Thermal Atropisomerization and Photoluminiscence Spectra of Very High Glass Transition Temperature Chiral Poly(binaphthoxyphosphazenes) with a Secondary Helicoidal Structure

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ABSTRACT: The optically active ([α] = −192°) and mesomorphic (2θ = 6°, d = 14.7 Å) isotactic poly(2,2′-dioxy-1,1′-binaphthylphosphazene) R-(−)-$[NP(O_2C_{20}H_{12})]_n$ (**1-R**) (M_w = 840 000) has a very high glass transition temperature, T_g (329 °C), and can be thermally degraded between 100 and 160 °C to lower M_w distributions without decomposition. The specific rotation in solution varied significantly with the M_w, with the temperature, and with the wavelength, while the specific rotation of the related random nonisotactic copolymer $[NP(O_2C_{20}H_{12})]_n$ (**2-R/S**) (M_w = 750 000, [α] = −50°), having different proportions of the chiral R and S repeating units (70% and 30%, respectively), was independent of the M_w and the temperature. Those observations are consistent with the secondary helicoidal structure for polymer **1-R** in solution. The steady-state and lifetime fluorescence measurements in various solvents and temperatures have shown that the lifetime of the excimers formed by the binaphthyl units are too short to evidence the effects of the helicity in the fluorescence spectra. Above 250 °C, a slow atropisomerization of the 2,2′-dioxy-1,1′-binaphthylphosphazene units takes place, which, supporting recent predictions on glassy polymer matrices, becomes much faster as the temperature approaches the T_g.

Introduction

Chiral macromolecules present an enormous interest in both fundamental and applied fields of modern chemistry. The chirality of the macromolecular compounds is related to their measurable optical activity, and, in fact, the synthetic polymers that are optically active may be divided into three groups depending on whether their optical activity arises: (a) from the presence of chiral centers in the chain or in the side groups; (b) from the presence of both asymmetric centers and macromolecular asymmetry; or (c) from macromolecular asymmetry alone.[1] A very important case of macromolecular asymmetry (main-chain chirality) arises when the polymer forms a helical conformation with a predominant screw sense in the helix.[2]

The synthesis of helical polymers with a controlled helix sense[3a] and the chiral amplification mechanisms[3b] have been widely reviewed. Many synthetic helical polymers[4] may be obtained by asymmetric polymerization techniques[5] and have received a great deal of attention due to their potential interest.[4] For example, they may exhibit a high optical resolving ability when used as chiral stationary phases in HPLC.[5] Chiral conducting polythiophenes with a helical structure are useful for enantioselective modified electrodes and membranes.[6] Other potential applications of helical polymers are the fields of catalysis,[7] nonlinear optical materials,[8] and the construction of novel dissymmetric architectures similar to those found in nature[9] and in the field of biomedical science.[10]

The incorporation of chiral 1,1′-binaphthyl groups into polymers is very relevant in molecular recognition, asymmetric catalysis, and new materials,[11] and in earlier papers,[12,13] we described the synthesis and characterization and solution properties of optically active polymers with 2,2′-dioxy-1,1′-binaphthylphosphazene structural units (Chart 1). Those materials showed a dependence of the specific rotation with the molecular weight, suggesting a helicoidal secondary structure. In fact, the polymer **1-R** is helical in the solid amorphous state, as found experimentally by large-angle X-ray scattering.[14] In solution they behave as random coils,[13] but as the molecular dynamics simulations confirm the possibility of conformations capable to produce helix-type sequences for this[14] and similar phosphazenes,[15] some of the chain fragments could contain short helices. Therefore, as they have a chiral unit in the main chain (with absolute configuration R or S),[16] the combination with the left-handed (s) or right-handed (r) orientations of the helix produces overall structures that are diastereoisomeric, and as in other related cases,[17] their properties would depend on the energy differences and on the helix inversion barriers. It is therefore expected that, as happened to certain helical polyolefins[4] and polyisocyanates,[18,19] and also to nonchiral polyphosphazenes in which helicity was induced by an interaction with optically active amines,[20] the specific rotation should be a function of temperature and wavelength.[21] Also, since chromophores are an intrinsic part of these polyphosphazenes, the temperature dependence of the fluorescence spectra might help to confirm the presence of the helicoidal fragments as recently observed in other cases.[22]

On the other hand, the atropisomerization of binaphthyl derivatives as a probe to study the polymeric glassy state[23] has led to the very interesting conclusion that a

