High Molecular Weight Phosphazene Copolymers Having Chemical Functions Inside Chiral Pockets Formed by (*R*)-(1,1′-Binaphthyl-2,2′-dioxy)phosphazene Units

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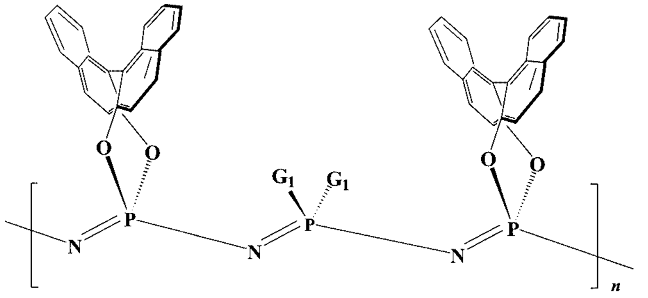
The polyphosphazene $\{[NPCl_2]_x[NP(O_2C_{20}H_{12})]_{1-x}\}_n$ ($O_2C_{20}H_{12}$ = 1,1′-binaphthyl-2,2′-dioxy) reacted in refluxing THF in the presence of Cs_2CO_3 with HOC_5H_4N or *para*-substituted phenols HOC_6H_4R to give the random copolymers $\{[NP(OC_5H_4N)_2]_x[NP(O_2C_{20}H_{12})]_{1-x}\}_n$ (**1**) or $\{[NP(OC_6H_4R)_2]_x[NP(O_2C_{20}H_{12})]_{1-x}\}_n$ [R = CN (**2**), COMe (**3**), CO_2nPr (**4**), PPh_2 (**5**)] and with H_2NnBu to give $\{[NP(NHnBu)_2]_x[NP(O_2C_{20}H_{12})]_{1-x}\}_n$ (**6**). The reaction of the polymer $\{[NPCl_2]_x[NP(O_2C_{20}H_{10}Br_2)]_{1-x}\}_n$ ($O_2C_{20}H_{10}Br_2$ = 6,6′-dibromo-1,1′-binaphthyl-2,2′-dioxy) with $HOC_6H_4PPh_2$ and Cs_2CO_3 gave $\{[NP(OC_6H_4PPh_2)_2]_x[NP(O_2C_{20}H_{10}Br_2)]_{1-x}\}_n$ (**7**). Those polymers have a very high glass-transition temperature (*Tg*) and a chemical function or ligand that is in the interior of a chiral pocket.

Introduction

Due to their growing interest in materials science, the chemistry of linear polyphosphazenes $(N{=}PX_2)_n$ containing halogen, pseudohalogen, alkoxy, aryloxy, amino, alkyl or aryl group have been very extensively reviewed.[1] Recently, a new type of phosphazene polymer was discovered containing cyclic repeating units with biphenyldioxy[2] $[NP(O_2C_{12}H_8)]_n$ or binaphthyldioxy[3] $[NP(O_2C_{20}H_{12})]_n$ groups. The latter could be obtained as isotactic chiral (*R*) or (*S*) polymers, or as (*R*/*S*) copolymers with different proportions of both chiral units.[3] The structural data of those polymers revealed that both in solution[4,5] and in the solid state[6] their chains are helicoidal and therefore they are a new type of interesting synthetic helical polymers.[7] These results led us to attempt the preparation of well-defined copolymeric phosphazenes of the general type $\{[NPX_2]_x[NP(O_2C_{20}H_{12})]_{1-x}\}_n$, where the X group supports a chemical functionality, useful as precursors for other derivatives or as ligands for transition metal complexes. As shown in Scheme 1, these polymers contain their chemical functions within a chiral environment that could be considered as a chiral pocket,[8] and therefore they may be potentially useful as supported catalysts (soluble or insoluble) for enantiomeric synthesis. From our previous knowledge[2,3] we anticipated that these polymers would have very high transition temperatures, i.e. they are stereochemically very rigid and the efficiency to induce chirality of the pocket could be modified by using derivatized binaphthols. Herein we describe the synthesis and full characterization of several chiral copolymers having (binaphthyldioxy)- or (dibromobinaphthyldioxy)phosphazene units and pyridine, nitrile, ketone, ester, phosphane or amine functions.



