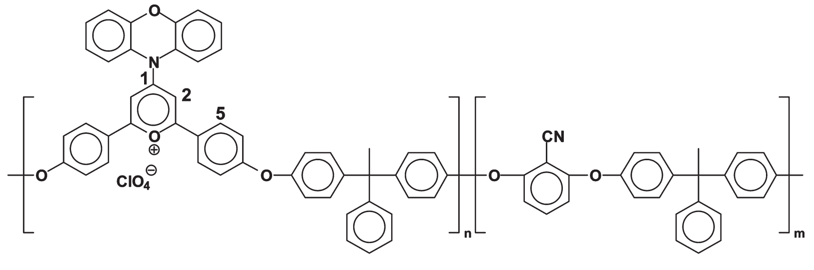
9: X = S; Y = CF_3; Z = OMe

obtain the maximum yield and purity. The optimization of the reaction conditions was very important because these conditions were applied to the copolymers, as described below. As an example, Figure 2 depicts the NMR spectra of the parent compound (**5**) and the modified model (**8**) and Figure 3 shows the NMR spectra of corresponding copolymers **V** and **Vc**.

Copolymer Synthesis, Modification, and Characterization. A copolymer containing homopolymer **II** was prepared from



V



Vc

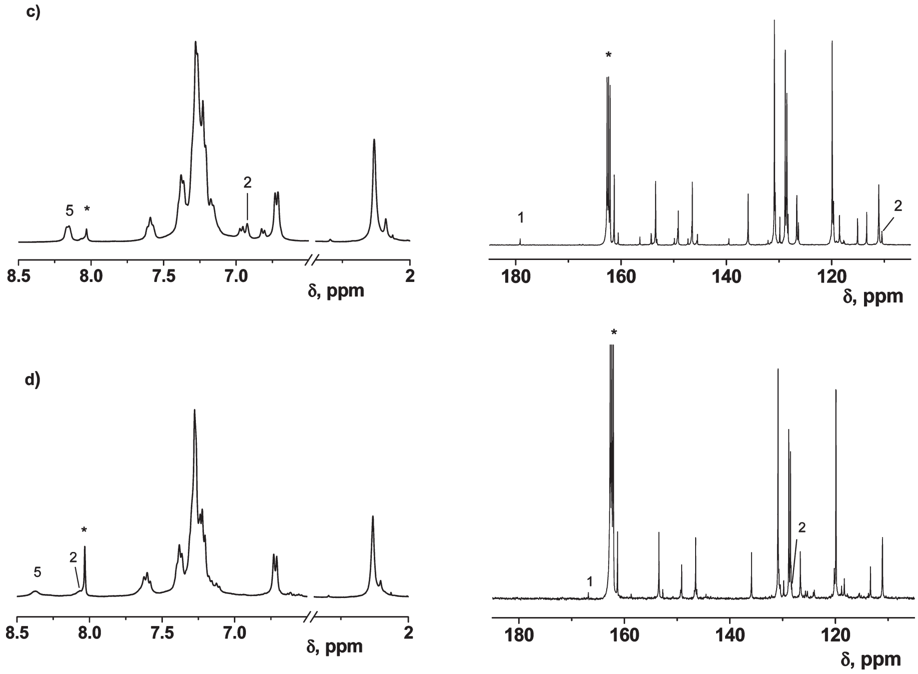


Figure 3. ^{1}H NMR and ^{13}C NMR: (a) copolymer **V**; (b) copolymer **Vc** (NMR solvent: $CDCl_3$).

the commercially available diphenol, 4,4′-(1-Phenylethylidene)bisphenol, and from the difluoro comonomers 2,6-difluorobenzonitrile and 2,6-bis(4-fluorophenyl)-4*H*-pyran-4-one (**4**) (Scheme 4). Because the copolyether was insoluble in $CHCl_3$ and other polar aprotic solvents under stoichiometric conditions, the polymer was prepared with a 4% excess of bisphenol to obtain a theoretical average degree of polymerization (X_n) of 25.