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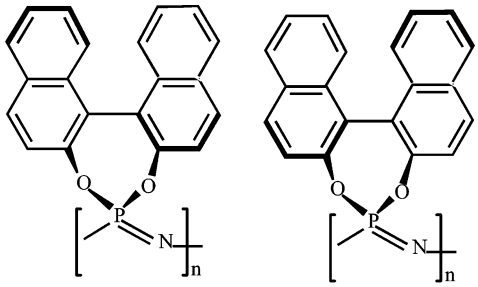
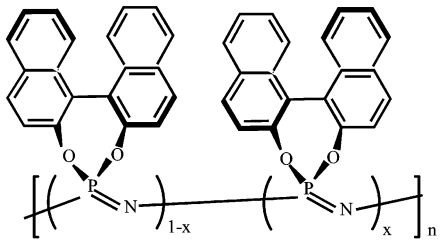
Chart 1



1-R **1-S**



2-R/S (x=0.5 or 0.3)

sudden increase in the isomerization rate is to be expected in the vicinity of the glass transition, and it has been also established that the atropisomerization of the 1,1′-binaphthyl is favored in the presence of nematic and ordered solid matrices.[24] In this report we present experimental evidence to support the secondary structure in solution of those 2,2′-dioxy-1,1′-binaphthylphosphazene polymers that form solid mesophases and that undergo a thermal atropisomerization that are much faster as the temperature approaches their T_g (near 330 °C), which are the highest ever recorded in polyphosphazenes.

Experimental Section

Materials. Cs_2CO_3 were dried at 140 °C prior to use. The acetone used as solvent (for analysis quality) was distilled from anhydrous $CaSO_4$. The THF was treated with KOH and distilled twice from Na in the presence of benzophenone. NMP (1-methyl-2-pyrrolydone) was used as received (Aldrich). The binaphthol R-(+)-1,1′-binaphthyl-2,2′-diol (VWR International) was used as purchased. Tetrabutylammonium bromide (TBAB) (Aldrich) was dried under vacuum at 50 °C. The cyclic trimer R-(−)-$[N_3P_3(O_2C_{20}H_{12})_3]$,[12] the homopolymer (+)-$[NP(O_2C_{20}H_{12})]_n$ [**1-S**],[12] and the copolymers [**2-R/S**] with $x = 0.5$ [12] and [**2-R/S**] with $x = 0.3$[13] were prepared as indicated in the given references. The THF solutions of the starting $[NPCl_2]_n$ were obtained as explained in refs 12 and 13. The homopolymer (−)-$[NP(O_2C_{20}H_{12})]_n$ [**1-R**] was prepared as already published[12] but with some modifications (see below). All reactions were carried out under a dry nitrogen atmosphere.

Measurements. NMR spectra were recorded on Bruker AC-200, AC-300, and DPX-300 instruments. $^{31}P\{^1H\}$ NMR are given in δ relative to external 85% aqueous H_3PO_4. C, H, N analysis was performed with a Perkin-Elmer 2400 microanalyzer. The chlorine analysis was performed by Galbraith Laboratories. GPC was measured with Perkin-Elmer equipment with a model LC 250 pump, a model LC 290 WV, and a model LC 30 refractive index detector. The samples were eluted with a 0.1 wt % solution of tetrabutylammonium bromide in THF through a Perkin-Elmer PLGel (Guard, 10^5, 10^4, and 10^3 Å) at 30 °C. Approximate molecular weight calibrations were obtained using narrow molecular weight distribution polystyrene standards. T_g values were measured with a Mettler DSC 300 differential scanning calorimeter equipped with a TA 1100 computer at 10 °C/min. Thermal gravimetric analysis were performed on a Mettler TA 4000 instrument. The polymer samples were heated at a rate of 10 °C/min from room temperature to 800 °C under a constant flow of nitrogen. The specific optical rotations [α] were measured with a Perkin-Elmer 343 polarimeter at the wavelength of the D line of Na or with a Perkin-Elmer 241 polarimeter at 578, 546, and 436 nm, near 25 °C in $CHCl_3$ or NMP.

The X-ray diffraction was measured between 25 and 300 °C with a Bragg−Brentano $\theta/2\theta$ Siemens D-500, using the Cu Kα (λ = 1.5418 Å), equipped with a Temperature Camera Anton Paar TTK(−196 to 300 °C).

