

Synthesis and Liquid-Crystalline Properties of Poly(4-vinylpyridinium) Bromides *N*-Substituted with Dialkyloxyterphenyl Groups

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ABSTRACT: Poly(4-vinylpyridine)s (P4VPs) fully and partially quaternized with dialkyloxyterphenyl groups were synthesized and characterized. These new polymers developed both liquid-crystalline (LC) properties and a light emission (luminescence) in the blue region. The mesomorphic behavior of the polymers was initially characterized by differential scanning calorimetry and polarizing optical microscopy and was further corroborated by X-ray diffraction analyses. The X-ray diffraction patterns showed in the low-angles region several equidistant diffraction peaks (d_{001} , d_{002} , d_{003} , ...) and in the wide-angles region a broad peak typical of nonordered mesophases. From d_{001} and the length of the monomers, we deduced that the molecular arrangement in the mesophase corresponded to a double-layered stacking of molecules with mesogens tilted

with respect to the smectic plane and the backbones sandwiched between. In this arrangement, the different parts of mesogens are segregated from one another in layered domains. The longer smectic periods observed for copolymers indicated that the nonsubstituted pyridine cycles were sandwiched between two smectic layers. The emission spectra of these polymers were characterized by a broad signal centered at 365 nm. The combination of LC properties with luminescence in the polymers is interesting for the preparation of thin films with aligned emitters, particularly for linearly polarized light emission. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 2074–2081, 2011

Key words: liquid-crystalline polymers (LCP); luminescence; thermal properties

INTRODUCTION

Unprecedented attention has been focused on π -conjugated polymers because the discovery of their light-emitting (LE) properties.¹ These polymers are fairly insoluble and normally they are modified with alkyl chains of different length for proper handling and processing.² The combination of alkyl chains with π -conjugated cores is interesting because it frequently leads to a liquid-crystalline (LC) behavior that increases the potential applications of the material, especially in devices requiring highly oriented molecular emitters, as is the case with linearly polarized LE diodes.^{3,4} On the other hand, π -conjugated molecules with few repeating units can be introduced into polymer chains through a flexible spacer, and the resulting polymer can also develop

LE and LC properties, along with some other interesting characteristics, such as good mechanical properties and easy processing; this makes possible the fabrication of large-area thin films.⁵

In a previous study, we observed 4-vinylpyridine (4VP) *N*-substituted with an alkyloxybiphenyl mesogen polymerizes spontaneously leading to a fully quaternized poly(4-vinylpyridine) (P4VP).⁶ This specific polymerization method was used to prepare P4VP *N*-substituted with different mesogens; however, there has been no report on the use of π -conjugated cores longer than a biphenyl group.^{7,8} P4VP *N*-substituted with biphenyl cores through a flexible spacer normally develops single-layer smectic phases with upright molecules (or mesogens) laterally arranged head to tail, as was deduced for pyridine *N*-substituted with similar mesogens.^{9,10} In a recent study on molecular liquid crystals, we observed that the pyridine *N*-substituted with longer rigid cores, such as terphenyls, developed double-layer smectic phases.¹¹ In such an arrangement, the ionic groups and elongated cores are fully segregated from one another in layered domains; this indicates that the π interactions of terphenyl cores are strong enough to counterbalance the interactions

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between the ionic species in such a way that the head-to-tail arrangement in these molecules is not developed. We thought it of interest to extend this work to polymers, so we synthesized and characterized ionic polymer liquid crystals based on poly(4-vinylpyridinium) bromides *N*-substituted with 4,4'-dialkyloxyterphenyl groups. The results of the LC properties of these new materials are presented and discussed in this article.

EXPERIMENTAL

Materials and instrumentation

4-Bromophenol, 4'-bromo-4-hydroxybiphenyl, 1-bromotetradecane, 1,8-dibromooctane, 1,12-dibromododecane, bromine, butyllithium (1.6M in hexanes), triisopropylborate, tetrakis(triphenylphosphine)palladium(0) or Pd(0) complex, *tert*-dodecanthiol, hydroquinone, pyridine and 4VP, sodium hydroxide, hydrochloric acid (37%), sodium carbonate, potassium carbonate, potassium iodide, azobisisobutyronitrile, dimethylformamide, tetrahydrofuran (THF), dichloromethane, methanol, and ether were used as received. THF was distilled from a sodium/benzophenone complex before use. 4VP was distilled at 80°C under reduced pressure from a 4VP/KOH mixture. All chemicals and solvents were purchased from Aldrich Co. (St Louis Missouri, USA) and J. T. Baker (Phillipsburg, NJ, USA).