Scheme 1

Results and Discussion

According to the partial substitution method previously described by us for functionalized phosphazene copolymers with biphenyldioxy[2,3] or binaphthyldioxy[4] units, the poly(dichlorophosphazene) $[NPCl_2]_n$ was treated first with *x* equiv. of (*R*)-(+)-1,1′-binaphthyl-2,2′-diol in the presence of Cs_2CO_3 [9] to give a THF solution of the intermediate $\{[NPCl_2]_x[NP(OC_{20}H_{12})]_{1-x}\}_n$ (see Scheme 2). The addition of 4-hydroxypiridine, a 4-substituted phenol HOC_6H_4R, or *n*-butylamine H_2NnBu, led to the new functionalized phosphazene random copolymers $\{[NP(OC_5H_4N)_2]_{0.1}[NP(O_2C_{20}H_{12})]_{0.9}\}_n$ (**1**), $\{[NP(OC_6H_4R)_2]_x[NP(O_2C_{20}H_{12})]_{1-x}\}_n$ [R = CN, *x* = 0.15 (**2**); R = COMe, *x* = 0.2 (**3**); R = CO_2nPr, *x* = 0.2 (**4**);

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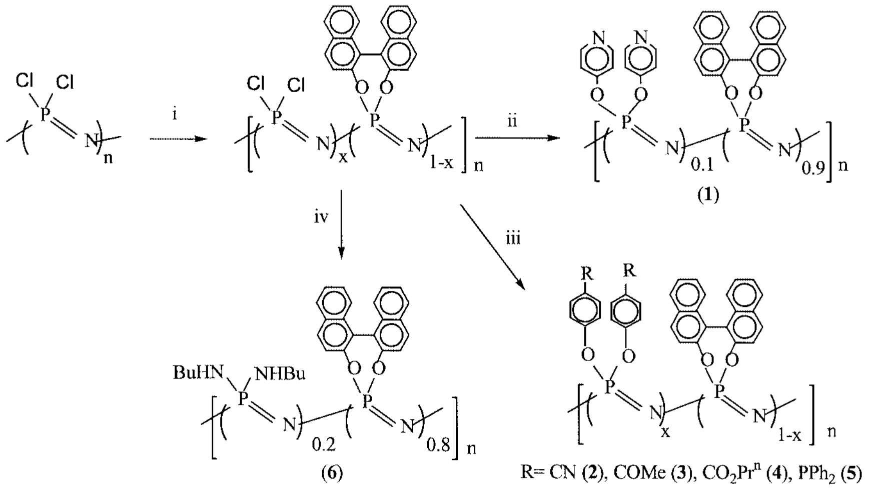


Scheme 2. i) (*R*)-(+)-$C_{20}H_{12}(OH)_2$, Cs_2CO_3; ii) HOC_5H_4N, Cs_2CO_3; iii) HOC_6H_4R, Cs_2CO_3; iv) H_2NnBu; for conditions see text

R = PPh_2, x = 0.1 (**5**)] and $\{[NP(NHnBu)_2]_{0.2}[NP(O_2C_{20}H_{12})]_{0.8}\}_n$ (**6**) (see Scheme 2, Table 1).

The actual x values observed in the isolated materials (see below) were close to the 0.2:0.8 ratio initially intended. The deviations in the cases of **1**, **2** and **5** are within the limits normally encountered in the synthesis of this kind of copolymer.[4]

The average *Mw* values, as determined by GPC, were of the order of 10^6. That of the amine derivative **6** was lower, however, in agreement with previous observations,[10] and this is due to some degradation of the chains during the aminolysis step. On the other hand, polymer **7** (Scheme 3) exhibits a higher *Mw*, namely 1.7 × 10^6. In all cases the specific rotation of the isolated polymers revealed their optical activity (Table 2).