Fluorescence measurements were performed using an SLM 8100 Aminco spectrofluorometer, equipped with a xenon lamp, a double (single) concave grating monochromator in the excitation (emission) path, and a cooled Peltier system photomultiplier. The excitation and emission slit widths were both selected at 8 nm. The polarizers were set at the magic angle conditions. Decay fluorescence measurements were performed on a time-correlated single-photon-counting FL900 Edinburgh Instruments spectrometer equipped with concave single grating monochromator at the excitation and emission paths with slits to 18 nm. The thyratron-gated lamp (nF900) was filled with hydrogen. No polarizers were used. The signal was also detected by a red-sensitive Peltier system cooled photomultiplier. The data acquisition was carried out by using 1024 channels of a multichannel analyzer with a time window width of 100 ns, and the stop condition was 10 000 counts in the maximum intensity channel. Instrumental response function was regularly achieved by measuring the scattering of a Ludox solution. Decay profiles were fitted to multiexponential trail functions. Right angle geometry and rectangular 10 mm path (triangular) cells were used for dilute (concentrate) solution measurements. Absorbances of dilute solution samples at the excitation wavelength of 325 nm were lower than 0.1. The solvents used in these measurements were THF, NMP, and/or 1,1,2,2-tetrachloroethane (TCE). Decay fluorescence measurements were performed on a time-correlated single-photon-counting FL900 Edinburgh Instruments spectrometer equipped with concave single grating monocromators at the excitation and emission paths with slits to 18 nm. The thyratron-gated lamp (nF900) was filled with hydrogen. No polarizers were used. The signal was detected by a red-sensitive Peltier system cooled photomultiplier. The data acquisition was carried out by using 1024−2048 channels of a multichannel analyzer with a variable time window width (100−200 ns), and the stop condition was 10 000 counts in the maximum intensity channel.

Synthesis and Data of (−)-$[NP(O_2C_{20}H_{12})]_n$ [1-R]. R-(+)-1,1′-Binaphthyl-2,2′-diol (8.36 g, 29.18 mmol) and Cs_2CO_3 (38.01 g, 116.66 mmol) were added to a solution of $[NPCl_2]_n$ (3.38 g, 29.17 mmol) in THF (200 mL) (obtained as indicated in refs 12 and 13). The mixture was vigorously stirred at the refluxing temperature for 19 h, allowed to cool to room temperature, and poured into water (1.5 L). The resulting white precipitate was washed with water, dissolved in THF (500 mL), and filtered. The slightly cloudy solution was concentrated at reduced pressure, giving a viscous liquid which was poured portionwise (with a Pasteur pipet) into water. Reprecipitation from THF/IPA and THF/hexane was repeated in the same manner, yielding an almost white slightly yellow solid which was dried at 70 °C in vacuo for 4 days (6.3 g, 65%). ^{31}P NMR ($CHCl_3$): δ (ppm) −1.2 (very broad) (no trimer [NP-$(O_2C_{20}H_{12})]_3$ was observed).

Anal. found (calcd): 70.3 (72.9)% C; 4.13 (3.67)% H; 4.25 (4.25)% N. Residual chlorine content: 0.39%. Solvents retained as calculated by ^1H NMR (see ref 11): 1.5% THF, 4.8% hexanes. Weight loss due to solvent evaporation in the TGA thermogram between 100 and 350 °C: 6.4%. M_w(GPC): 840 000 (PDI = 2.5). TGA: From 30 to 350 °C a weight loss of 6.4%. The weight remained constant under continuous heating at the constant temperature of 350 °C. T_g (DSC): 329 °C. Specific rotation in $CHCl_3$ (c = 1) at 20 °C: $\alpha = -192°$.

Table 1. M_w and [α] after the Thermal Degradation and Atropisomerization of 1-R (Initial Values M_w = 840 000, [α] = −192°)

temp (°C)	time	M_w	[α] (deg)
130	7 days	617 000	−164
130	22 days	522 000	−159
130	30 days	487 000	−148 (**1-R-a**)
160	6 days	400 000	−124
160	12 days	350 000	−116 (**1-R-b**)
250	10 min	210 000	−77
300	10 min	85 000	−3
350	10 min	80 000	0

Table 2. M_w and [α] after the Thermal Degradation and Atropisomerization of 2-R/S(x = 0.3) (Initial Values M_w = 750 000, [α] = −50°)

temp (°C)	time	M_w	[α] (deg)
130	3 days	253 000	−50
160	10 min	420 000	−50
160	12 days	150 000	−48
250	10 min	110 000	−40
300	10 min	70 000	−5

Data for the Thermal Degradation and Atropisomerization of [1-R] and 2-R/S(x = 0.3). Solid samples of **1-R** or **2-R/S**(x = 0.3) were heated in an oven at reduced pressure at the temperatures and times (in days) indicated in Tables 1 and 2. No trimer formation was detected by ^{31}P NMR spectroscopy. The TGA of the polymeric samples revealed no significant weight loss in the range studied. The C, H, N analysis of the final products also confirmed that no decomposition took place during the thermal treatments. For example, the analysis found (calculated) for the product heated at the higher temperature (350 °C) was 70.0 (72.9) % C; 3.51 (3.67) % H; 4.26 (4.25) % N.