¹H-NMR spectra were recorded with a JEOL (Akishima Tokyo, Japan) spectrometer (300 MHz) with CDCl₃, tetrahydrofuran-*d*₈, and CDCl₃/CD₃OD as solvents. Thermograms were registered from an open Mettler FP94HT differential scanning calorimeter (or an MDSC 2920 from TA Instruments) (New Castle DE, USA) at heating and cooling rates of 5°C/min. Thermogravimetric analysis was performed on vacuum-dried samples with a TGA Q500 (TA Instruments) with a nitrogen vector gas at a heating rate of 10°C/min. Optical textures of the mesophases were registered upon cooling in an Olympus (Tokyo, Japan) BH-2 polarizing optical microscope coupled with a Mettler (Greifensee, Switzerland) FP82HT hot stage. X-ray diffraction analyses were performed with an INEL (Artenay, France) CPS120 diffractometer with K α ₁ copper radiation and a homemade electrical oven. The ultraviolet-visible (UV-vis) absorption spectra were recorded on a Shimadzu (Kyoto, Japan) 2401PC UV-vis spectrophotometer (250–450 nm), whereas the emission spectra were obtained with a PerkinElmer (Seer Green U.K.) LS 50B spectrofluorimeter (350–500 nm). Polymer solutions were excited with a UV light of 304 nm. Solutions for the optical characterization were prepared with spectroscopic-grade chloroform at concentrations around 0.04 mg/mL.

Synthesis of polymers

The intermediates and final polymers were prepared through the synthetic route outlined in Scheme 1. Initially, an alkyl chain was introduced into the 4-bromo-4-hydroxybiphenyl through a Williamson reaction.¹² The resulting molecule (I) was then reacted with butyllithium and triisopropylborate to obtain an arylboronic acid (II).¹³ The 4-bromophenol was reacted with α,ω -dibromoalkanes to obtain the 4-(ω -bromoalkoxy) bromobenzene (III), which was, in turn, coupled with II to prepare the 4''-(ω -bromoalkoxy) 1-alkyloxyterphenyl (IV; Suzuki reaction).¹⁴ The experimental conditions for the synthesis and purification of the intermediates were similar to those described in previous articles.¹⁵

The quaternization/polymerization reaction was carried out by the introduction of compound IV (1 mmol) into freshly distilled 4-vinyl pyridine (50 mL), and the mixture was heated at 80°C and stirred for 20 h. The molecular weight of the polymers was not determined because of solubility problems; however, the feature of the ¹H-NMR spectrum was typical of polymeric materials. On the other hand, P4VP was synthesized by free-radical polymerization (azobisisobutyronitrile as initiator) to further prepare polymers that were partially quaternized with dialkyloxyterphenyl mesogens. The molecular weight of the nonquaternized P4VP, as determined by solution viscosimetry in ethanol at 25°C, was 2.2×10^4 g/mol.¹⁶ The quaternization degree (or percentage quaternization) was calculated from the ratio of the integrals of the peaks centered at $\delta = 4.5$ ppm ($-\text{CH}_2-\text{N}^+$) and $\delta = 6.8$ ppm (4CH, Ar, in ortho position to C—O).