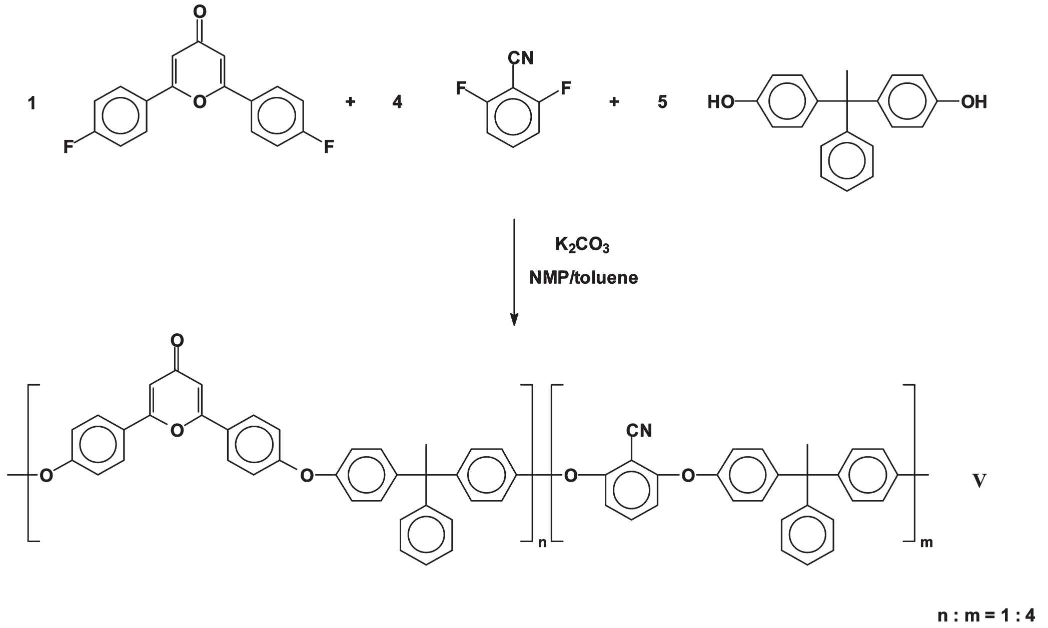
To obtain materials that could be used in sensing or optical applications, the ratio of comonomers was selected to obtain soluble polymers with an appropriate number of pyranone groups, which were subsequently transformed into pyrylium rings.

Functional copolyether **V** was transformed into pyrylium-based polymers by reacting the pyranone ring with different reagents. The synthesis was conducted according to the optimized conditions, which were obtained through the modification of polyether model compound **5**. Following this approach, copolyether **V** was transformed into copolyethers **Va**, **Vb**, and **Vc** (Scheme 5). The chemical modification could be followed by NMR, as depicted in Figure 3 for copolymer **Vc**.

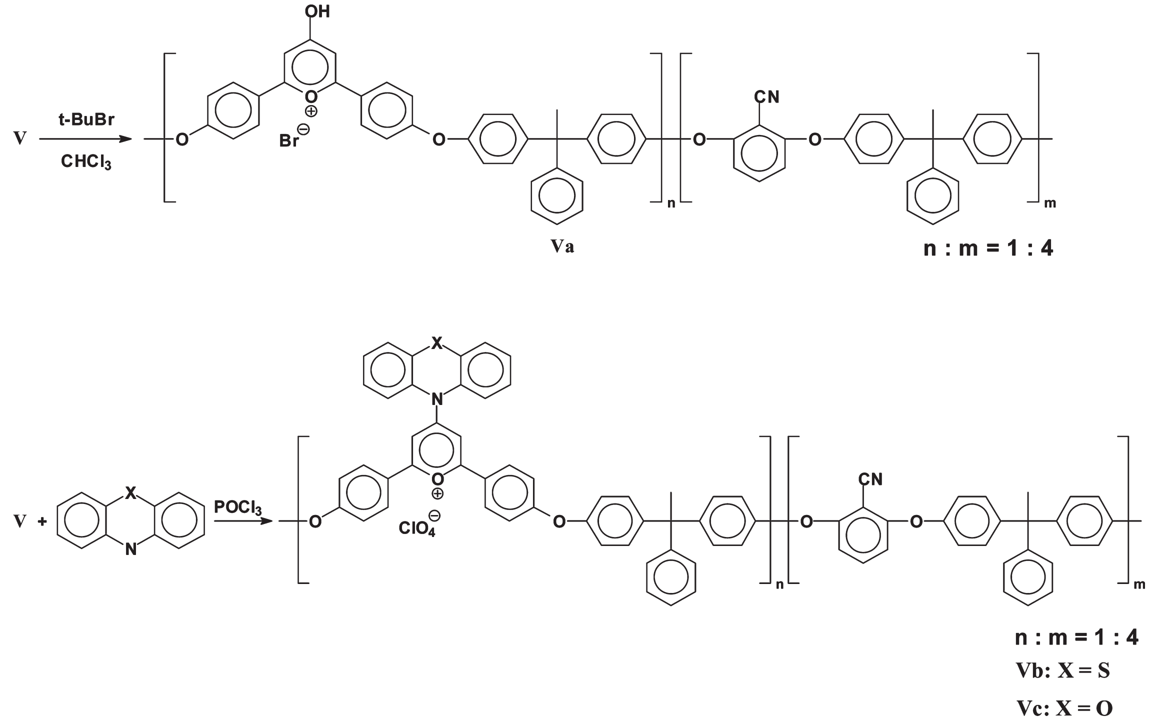
Properties of the Polymers. *Thermal Properties.* The thermal behavior of the polyethers and copolyethers was evaluated by DSC and TGA. The polyethers possessed high glass transition temperatures (T_g), from 209 to 238 °C, whereas the T_g of copolyethers ranged from 181 to 200 °C (Table 3).