Results and Discussion

The samples of the chiral poly(2,2′-dioxy-1,1′-binaphthylphosphazene) R-(−)-[NP($O_2C_{20}H_{12}$)]$_n$ (**1-R** in Chart 1) used in this study were prepared by the method published previously[12] with some slight modifications (see experimental part). The average M_w (GPC) was 840 000 and the specific rotation [α] = −192°. Heating **1-R** at 130 or 160 °C gave lower M_w distributions with lower specific rotations (see Table 1). The TGA of **1-R** revealed no significant weight loss in the range studied. The ^{31}P NMR spectra of the products showed only the broad signal at −1.2 ppm of the polymer, indicating that no decomposition or formation of the trimer R-(−)-[N_3P_3-($O_2C_{20}H_{12}$)$_3$] (for which [α] = −77°) [12] took place during the thermal treatment of **1-R**. The elemental analysis also confirmed that the chemical composition remained unaltered during the thermal treatments. The overall decrease in M_w was less pronounced than the previously observed,[12] but this is not surprising since the thermal degradation of this type of polyphosphazenes strongly depends on the initial M_w and on the residual chlorine content.[15]

The observed decrease of the [α] may be due to the following effects: (a) the atropisomerization of the binaphthoxyphosphazene units; (b) the helicoidal nature of the polymer, the degree of which might be dependent on the average chain length.

The decrease by thermal atropisomerization below 160 °C could be ruled out by heating the previously reported[13] random copolymer **2-R/S**(x = 0.3) (Chart 1), having R- and S-[NP($O_2C_{20}H_{12}$)] repeating units in different proportions (70% and 30%, respectively). Between 130 and 160 °C and various periods of time (Table 2) the average M_w was reduced from 750 000 to 150 000 without a significant change in the specific rotation, which remained constant at −50°. In fact, the atropisomerization of the binaphthoxyphosphazene units was only detectable above 250 °C and was very fast at 300 °C (see Table 2). The same was observed with the homopolymer **1-R** (see Table 1).

It is known[11] that 2,2-substituted 1,1′-binaphthyls may be configurationally stable at high temperatures and that the atropisomerization rate of binaphthyls incorporated in a polymeric matrix with high T_g should increase precisely near the T_g.[23] It has been also established that the atropisomerization of the 1,1′-binaphthyl is favored in the presence of nematic and ordered solid matrices.[24]

Interestingly, although earlier attempts to observe the glass transition were unsuccessful,[12] the DSC of **1-R**, measured from 0 to 350 °C, showed a clearly defined C_p step with a T_g of 329 °C. As expected, the same T_g was observed in the DSC thermograms of the thermally atropisomerized samples and of the nondegraded but "racemic" polymers **2-R/S**(x = 0.5 or 0.3) (Chart 1). Therefore, the rapid atropisomerization observed at 300 °C for **1-R** can be related with the high T_g of this polymer.

On the other hand, the X-ray diffraction of the solid samples of **1-R** from 25 to 300 °C (Figure 1) clearly showed a wide-angle reflection at $2\theta = 6°$, corresponding to a mesophase with an interplanar distance of 14.7 Å. Its intensity relative to that of the wide halo centered at 20° did not vary significantly with the temperature. On cooling to room temperature, the diffractogram coincided with that obtained before the heating cycle. The formation of bidimensional mesophases is very common among polyphosphazenes,[25] but in this case, it may be interesting because, according to the literature, the atropisomerization of the binaphthoxyphosphazene units may be favored in ordered solid phases by flattening the naphthyl rings.[24]

Taking all these results into account, the aforementioned conspicuous dependence of the optical rotation of **1-R** with the M_w in a temperature range where no atropisomerization takes place supports the assumption of a secondary helicoidal structure for this polymer. It is therefore expected that, as observed in other polymers,[4,18−20] the optical rotation should change with the temperature, and in fact, as shown in Figure 2, a very significant reduction of the absolute value of the specific rotation was observed by heating a solution of **1-R** in 1-methyl-2-pyrrolidinone (NMP) from room temperature to 140 °C. The line plot was perfectly reproduced by cooling the solution back to room temperature and repeating the cycle several times; i.e., no other process able to decrease the specific rotation took place during the heating. The specific rotation of the thermally degraded samples of **1-R** also decreased with the temperature, but the effect was less pronounced than in the case of the starting polymer, which is also consistent with the helical hypothesis.