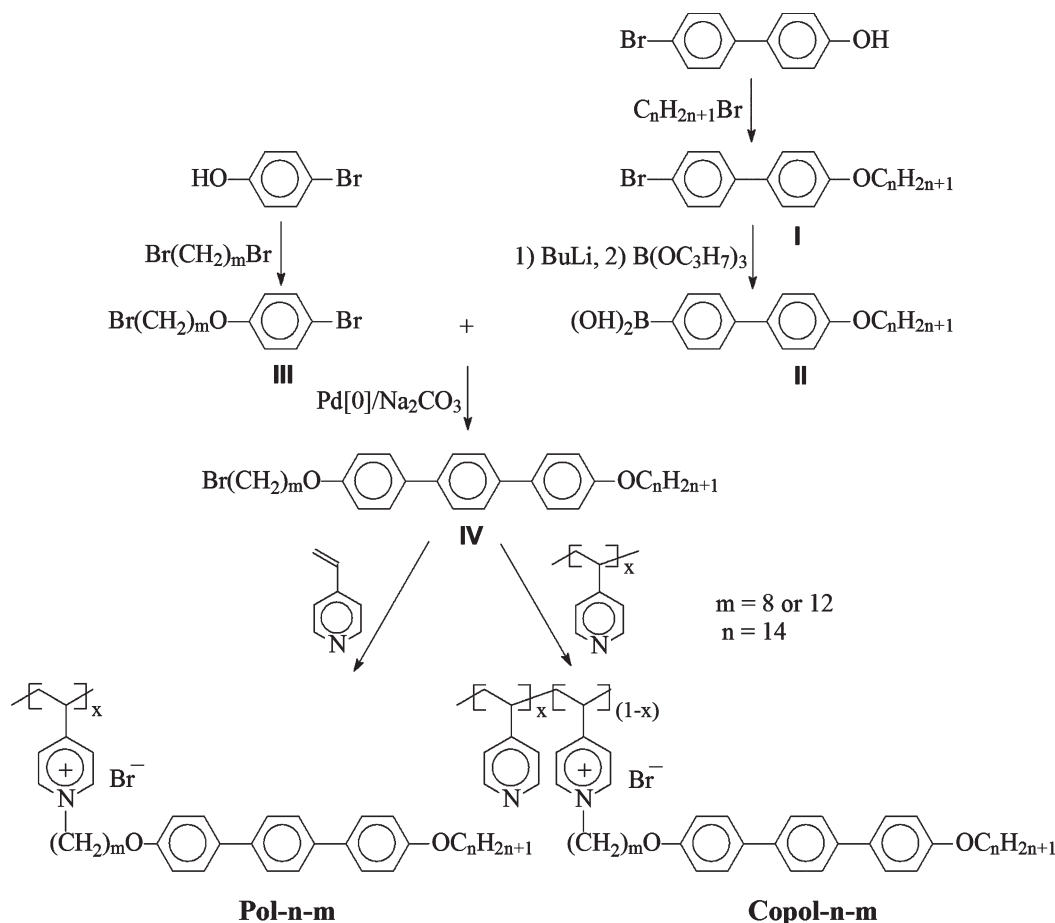
For the sake of brevity, the fully and partially quaternized polymers were labeled Pol-*n-m* and Copol-*n-m*, respectively. As indicated in Scheme 1, *n* and *m* are the lengths of the terminal alkyl chain and the spacer, respectively. The partially quaternized polymers are also referred as the copolymers.

RESULTS AND DISCUSSION

Synthesis of the polymers

The synthesis, purification, and characterization of the intermediates (I–IV in Scheme 1) were described in detail in previous reports.^{15,17} The intermediate IV was used to quaternize both 4VP and P4VP to obtain the fully and partially quaternized side-chain LC polymers, respectively.

The quaternization of 4VP with bromoalkyl derivatives produced *N*-alkyl-substituted 4-vinylpyridinium bromides, which were unstable and polymerized spontaneously; this led to fully quaternized polymers.¹⁸ To prevent a parallel thermal free-



Scheme 1 Synthetic route for the preparation of P4VPs fully and partially quaternized with terphenyl groups through a flexible spacer.

radical polymerization of the nonquaternized 4VP, a small amount of hydroquinone was added to the reaction. Through this method, the polymers Pol-14-8 and Pol-14-12 were obtained at relatively high yield (ca. 83%). Both polymers were analyzed by $^1\text{H-NMR}$ spectroscopy; however, because of their similarity, only the spectrum of Pol-14-12 is presented and discussed (Fig. 1). In this spectrum, the two broad peaks located between 7.8 and 9 ppm corresponded to protons of the pyridinium ring. The presence of only these two signals in this region of the spectrum indicated that all pyridine cycles in the polymer were quaternized.¹⁹ The peaks centered at 6.8 and 7.6 ppm corresponded to protons of the terphenyl group. The small and broad signal observed at 4.5 ppm was assigned to protons of the methylene attached to the nitrogen atom ($-\text{CH}_2-\text{N}^+$), whereas the peak at 4 ppm was attributed to protons of the two methylenes in α to the oxygen atom ($-\text{CH}_2-\text{O}$). Finally, the signals at 1.2–1.6 ppm corresponded to protons of the internal methylenes, whereas that at 0.9 ppm corresponded to those of the methyl group. The spectrum also showed a small peak at 3.4 ppm, which was attrib-

uted to the protons of methanol (traces from deuterated methanol), and a big peak at 2.5 ppm, which was assigned to the protons of water. Alkyl pyridinium salts are hygroscopic molecules and are used to crystallize with half of the molecules of water; these were difficult to remove.²⁰