All the spectroscopic data of the new polymers (Exp. Sect., Tables 2 and 3) are in agreement with their formulation and confirmed their expected stereochemical rigidity. The IR spectra (in KBr pellets) show, along with the expected bands of the $[NP(O_2C_{20}H_{12})]$ units, the specific absorptions corresponding to the other $[NP(OC_5H_4N)_2]$, $[NP(OC_6H_4R)_2]$ or $[NP(NHnBu)_2]$ repeating units (see Exp. Sect.). No significant changes on either group of frequencies were observed when compared with those of the $[NP(O_2C_{20}H_{12})]_n$ homopolymer (given in the Exp. Sect.) or other copolymers containing similar pyridinoxy[11] or (diphenylphosphanyl)phenoxy groups.[12] However, a rather conspicuous difference was observed between the ν(NH) stretching frequency in **6** (3396 cm^{-1}), and that normally found in poly[(dibutylamino)phosphazenes] (3330 cm^{-1}).[13] This might be due to the effects of the environment on the NPNHBu groups provided by the two binaphthoxyphosphazene units surrounding them, but it could also indicate that, being more isolated within the chains, their participation in H-bonding interactions is precluded. In fact, the ν(NH) band in **6** is rather sharp in contrast with the broad one observed in the poly[(dibutylamino)phosphazenes] previously reported by us.[10]

The ^1H, ^{13}C and ^{31}P NMR spectra are broad, as expected for these types of polymers, but they sharpen significantly upon heating above 110 °C in [D$_6$]DMSO. The integration of the ^1H and ^{31}P NMR spectra at high temperature confirmed the chemical composition of the copolymer and allowed the quantitative determination of the relative amounts of the two repeating units. In those cases where x could be obtained form both the ^1H and the ^{31}P NMR spectra (i.e. polymers **3** and **4**), the results were practically identical. Moreover, in the case of the high-temperature ^{31}P NMR spectrum (Figure 1) the distribution of the chemical shifts of the phosphorus atom bearing the $[NP(O_2C_{20}H_{12})]$ units along the chain ($\delta \approx -5$ ppm) was clearly evidenced by two distinct main signals, one sharper (units mainly surrounded by the same units) and another much broader (units nearer the other repeating units).

Similarly, the high-temperature ^1H and ^{13}C NMR spectra show the main signals for the statistical distribution of the (binaphthoxy)phosphazene units and, among them, the much weaker signals corresponding to the other aryl groups present in the chain (see Exp. Sect.). Only in the

Table 1. Experimental data for the synthesis of the polymers **2**−**5**

Polymer	PDCP [g (mmol)]	THF [mL]	RBIN [g (mmol)]	Cs_2CO_3 [g (mmol)]	t_1 [h]	HOC_6H_4R [g (mmol)]	t_2 [h]	DT [d]	Yield [g (%)]
2	1.50 (12.94)	200	2.96 (10.34)	16.87 (51.78)	4	0.92 (7.72)	18	1	3.20 (77)
3	1.40 (12.08)	150	2.77 (9.70)	17.96 (55.12)	12	0.99 (7.27)	83	3	2.62 (66)
4	2.12 (18.29)	250	4.19 (14.63)	23.84 (73.17)	4	1.98 (11.00)	13	1	5.3 (80)
5	2.40 (20.71)	230	4.75 (16.59)	29.24 (89.74)	17	3.46 (12.43)	46	1	3.53 (48)

Table 2. Analytical, molecular weight, glass transition, and specific rotation for the polymers

Polymer	Colour	C calcd. (found)	H calcd. (found)	N calcd. (found)	Cl	Mw (Mw/Mn)	Tg [°C] (ΔC_p [J $g^{-1}K^{-1}$])	$[\alpha]_D^{20}$ [a]
1	white	71.4 (67.0)	3.66 (3.65)	5.26 (5.36)	0.11	930 000 (2.4)	296 (0.24)	−160
2	pale creme	71.2 (71.3)	3.57 (3.42)	5.65 (5.16)	0.21	1 100 000 (1.8)	293 (0.17)	−145
3	white	70.6 (68.3)	3.83 (3.90)	4.29 (4.25)	0.17	1 100 000 (2.3)	271 (0.14)	−150
4	white	69.8 (69.2)	4.10 (3.96)	4.07 (4.14)	0.04	1 200 000 (2.5)	227 (0.18)	−116
5	white	72.7 (70.1)	3.84 (3.24)	3.92 (3.71)	0.07	940 000 (2.3)	268 (0.29)	−66
6	white	70.2 (67.8)	4.55 (4.77)	6.51 (6.94)	0.1	470 000 (4.9)	236 (0.12)	−186
7	yellow	54.6 (53.7)	2.69 (2.68)	2.74 (2.85)	[b]	1 760 000 (1.9)	256 (0.20)	9.7[c]