The T_g of homopolyethers with a 4-pyranone subgroup in the polymer backbone was higher than the T_g of related polyethers synthesized by the polycondensation of activated aromatic dihalides such as 2,6-dihalobenzonitrile and bisphenol A or bisphenol AF, which have a T_g of 180 °C.[17] On the other hand, the T_g of copolyether **V** was less than the T_g of other homopolyethers, indicating that molecular order and regularity had a strong effect on the glass transition temperature.

Scheme 4. Synthesis of Copolyethers



Scheme 5. Synthesis of Pyrylium-Based Copolyethers



The transformation of pyranone moieties to pyrylium rings had little effect on the T_g of the polymer due to the low molar percent of the pyrylium subunits. Moreover, the T_g of the copolymers was similar due to two counteracting effects in the thermal transition. Namely, the pyrylium ring is more polar and possesses a greater lateral volume than the pyranone moiety, which impairs interchain interactions.

In DSC experiments, an endothermic peak corresponding to the melting temperature of the polyethers was not observed, indicating that the polymers are amorphous. Moreover, in wide-angle X-ray scattering (WAXS) experiments, all of the polymers except for polyether **IV** displayed an amorphous pattern with a small semicrystalline peak and a dominant amorphous halo. The WAXS measurements were carried out with as obtained polymers, meaning that the development or not of crystalline regions upon annealing was not verified.

The results of thermogravimetric analysis, summarized in Table 3, confirmed that the aromatic polymers were heat resistant materials. Thus, the temperature corresponding to 10% weight loss (T_{10}) of the homopolyethers was greater than 400 °C under a nitrogen and oxygen atmosphere. Figure 4 depicts the TGA degradation pattern of polyether **III,** which possessed the highest decomposition temperature, due to the presence of halide atoms.

Table 3. Thermal DSC and TGA Data of the Polymers and Copolymers

		TGA					
		N_2 atmosphere			O_2 atmosphere		
polymer	DSC T_g (°C)	T_5[a] (°C)	T_{10}[b] (°C)	char yield[c] (%)	T_5[a] (°C)	T_{10}[b] (°C)	LOI[d]
I	236	404	437	47	386	422	36.3
II	238	410	454	50	396	430	37.5
III	209	412	462	55	398	433	39.5
IV	219	383	425	43	383	420	34.7

		TGA					
		N_2 atmosphere			O_2 atmosphere		
copolymer	DSC T_g (°C)	T_5[a] (°C)	T_{10}[b] (°C)	char yield[c] (%)	T_5[a] (°C)	T_{10}[b] (°C)	LOI[d]
V	193	383	428	38	362	430	32.7
Va	200	409	463	46	410	467	35.9
Vb	192	278	390	41	284	410	33.9
Vc	181	263	379	44	271	371	35.1

[a] Temperature at which 5% weight loss was observed. [b] Temperature at which 10% weight loss was observed. [c] Residue (wt %) at 800 °C. [d] Calculated limiting oxygen index (LOI).