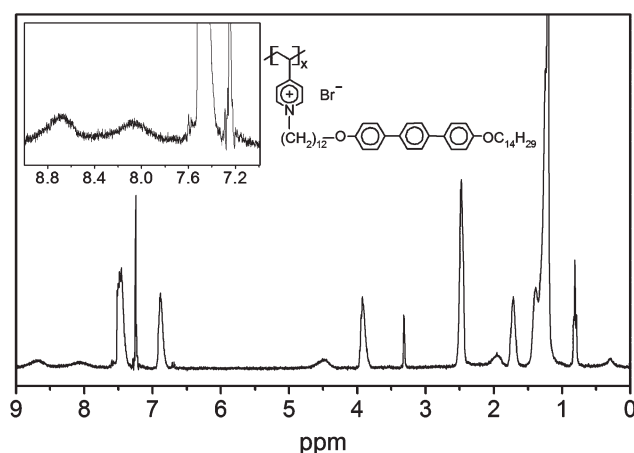


Figure 1 $^1\text{H-NMR}$ spectrum of Pol-14-12 obtained in $\text{CDCl}_3/\text{MeOD}$ at 60°C .

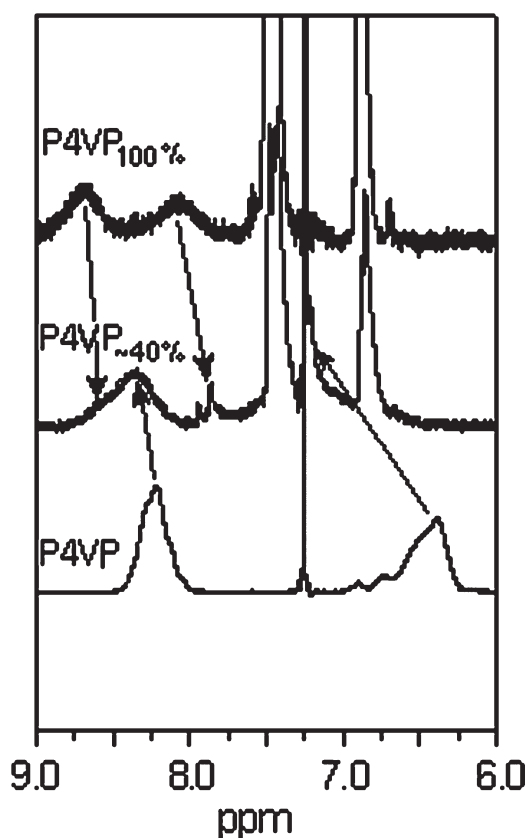


Figure 2 Amplification ($\delta = 6-9$ ppm) of the ^1H -NMR spectra of P4VP, Pol-14-12, and Copol-14-12 measured in $\text{CDCl}_3/\text{MeOD}$ at 60°C . The percentages indicate the extent of quaternization.

A second strategy for preparing poly(vinylpyridinium) salts *N*-substituted with mesogenic groups is the quaternization of a previously synthesized P4VP. Through this method, only partially quaternized polymers can be obtained because of the steric hindering effect produced by the already substituted cycles; this becomes more and more important as the degree of quaternization increases. This effect is more pronounced when voluminous mesogens are used as quaternization agents.²¹

The ^1H -NMR spectrum of the partially quaternized P4VP showed the same signals compared to that of the fully quaternized polymer, except for those signals corresponding to the pyridinium ring, which are shifted and overlapped. Figure 2 shows the expanded ^1H -NMR spectra (from 6 to 9 ppm) for the fully and partially quaternized polymers; the ^1H -NMR spectrum of the nonquaternized P4VP is also shown. Signals of the nonquaternized P4VP were centered around 6.4 and 8.2 ppm, whereas those for a fully quaternized P4VP (100%) shifted and appeared around 8.1 and 8.7 ppm; however, for the partially quaternized P4VP (ca. 40% in this study) the corresponding signals shifted and overlapped. The shifting of signals in these polymers was com-

pared with those observed in previous studies for similar systems (from 5 to 80%), and good concordance was found with respect to the polymer quaternized around 40% with mesogenic groups.¹⁹

Thermal behavior

The initial decomposition temperatures (T_d 's) for polymers Pol-14-8 and Pol-14-12 were 220 and 238°C , respectively. This relatively poor thermal stability arose primarily from the poor heat resistance of the CH_2-N^+ bond.²² The T_d values for Copol-14-8 and Copol-14-12 were 246 and 250°C , respectively. The relatively lower T_d observed for the fully quaternized polymers indicated that the close vicinity between the pyridinium rings had a negative effect on the thermal stability, as was previously observed for partially substituted P4VPs with methoxybiphenyl groups.²³ To prevent the thermal decomposition of the polymers, the T_d was used as the maximum temperature for the differential scanning calorimetry (DSC) analyses.