[a] [° mL·dm^{-1}·g^{-1}]. [b] Br calcd. 25.05; found 24.02. [c] At Hg line (578 nm).

Table 3. $^{31}P\{^1H\}$ NMR spectroscopic data of the polymers (see Figure 1)

Polymer	In $CDCl_3$ at room temp.		In $[D_6]$DMSO at 110 °C		
	NPOAr	$NP(O_2C_{20}H_{12})$	**A**[a]	**B**	**C**
1	−26	−2.6	−26.2, −25.6, −25.1	−5.0, −4.7,	−4.0, −3.7
2	−25	−2.5	−26.6, −26.0, −25.4	−5.4	−4.0
3	−25.1	−2.7, −4.0	−25.1	−5.0	−3.9
4	−25.0	−3.0	−25.6, −25.1, −24.5	−5.1	−4
5	−25.0	−3.0[b]	−25.7[c], −25.0, −24.3	−6.0	−4.0
7[d]	−22.3	−4.0[e]	−23[f]	−5.7	−4.4

[a] The signals A correspond to $NP(OAr)_2$ groups, where Ar = C_5H_4N or C_6H_5-R. The signals B are due to $NP(O_2C_{20}H_{12})$ units surrounded by $NP(OAr)_2$ groups. The peaks C correspond to $NP(O_2C_{20}H_{12})$ units which are located between other $NP(O_2C_{20}H_{12})$ units. [b] At δ = −6.2 $[OC_6H_4\mathit{P}(C_6H_5)_2]$, 28.3 $[OC_6H_4\mathit{P}\{O\}(C_6H_5)_2]$ ppm. [c] At δ = −4.4 $[OC_6H_4\mathit{P}(C_6H_5)_2]$, 25.1 $[OC_6H_4\mathit{P}\{O\}(C_6H_5)_2]$ ppm. [d] Polymer **6** exhibits a very broad signal with two maxima at δ = −2.7 and −1.6 ppm in its $CDCl_3$ spectrum, measured at room temp.; in $[D_6]$DMSO at 120 °C its spectrum shows a very broad peak centered at δ = −3.4 ppm. [e] At δ = −6.3 $[OC_6H_4\mathit{P}(C_6H_5)_2]$, 28.0 $[OC_6H_4\mathit{P}\{O\}(C_6H_5)_2]$ ppm. [f] At δ = −4.4 $[OC_6H_4\mathit{P}(C_6H_5)_2]$, 25 $[OC_6H_4\mathit{P}\{O\}(C_6H_5)_2]$ ppm.

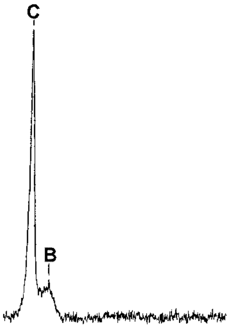


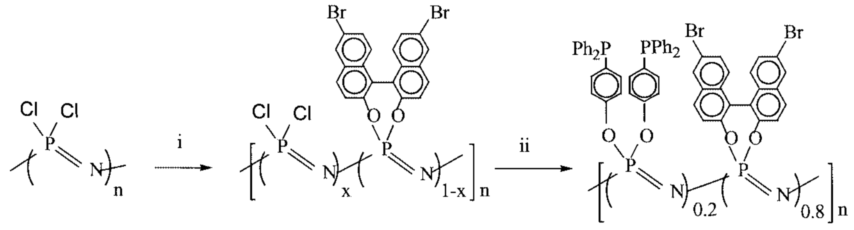
Figure 1. $^{31}P\{^1H\}$ NMR spectrum of $\{[NP(O_2C_{20}H_{12})]_{0.85}$-$[NP(OC_6H_4CN)_2]_{0.15}\}_n$ (**2**) in $[D_6]$DMSO at 110 °C; δ_A = −26.6, −26.0, −25.4 ppm; δ_B = −5.4 ppm; δ_C = −4.0 ppm (see Table 3)