Table 4. Solubility of the Polymers[a]

polymer	DMSO	DMF	NMP, DMA	*m*-cresol	$CHCl_3$	CH	THF	dioxane	AcOH, acetone
I	+	+−	++	++	+−	+−	+−	+−	+−
II	+	−	++	++	++	+	+−	+−	−
III	+	++	++	++	−	++	+−	+−	+−
IV	+	+	+	++	+−	+	+−	−	−

copolymer	DMSO	DMF	NMP, DMA	*m*-cresol	$CHCl_3$	CH	THF	dioxane	AcOH, acetone
V	++	++	++	++	++	+	+−	+−	+−
Va	++	++	++	++	++	+	+−	+−	+−
Vb	−	+	+	−	−	−	−	+−	−
Vc	−	+	+	−	−	−	−	+−	−

[a] Key: DMSO = dimethyl sulfoxide; DMF = dimethylformamide; NMP = *N*-Methyl-2-pyrrolidone; DMA = dimethylacetamide; CH = cyclohexanone; ++ = soluble at room temperature; + = soluble upon heating; +− = partially soluble; − = insoluble

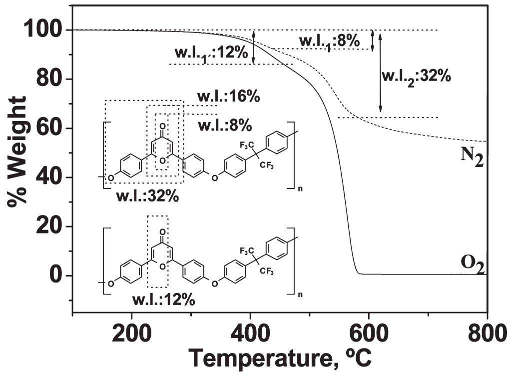


Figure 4. TGA of polyether **III** under an atmosphere of nitrogen and oxygen (w.l.: percent weight loss).

Table 5. Water Absorption of the Polyethers

polymer	water uptake (%)	molecules of H_2O/repeating unit
I	1.6	0.42
II	2.7	0.79
III	5.2	1.67
IV	6.1	1.75

copolymer	water uptake (%)	molecules of H_2O/repeating unit
V	3.6	--
Va	4.7	--
Vb	2.9	--
Vc	2.7	--

The chemical modification of the pyranone subunit to pyrylium rings slightly increased or drastically decreased the T_{10}, depending on the substitution on the pyrylium ring. The T_{10} displayed a slight increase when small and polar functional groups such as hydroxyl were introduced onto the pyrylium ring. Alternatively, the latter effect was observed with bulky organic substituents such as phenoxazin or phenothiazin moieties.

The char yield at a given temperature is intimately related to the thermal behavior of the polymers. The results indicated that the char yield of the polymers was greater than 38% at 800 °C under a nitrogen atmosphere. With the Van Krevelen equation, the char yield can be used to estimate the limiting oxygen index (LOI) of the polymers ($LOI = 17.5 + 0.4\,CR$, where CR is the char yield in % weight).[18] The LOI obtained with this equation were greater than 32, indicating that the polymers can be classified as self-extinguishing (LOI is defined as the minimum fraction of oxygen in an oxygen and nitrogen atmosphere that will support combustion after ignition. Air contains approximately 21% oxygen; thus, a material with a LOI less than 21 will not burn under open air conditions).

Solubility. The solubility of the copolymers is shown in Table 4. The polyethers were soluble enough to allow transformations to be conducted in solution (i.e., *casting* to yield films, dense membranes or enamels). The solubility of copolymer **V** was significantly greater than the solubility of the homopolyethers because the polymer chains of the copolymer were asymmetric. Moreover, the use of nonequimolecular concentration of comonomers led to a lower molecular weight, which increased the solubility (see Experimental Section). Surprisingly, the chemical modification of copolymer **V** to yield copolymers **Vb** and **Vc** dramatically decreased the solubility; however, this effect was not observed with copolymer **Va**.