The DSC thermograms (cooling scans) of the fully and partially quaternized polymers are shown in Figure 3. The fully quaternized polymers showed quite diffuse exotherms, whereas the partially quaternized ones developed relatively well-defined exotherms: one around 100°C and one or two located between 150 and 200°C . Through polarizing optical microscopy, we observed that both the fully and partially quaternized polymers remained birefringent after they melted and at temperatures close to their T_d values. On cooling from the isotropic state, batonnets and homeotropic zones were observed,

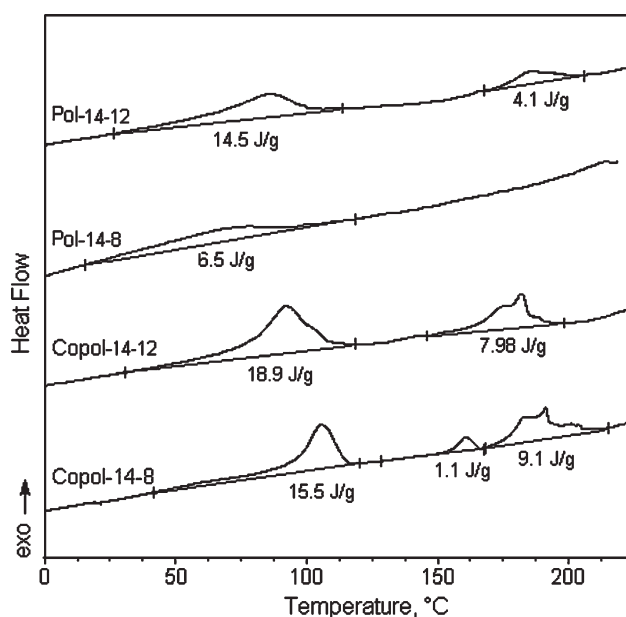


Figure 3 DSC traces registered on cooling ($5^\circ\text{C}/\text{min}$) for Pol-14-8, Pol-14-12, Copol-14-8, and Copol-14-12.

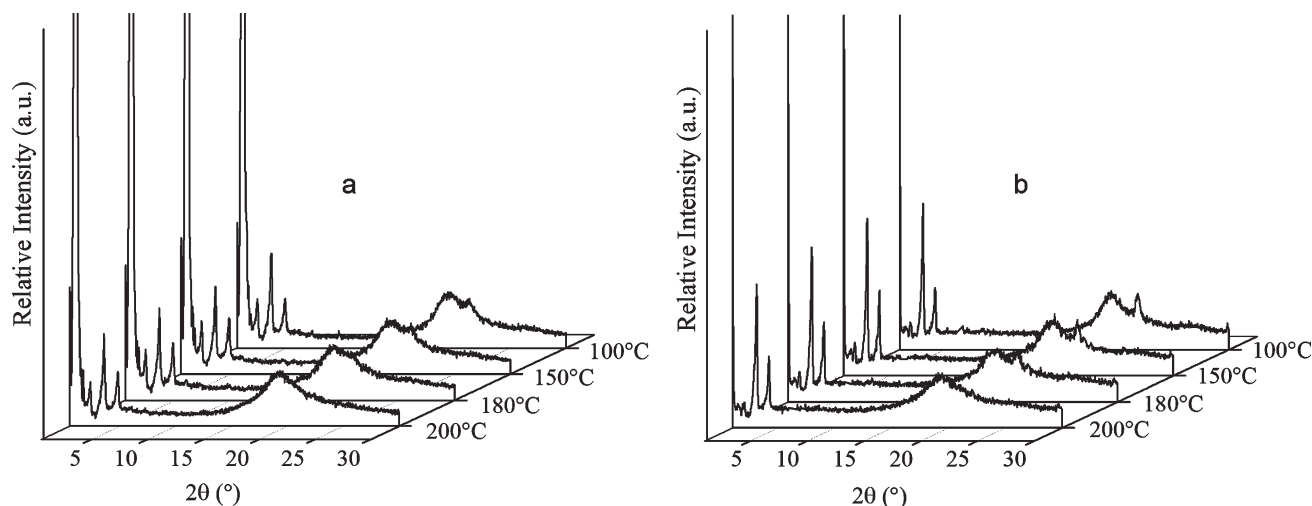


Figure 4 X-ray diffraction patterns of (a) Pol-14-8 and (b) Pol-14-12 registered at different temperatures on cooling.

and although some focal conic objects were (hardly) distinguished, the registered optical textures were rather nonspecific. To corroborate the LC nature of these polymers, X-ray diffraction experiments were conducted at different temperatures, and the results are described in the following section.