We have previously shown that the polymers **1-R** behave as random coils in a good solvent.[13] This is compatible with the occurrence of helical segments throughout the chains, producing an overall degree of helicity that would increase with the average M_w leading to higher [α] values. This effect would be eliminated by the faster conformational changes of the chains that occur at high temperatures, explaining the variation of the specific rotation with the temperature

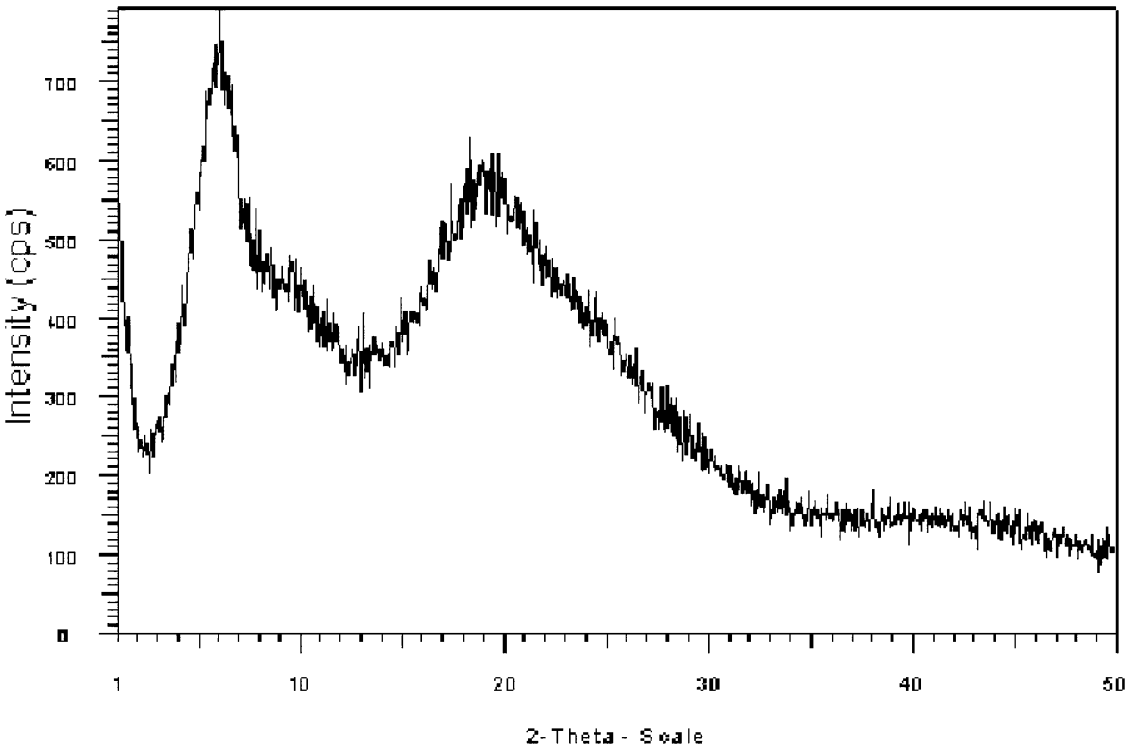


Figure 1. X-ray diffraction of the solid samples of **1-R** at 25 °C.