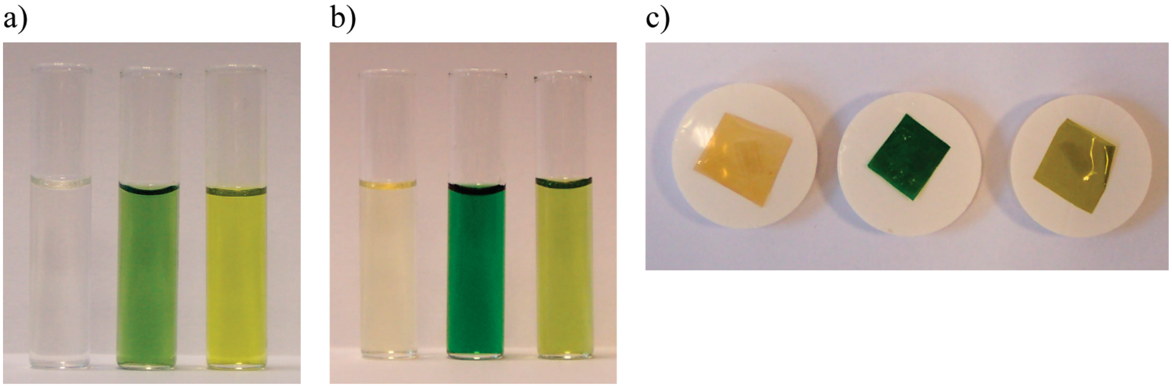


Figure 5. (a) Solutions of models **6**, **7**, and **8** (from left to right) in NMP (5×10^{-3} M); (b) solution of copolyethers **Va**, **Vb**, and **Vc** (from left to right) in NMP (5×10^{-3} equivalents of pyrylium per liter of NMP); (c) films of copolymers **Va**, **Vb**, and **Vc** (from left to right).

Table 6. Fluorescence Emission Maxima (nm) of Copolymers and Models

		$\lambda_{\text{emission}}$, nm	
models	$\lambda_{\text{excitation}}$, nm	solution	solid state (film)
6	362	476	--
7	452	526	--
8	504	597	--
		$\lambda_{\text{emission}}$, nm	
copolymers	$\lambda_{\text{excitation}}$, nm	solution	solid state (film)
Va	364	469	514
Vb	452	520	528
Vc	504	553	561

Water Sorption. The hydrophilic or hydrophobic character of organic molecules arises from the presence or absence of hydrophilic groups. In the aromatic polyethers, the ether linkage is not highly polar and water uptake is low, as shown in Table 5. The water uptake of the polymers can determine the final application of the materials because absorbed water decreases the T_g and affects the mechanical, electrical and dielectrical properties of the material. For instance, membranes with selective chromogenic or fluorogenic groups can be used as sensing materials in aqueous environments, where greater water uptake leads to superior performance because the diffusion of guest molecules or analytes into a swollen polymer matrix is improved. This effect is significant because sensing occurs in the polymer matrix, where solvated analytes and the sensing moiety of the polymeric material interact.

The water uptake of copolyether **V** was 3.6%, which was greater than the water absorption of polyether **I** but less than the uptake of polyether **IV**. The water uptake results indicated that substitution on the pyrylium rings affected the amount of water absorbed by the polymer. Specifically, polymers containing hydroxypyrylium rings displayed the greatest water uptake (**Va**). Dense membranes or films of the copolymers were used to test the materials as colorimetric sensors for amines, as described below.

Chromogenic and Fluorescence Behavior. The chromogenic and fluorescence behavior of high performance polymers is a fundamental property that is necessary for applications such as chromogenic and fluorogenic sensing materials and hybrid LUCO/LED emitting devices.

Solutions of models **6-8** and copolymers **Va-Vc** in solution and in the solid state ranged from colorless to deep green (Figure 5).

Polymers and models displayed fluorescence behavior, where the maximum fluorescence emission was observed between 476 and 597 nm (Table 6). Figure 6 depicts the fluorescence spectra of the models and copolymers in solution, and Figure 7 illustrates the fluorescence behavior of the copolymers in solution and in the solid state. Moreover, the batochromic shift and broaden of the emission band of the films with respect to the solutions, ascribed to the inter and intrachain interactions in the solid state, is shown in Figure 7.[19] The films, especially polymer **Vb**, displayed fluorescence emission maxima at the wavelength of yellow light, which allows these materials to be combined with a blue LED pumping source to yield white lighting for lighting and backlighting applications. Currently, investigations on the use of pyrylium polymers in LED applications are underway. Nevertheless, further improve in the polymer structure are needed to achieve material with commercial application in the field of LUCO technologies because the quantum yield of the polymers and models is lower than 0.1.