Structure of the mesophases

The X-ray patterns of polymers Pol-14-8 and Pol-14-12, registered at different temperatures, are shown in Figure 4. To prevent the thermal degradation of the polymers, a maximum temperature of 220°C was used for the X-ray data acquisition.

All of the patterns in Figure 4 show in the low-angles region one sharp Bragg reflection (d_{001}) and several equidistant peaks (d_{002} , d_{003} and d_{004}); these reveal the layered structure (smectic) of the LC phases. The smectic period (d_{001}) was compared with the length of the monomer (L) in its most extended conformation ($L = 44.3$ and 49.3 Å for n - m values of 14-8 and 14-12, respectively), which was calculated with molecular modeling software (Spartan 4, Irving California, USA), and we considered as a model molecule the monomer 4-vinylpyridinium N -substituted with the corresponding mesogenic

group (Table I). d_{001} was almost twice L for both polymers; this indicated that the molecular arrangement corresponded to a double-layered smectic phase. According to this result, the mesogenic groups of neighboring chains were not interdigitated. The $\cos^{-1}(d_{001}/2L)$ value indicated that the molecules were tilted with respect to the normal of the smectic plane at angles of around 28 and 24° for Pol-14-8 and Pol-14-12, respectively. The angle decreased by 2 or 3° with decreasing temperature from 200 to 150°C. According to these results, the smectic structure may have consisted of double

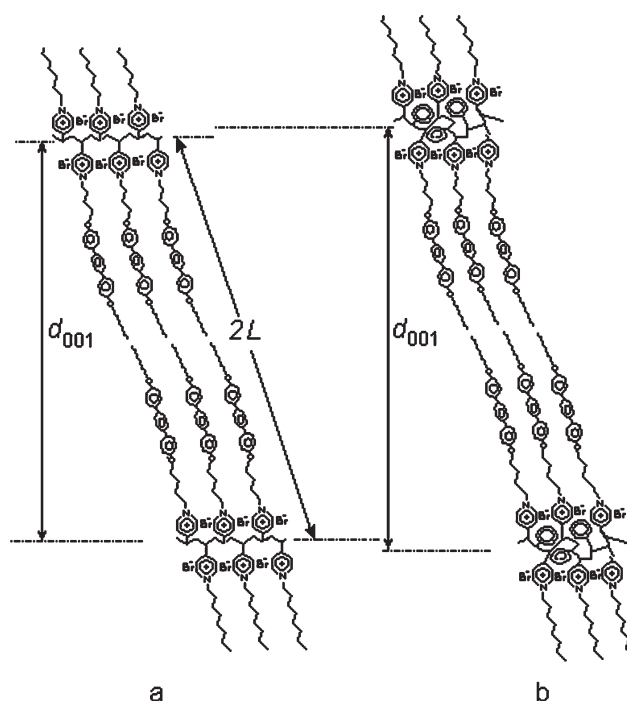


Figure 5 Schematic representation of tilted smectic structures of (a) fully and (b) partially quaternized P4VP with dialkyloxyterphenyl groups through a flexible spacer.

TABLE I
Smectic Periods (d_{001}) and $d_{001}/2L$ Ratios Calculated from the X-Ray Diffraction Patterns Registered at Two Different Temperatures

Polymer	d_{001} (Å)		L (Å)	$d_{001}/2L$	
	200°C	150°C		200°C	150°C
Pol-14-8	78.0	78.7	44.3	0.880	0.888
Pol-14-12	89.2	91.0	49.3	0.904	0.922
Copol-14-8	97.9	101.8	44.3	1.105	1.148
Copol-14-12	101.3	105.8	49.3	1.027	1.073