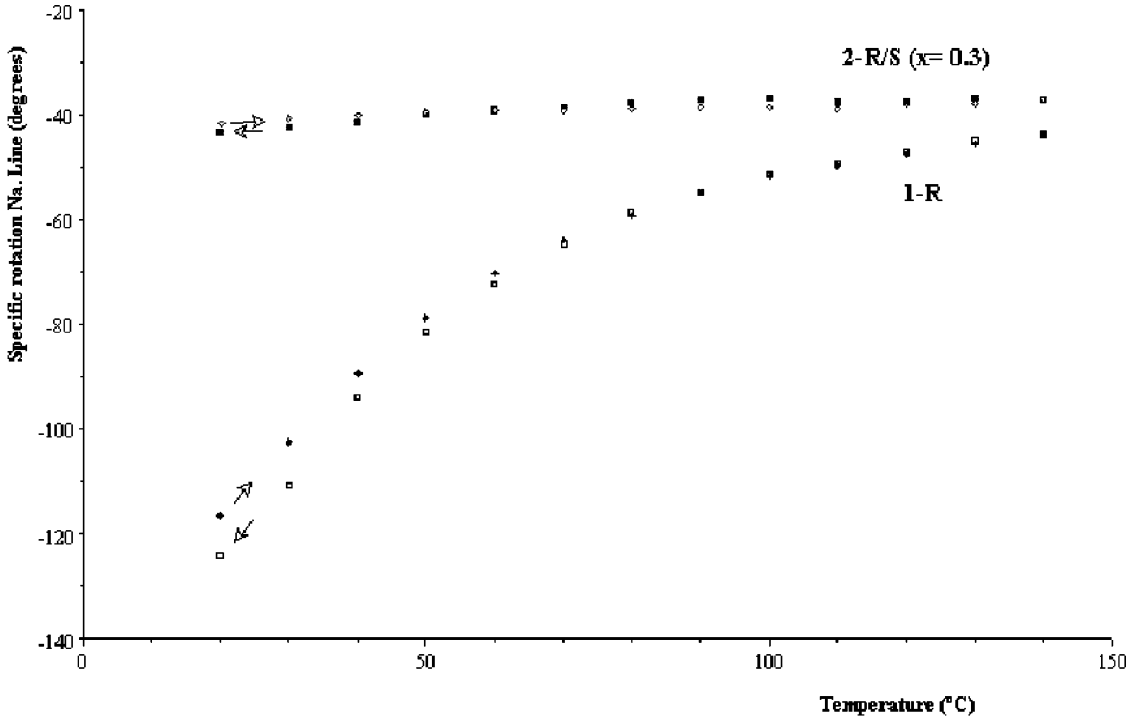


Figure 2. Specific rotation as a function of temperature for the polymers in NMP.

in Figure 2. The process could be described as a transformation of helical to nonhelical fragments along the chains of the overall random coil, like the reverse to the first step in the solvent-induced crystallization[26] or gelation[27] of the polystyrene, which is related to a helix−coil transition frequently observed in poly(amino acid)s.[28] Thus, for the nonisotactic copolymer (**2-R/S**, $x = 0.3$) (Chart 1) the specific rotation in NMP (near −40°) is almost independent of the temperature in the range 25−150 °C (see Figure 2), showing that, in this much less regular structure, the excess of a preferred helical sense in the short helicoidal fragments is almost absent.

In well agreement with all expectations, the specific rotation of **1-R** in NMP changed with the wavelength as well as with the temperature (Figure 3), and a comparison with the similar graphs published for poly(bisoxazolines) with pendant binaphthoxy groups[29] showed the 436 nm lines are very different from those for the other wavelengths. In the case of **1-R** the specific rotation at 436 nm was more negative at room temperature than at the other wavelengths, but because of its stronger temperature dependence, the situation is re-

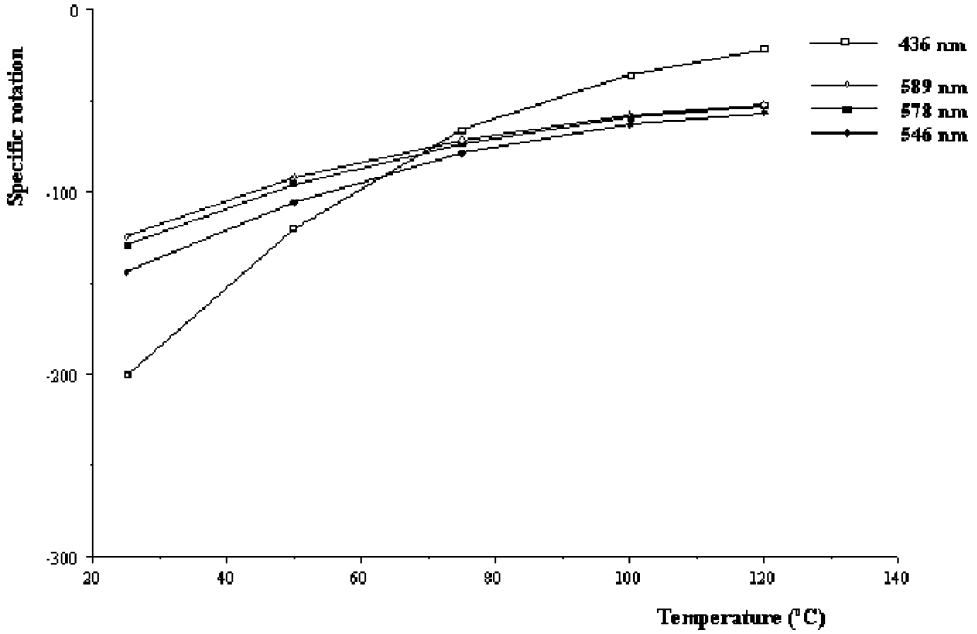


Figure 3. Specific rotation on vs temperature at various wavelengths for polymer **1-R** in NMP.