Sensing Behavior of Copolyether Films. Once the characterization of functional polymers was complete, a preliminary study was conducted to investigate the use of polymer films as chemosensing materials. Previous research has shown that pyrylium rings can react with amines to produce color changes and fluorescence modulations, which may be useful for the design of optical chemosensors.[20] The determination of toxic substances such as amines has become relevant in recent years.[21−23] For instance, amines are used in fertilizers and in the pharmaceutical and dye manufacturing industries. Moreover, amines can be found in industrial wastewater. Common methods for the detection and determination of amines include chromatographic methods,[24−26] potentiometric techniques,[27−30] piezoelectric sensors and quartz crystal microbalances.[31,32] An alternative to these high-cost techniques is the development of optical sensors for the *in situ* and rapid identification of amines.[33,34]

Copolyether **Vb** was further evaluated in sensing studies. Changes in the color or fluorescence of this film were tested in the presence of butylamine, dibutylamine, triethylamine and aniline, as well as OH^-, CO_3^{2-}, HCO_3^-, CN^-, SCN^-, $H_2PO_4^-$, F^-, Cl^-, Br^-, I^-, acetate, and benzoate, which were dissolved in solutions of H_2O:CH_3CN (60:40 v/v). The chromomeric response of the polymer to the aforementioned analytes is depicted in Table 7. The color of the film changes in the presence of primary and secondary amines including butylamine and dibutylamine, whereas tertiary amines, aromatic amines and a number of anions did not induce a color change. Figure 8 shows the UV−vis spectra of **Vb** in the absence and presence of butylamine. Besides the change in

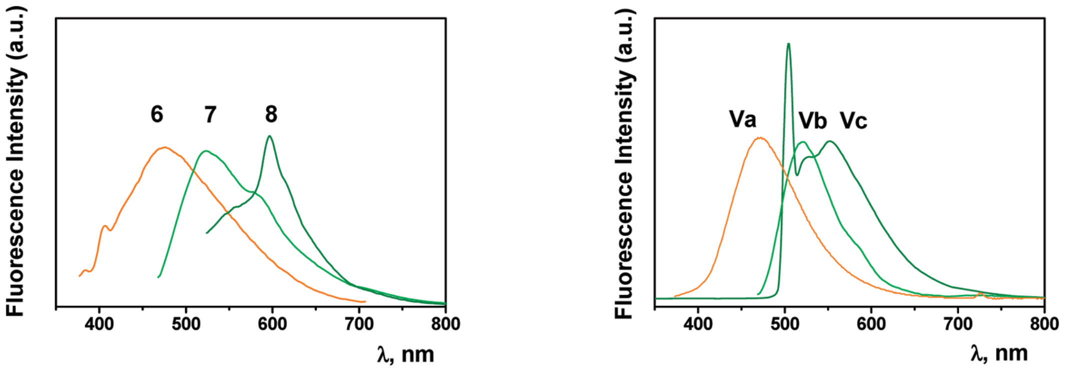


Figure 6. Fluorescence emission of pyrylium models (left) and pyrylium polyethers in solutions of NMP (right). The sharp fluorescence peak observed at ca. 500 nm for polymer **Vb** corresponds to Rayleigh's diffraction.

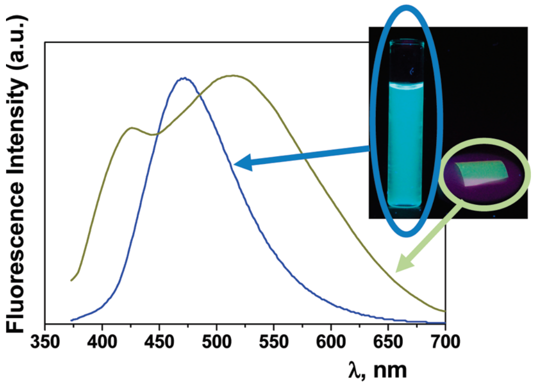
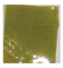


Figure 7. Fluorescence emission spectra of copolymer **Va** in solutions of NMP (continuous lines) and in the solid state (film).

Table 7. Chromogenic Response of Copolyether Vb upon Immersing a Film of the Polymer in Solutions of H_2O:CH_3CN and Several Amines or Anions for 30 min (the Images Correspond to Pictures of the Films Taken with a Digital Camera)

Vb (raw material)	
Butylamine	
Dibutylamine	
Triethylamine	
Aniline	
CO_3^{2-}, HCO_3^-, CN^-, SCN^-, $H_2PO_4^-$, AcO^-, benzoate$^-$, F^-, Cl^-, Br^-, I^-	

color, a modulation in the fluorescence behavior of the film (see Figure 9) was observed, where green fluorescence was transformed into orangish/red emissions.