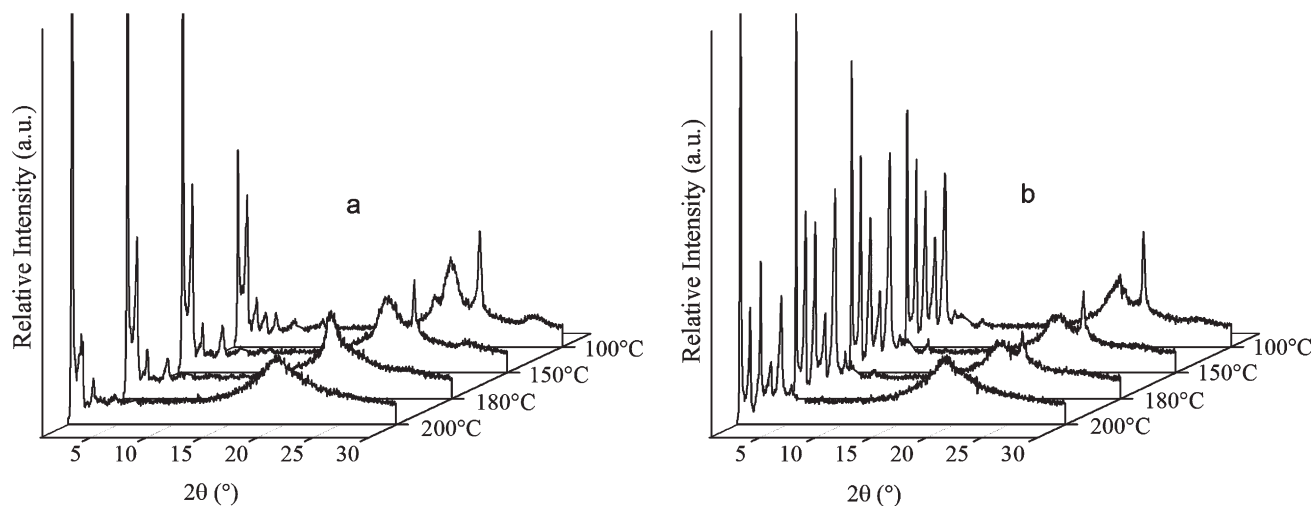


Figure 6 X-ray diffraction patterns of (a) Copol-14-8 and (b) Copol-14-12 registered at different temperatures upon cooling.

layers of tilted molecules with the ionic species; the aromatic cores and the alkyl chains were fully segregated in three microdomains periodically arranged in space, as schematized in Figure 5(a). In such an arrangement, the negative and positive ionic species may be positioned facing each other to satisfy the electrical interactions. The polymer backbone, $-(\text{CH}_2-\text{CH})_n-$, to which the pyridinium rings are attached may be sandwiched between the smectic layers.

On the other hand, the arrangement of molecules within the smectic layers was determined from the signal appearing in the wide-angles region of the X-ray diffraction pattern. At 200°C, the patterns of both polymers showed a broad diffraction peak; this indicated a liquidlike ordering of the molecules within the smectic layers. On cooling to 150°C, this broad peak remained almost unchanged, except for the small sharp peak appearing at 4 Å, and that is normally associated with the π stacking of aromatic cores. Most studies on the π stacking of aromatic cores have reported distances ranging between 3.3 and 3.6 Å; however, we found some publications reporting π -stacking distances of 3.8 and 4 Å; these were close to the values found in this study. Such π -stacking distances concern phenylenethynylene oligomers and conjugated oligoquinolines bearing a π -conjugated phenylene group.^{24,25} No reports were found in the literature about distances associated with π stacking in terphenyls. In conjugated aromatic cores, the contiguous rings are twisted from one another to a certain dihedral angle because of the repulsion forces between hydrogen atoms in the ortho position. This nonplanar molecular conformation could have been related to the relatively big distance (~ 4 Å) observed in the polymers studied

here. Finally, the layered structure, developed from the isotropic state, was retained at room temperature, as is typical in polymers bearing lateral mesogenic groups and which was certainly related to the rigidity of the polymer chain at low temperature.

The presence of sharp equidistant Bragg reflections in the X-ray pattern of partially quaternized polymers (Copol-14-8 and Copol-14-12) also revealed a layered structure for their LC phases (Fig. 6). The intensities of d_{002} , d_{003} , and d_{004} for Copol-14-12 were higher than those for the corresponding reflections of Copol-14-8; this indicated a longer correlated layer stacking for the former. The smectic periods (d_{001}) of these copolymers were also compared (Table I) with L in its most extended conformation (4VP N -substituted with the corresponding mesogenic group), and $d_{001} > 2L$. One possible reason for such a longer stacking period was the localization of the nonquaternized monomers between two smectic layers, as schematized in Figure 5(b). In a previous study, the expansion of the smectic period was studied in detail for a series poly(4-vinylpyridinium) salts partially substituted with methoxybiphenyl groups.⁹ In that study, two antagonist effects were considered to explain the apparent inconsistency of the variation of d_{001} as a function of the quaternization degree: First, the exclusion of the nonsubstituted pyridine rings from the sublayer of the mesogenic groups, which contributed to the thickening of the smectic layers, and second, the tilting of the mesogenic groups, which contributed, on the contrary, to the thinning of the smectic layers. This interpretation certainly applied to copolymers Copol-14-8 and Copol-14-12, whose mesogens may have been tilted, as was already deduced for the fully quaternized polymers Pol-14-8 and Pol-14-12.