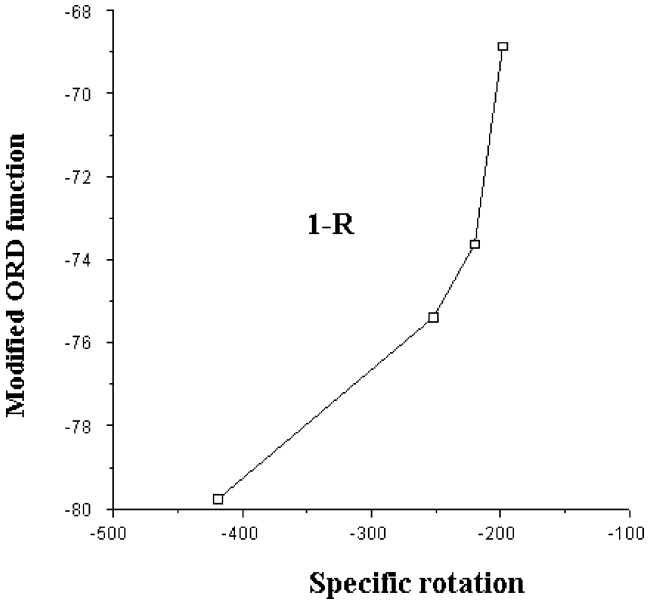


Figure 4. Modified ORD function ($[\alpha]\lambda^2$) vs $[\alpha]$ for **1-R** in $CHCl_3$ solution at 25 °C (λ in nm and the function is $\times 10^{-6}$).

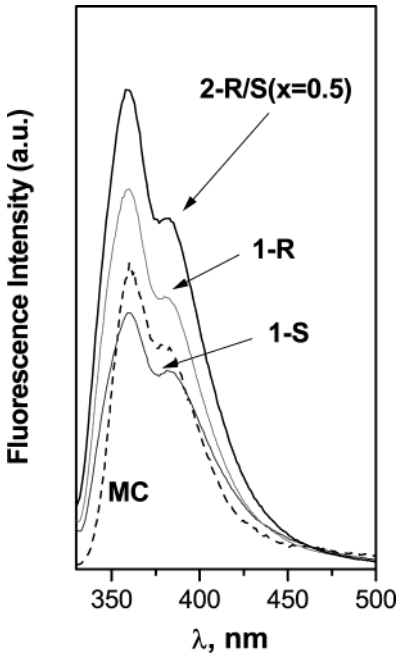


Figure 5. Emission spectra for dilute solutions of model compound R-(+)-1,1′-bi-2-naphthol (MC) and polymers **1-R**, **1-S**, and **2-R**/**S**($x = 0.5$) in TCE at 25 °C upon $\lambda_{exc} = 325$ nm.

versed at higher temperatures (which is not observed in the oxazolines) (see Figure 3).

We also observed that the "modified" $[\alpha]\lambda^2$ function (ORD)[21] for **1-R** in NMP varied with $[\alpha]$ and with the temperature. The data (limited to the usual values $\lambda =$ 436, 546, 578, 589 nm) suggested that at 25 °C the variation with $[\alpha]$ was, as expected, not linear ($R^2 =$ 0.97) and that the nonlinearity was much more pronounced in $CHCl_3$ as solvent (Figure 4). However, the data obtained at various temperatures did not show definite trends evidencing the effects of the gradual disappearance of the helical fragments on the linearity of the ORD plots.

To study the possibility of excimer formation in the polymeric binaphthhoxyphosphazene chains and its relation to the helicoidal nature of the poly(binaphthoxy)phosphazenes, we performed steady-state as well as lifetime fluorescence measurements in several solvent solutions at various temperatures. The results are shown below.

Fluorescence excitation spectra of dilute solutions of the binaphthol R-(+)-1,1′-binaphthyl-2,2′-diol used as model compound (**MC**) show peaks (p) and shoulders (s) centered at ∼338 (p), ∼320 (p), and ∼290 nm (p) in THF at 25 °C. These peaks are slightly shifted (by about 5 nm) to the red in NMP and to the blue in TCE. The cyclic trimer R-(−)-$[N_3P_3(O_2C_{20}H_{12})_3]$ and the polymer dilute solutions present similar bands centered at ∼325 (p), ∼318 (s), ∼308 (p), and ∼290 nm (p) in any of the solvents used. All of the excitation spectra present features similar to the absorption spectra.