To interpret the chromo-fluorogenic behavior of copolyether **Vb**, one must consider that the α or γ position of the pyrylium ring reacts with nucleophiles to afford a variety of acyclic or cyclic products. Attack at the α position is preferred because this site is more electron deficient than the γ position. Under basic or acidic conditions, nucleophilic attack in aqueous solution leads to the diketone, as shown in Scheme 6. On the other hand, primary and secondary amines behave as nucleophiles in aqueous solution, leading to pseudobase formation that, in the case of primary amines, may lead to the formation of a pyrydinium salt (Scheme 6).[35-37]

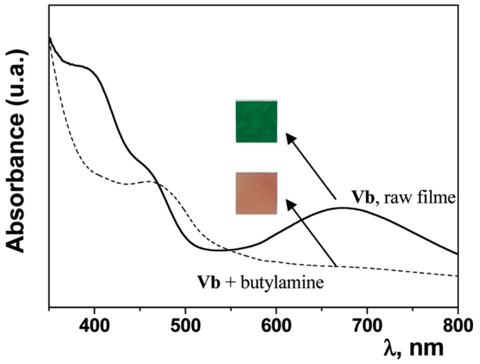


Figure 8. UV−vis spectra of copolyether **Vb** upon soaking the film in a 5×10^{-2} M solution of butylamine in H_2O:CH_3CN (60:40 v/v). The film was immersed in the solution for 24 h, which caused the polymer to swell by 16% (by weight). Similar spectra were obtained in the presence of dibutylamine.

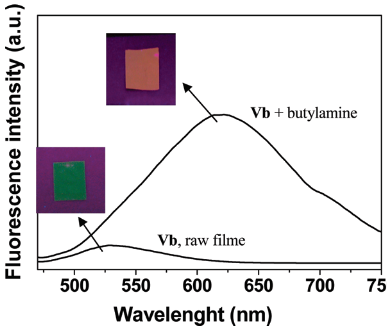
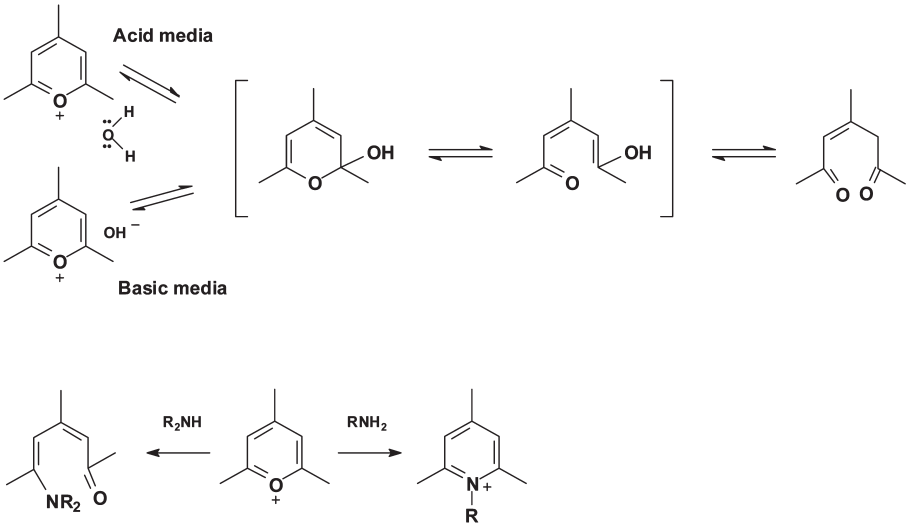


Figure 9. Fluorescence emission spectra of copolyether **Vb** upon soaking the film in a 5×10^{-2} M solution of butylamine in H_2O:CH_3CN (60:40 v/v). The film was immersed in the solution for 24 h, which caused the polymer to swell by 16%.