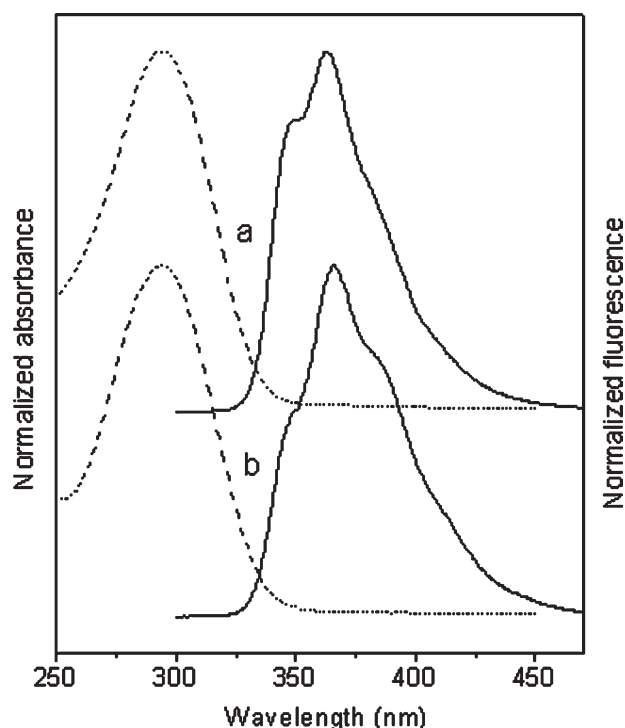


Figure 7 UV-vis absorption (dashed line) and emission (solid line) spectra for (a) Pol-14-8 and (b) Copol-14-8 dissolved in CHCl_3 .

On the other hand, the X-ray patterns obtained at 200°C showed a broad peak in the wide-angles region; this indicated a liquidlike ordering of mesogens for both copolymers. Although on cooling to 180°C , the broad peak of Copol-14-8 became a little bit sharper; this indicated a tendency to develop a hexatic order. The small peak associated with the π stacking of conjugated cores was also observed in the wide-angles region ($\sim 4 \text{ \AA}$) of the X-ray patterns of the copolymers.

According to the X-ray analyses of both the fully and partially quaternized polymers, the π stacking of terphenyls and the electric interactions of the ionic groups were determining interaction forces and led to a double-layered smectic structure in which the different parts of mesogens may have been completely segregated from one another.

Absorption and emission properties

UV absorption and emission spectra of the fully and partially quaternized P4VP were obtained from dilute solutions in spectroscopic-grade CHCl_3 . For both polymers, the absorption and emission spectra showed maxima centered around 294 and 364 nm (blue light), respectively (Fig. 7).²⁶ The absorption/emission process is associated with electronic excited states occurring in the π -conjugated core. The Stokes shift of around 70 nm, which was calculated from the absorption and emission spectra, indicated

that the ground and excited states were different and were probably associated with the torsion of adjacent phenylene rings due to excitation. The shape of the emission spectra changed as a function of the quaternization degree. The observed left-side shoulder (blueshifted) was more pronounced for the fully quaternized polymer, which in solution (with CHCl_3 as the solvent), showed a deep blue color under the illumination of a UV lamp (365 nm). On the contrary, the right-side shoulder (redshifted) was less pronounced for this polymer, and the color of the solution was blue green. To give a convincing explanation of the photophysical properties as a function of the quaternization degree, much more study is still necessary on the optical characteristics of this kind of polymer.

CONCLUSIONS

The polymers synthesized in this study are new liquid crystals bearing both ionic groups and π -conjugated moieties. Fully quaternized polymers were obtained through the unconventional spontaneous polymerization of *N*-substituted pyridinium salts, whereas partially quaternized polymers were prepared by the quaternization of P4VP with bromodialkylxytrephenyl derivatives. Both the fully and partially quaternized polymers showed two or more thermal transitions, which revealed their mesomorphic behavior. By comparing d_{001} with L , we deduced a double-layered smectic structure for the LC phases, with pending mesogens tilted with respect to the smectic plane. On the other hand, the polymers showed luminescence in the blue region (ca. 360 nm). Finally, we believe that this study will contribute to the understanding of the properties of comblike polymers showing both LC and luminescent properties, particularly of those polymers bearing ionic groups.

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