Figure 5 depicts uncorrected emission spectra for dilute solutions of **MC** and the polymers **1-R**, **1-S**, and the "racemic" optically inactive **2-R/S**($x = 0.5$) in TCE

at 25 °C upon 325 nm as excitation wavelength. The spectrum for **MC** shows two bands placed at approximately 360 and 380 nm. The emission spectra of polymers are very similar. They do not show any broadening to the red of the monomer bands observed for **MC** that could indicate the presence of excimers. Ratios of intensity of the bands placed at 380 and 360 nm do not significantly differ from the ratio obtained for the **MC**. Relative intensities of both peaks do not change significantly either upon changing the excitation wavelength. This denotes that both bands that appear in the emission spectra come from a single ground-state species, the monomer.

These results can be extended to the cyclic trimer R-(−)-[$N_3P_3(O_2C_{20}H_{12})_3$] and any of the other polymers investigated, the nonisotactic **2-R/S**($x = 0.3$), and the products **1-R-a** and **1R-b** resulting from the thermal degradation of the homopolymer **1-R** (see experimental part), the emission spectra of which (not included in Figure 5) show similar characteristics with only small changes of a few nanometers in the placement of both bands.

The absence of intramolecular excimers should be mainly due to two reasons: either the naphthalene groups of binaphthyl chromophores, for any of the conformations adopted by the polymers, are too far away to fulfill the excimer sandwich-type geometry, or satisfying these requirements, the excimer is not stable in solution.

Simple molecular models on these polymers show that the adoption of a helix structure may involve conformations where there is a possibility of the partial overlapping of naphthalene groups between next-to-nearest-neighbor binaphthol units, which could be the origin of the intramolecular excimers for this helix type of structures.

The stability of binaphthoxyphosphazene excimers was studied by comparison of steady-state emission spectra and fluorescence decay measurements on concentrate solution (0.25 M) of **MC** and 2-naphthol at 25 °C. Emission spectra for **MC** showed similar characteristics to the spectra for dilute solutions. Ratios of intensities for both bands placed at 380 and 360 nm are independent of temperature. Lifetime measurements showed a single decay component of approximately 1.4 ns, which is independent of the emission wavelength selected. Both results denote the absence of intermolecular excimers. The emission spectrum for the 0.25 M solution of 2-naphthol in THF exhibits bands around 348 and 370 nm and a shoulder around 385 nm. Fluorescence decays now showed two lifetime components of ∼2.5 and ∼7.5 ns. The proportion of the long-lived components relative to the short ones increases with the emission wavelength. The long component can thus be ascribed to the intermolecular excimer. 2-Naphthol can form excimers in solution. These results, however, indicate that the binaphthol intermolecular excimer, like biphenyl excimers,[30] are not stable, and they are not found in homogeneous solutions. This nonstability should reasonably be extended to the intramolecular binaphthol excimers.

Therefore, the absence of excimers in the polymeric binaphthoxyphosphazene chains and the fact that all the chromophores behaved as if they were isolated are probably a consequence of the nonstability of the binaphthyl excimer.

The fluorescence decays for **1-R**, **1-S**, and **2-R/S**($x = 0.5$) were complicated, and they require a three-exponential decay function to fit the emission satisfactorily. The three lifetime components observed were in the 0.5−0.8, 2.2−2.6, and 5−8 ns ranges, at the emission of 360 nm for any of the polymer investigated. Disregarding the possibility of excimers, this fact should denote the presence of intramolecular energy transfer between binaphthyl chromophores. The weighted average of the individual components $\langle\tau\rangle$ (around 2.8−2.5 ns) showed, as expected, a small decrease with temperature. Therefore, fluorescence measurements have shown the instability of the excimers without supporting the existence or the absence of helical fragments on the chains of poly(binaphthoxyphosphazenes).

Conclusions

The chiral binaphthoxyphosphazene units [NP-($O_2C_{20}H_{12}$)] are configurationally stable up to 160 °C, and the isotactic lineal homopolymers formed with them adopt a secondary helical structure along the fragment chains of the ramdom coil in solution that, due to the nonstability of the binaphthyl excimers, is not manifested in the fluorescence spectra. The high T_g of these polymers (ca. 330 °C) and the existence of mesophases at high temperature favor their solid-state thermal atropisomerization, which supports previous works on glassy polymer matrices.

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