To study the chromogenic response of pyrylium copolyether **Vb** to specific amines, the reactivity of model compound **7** was studied in the presence of butylamine. Upon reacting **7** with butylamine, a compound containing a pyrydinium ring was formed (**10**) (see Scheme 7). The product was isolated and fully characterized by ^1H and ^{13}C NMR. Figure 10 shows the UV−vis spectra of pyrylium (**7**) and pyrydinium (**10**) derivatives in H_2O:CH_3CN (60:40 v/v). Compound **7** shows a visible band at 650 nm that is similar to the band observed in polymer

Scheme 6. Reaction of Pyrylium Rings with Nucleophiles



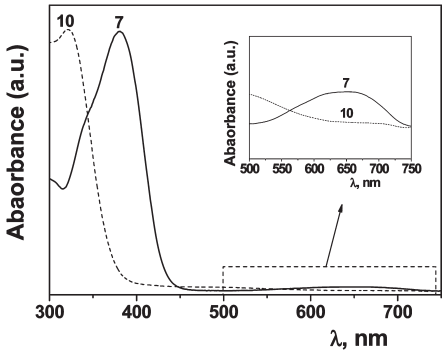
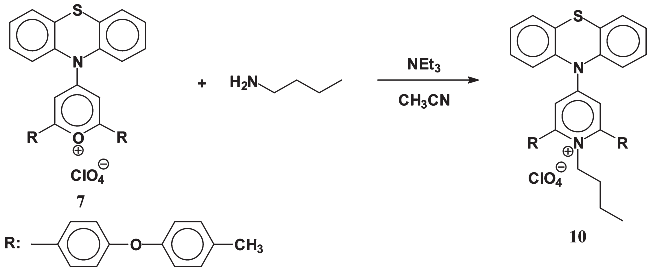


Figure 10. UV−vis spectra of a 2.5 × 10^{-5} M solution of pyrylium model **7** and pyrydinium **10** in H_2O:CH_3CN (60:40 v/v).

Scheme 7. Synthesis of the Pyrydinium Model



Vb (see Figure 8). In the presence of butylamine, this band disappears due to the formation of pyrydinium derivative **10**. Similar behavior (i.e., the disappearance of the visible band at 650 nm) was observed for **Vb** in the presence of butylamine, suggesting that the chromogenic response of the polymer was due to the transformation of the pyrylium ring to a pyrydinium moiety. Finally, the color of polymer **Vb** changed in the presence of dibutylamine. As shown in Scheme 2, the reaction between a pyrylium ring and a diamine is expected to result in the formation of a divinylogous amide. Moreover, the rupture of the pyrylium ring is expected to cause the band at 680 nm to disappear; thus, the formation of the divinylogous amide is in agreement with the observed color change. The reactivity of the pyrylium ring is also in agreement with the lack of reaction in the presence of triethylamine, a tertiary amine.

The results indicated that the chromogenic response of pyrylium films toward primary amines was due to the transformation of pyrylium rings to pyrydinium moieties. Moreover, the chromogenic response of the polymer to secondary amines leads to similar UV−vis spectra. Primary amines and pyrylium groups present in the polymer film react to form a divinylogous amide, which also occurs with secondary amines.

Conclusion

In this study, the synthesis and characterization of eight new fluorescent polyethers, copolyethers and polyether models was achieved. The pyranone ring in the polymers could be chemically transformed into substituted pyrylium groups, which can be used as chromogenic and fluorogenic receptors in supramolecular chemistry.

The parent copolyether can be easily modified to yield pure, high performance polyethers with "a la carte" fluorescent and chromogenic properties. The inherent difficulty associated with clean and high yielding chemical modifications of polymers was overcome by optimizing the reaction conditions with polyether models. Upon determining the optimal conditions, the reactions were applied to functional polymers, and the desired chemical modifications were effected. The influence of the pyranone and pyrylium rings was evaluated, and the thermal properties, solubility and water uptake of the polymers was determined.

In short, a clean and easy preparation of functional polymers was achieved, and the synthesis of high value, high performance materials was attained by subsequent modification of parent polymers. The results of this study suggested that the characteristics of these materials are applicable to innovative technologies associated with the fluorescence and chromogenic characteristics of the pyrylium moiety. Moreover, the host behavior of pyrylium rings can be applied to the fluorescent and chromogenic-naked eye-sensing of amines or hybrid luminescent converter (LUCO) and LED systems. Further investigations on the applications of the polymers are currently in progress.

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Supporting Information Available: Text giving synthetic details and characterization of the monomer, polyether models, amine sensing related molecules, polymers, and copolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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