case of **6** are significant differences found between the signals corresponding to the butyl protons of NHBu (δ = 2.2, 0.6 and 0.4 ppm) and those observed in other poly[(dibutylamino)phosphazene] polymers (δ = 3.0, 1.5 and 1.05 ppm).[10] However, the shift of the amine proton PNHR in **6** (δ = 2.6 ppm), which was unambiguously identified by its disappearance in the presence of D_2O, is very similar to that of the other aminophosphazenes (e.g., δ = 2.67 ppm in ref.[10]).

The *n*-butyl group was also easily detected in the ^{13}C NMR spectrum by the signals at δ = 15, 21, 35 and 42 ppm, of decreasing intensity, that are very close to those published for other polymers containing (butylamino)phosphazene units.[14]

The ^1H and ^{13}C NMR spectra also showed that all the isolated materials were perfectly free of any solvents, a fact that was confirmed by the TGA analysis (see below). This is important since poly(binaphthoxyphosphazene) polymers tend to retain solvent molecules even after having been dried in vacuo at 70 °C.[3,4] The only impurity present was a very small amount of the cyclic trimer $[N_3P_3(O_2C_{20}H_{12})_3]$ that in no case was higher than one molecule of the trimer for every 100 polymeric units [to be exact 1 (**1**), 0.5 (**2**), 0 (**3**), 1 (**4**), 1 (**5**), 0 (**6**), and 0.1 (**7**) molecules of the trimer].

In the case of the phosphane derivative **5**, the ^{31}P NMR spectrum (Table 3) revealed that 20% of the PPh_2 groups had been oxidized to $P(O)Ph_2$. Therefore, the exact chemical formula of **5** would be $\{[NP(OC_6H_4PPh_2)_{1.6}$-



(7)

Scheme 3

$(OC_6H_4POPh_2)_{0.4}]_{0.1}[NP(O_2C_{20}H_{12})]_{0.9}\}_n$. The formation of oxidized phosphane sites also noted in other similar phosphazene polymers with PPh_2 ligands could not be prevented even under careful workup.[15]

All the polymers exhibit an increase in C_p corresponding to the glass transition at rather high temperatures ranging from 227 to 296 °C (Table 2) in their DSC thermograms. In fact, the *Tg* of **1** (296 °C) is the highest glass transition recorded for a phosphazene high molecular weight polymer [up to now the highest reported *Tg* is 220 °C for a poly(aminophosphazene)].[16] This, together with the broad NMR spectra at room temperature and the observed sharpness upon heating evidenced the high stereochemical rigidity of the polymeric chains, which, in principle, is helpful in their potential use as ligands to support catalysts for asymmetric reactions.

In order to synthesize similar polymers with a chiral pocket with different electronic and steric characteristics, we extended the reactions of Scheme 2 to the preparation of the polymer **7** (see Scheme 3), which is a brominated derivative of **5**. The data of the isolated product are in agreement with the formula given in the Scheme 3. In spite of the presence of the Br atoms in the binaphthyl units, the *Tg* of **7** (256 °C) is not higher than that of **5**. However, this is due to the lower content of binaphthyl groups — 0.8 in **7** and 0.9 in **5**. The oxidized phosphanes make up 12.5% of the PPh_2 groups, and therefore the exact formula is $\{[NP(OC_6H_4PPh_2)_{1.75}(OC_6H_4POPh_2)_{0.25}]_{0.2}[NP(O_2C_{20}H_{10}Br_2)]_{0.8}\}_n$.

The TGA thermograms show that the copolymers **1**−**3**, **5** and **7** have a high thermal stability, losing weight around 500 °C, near to the decomposition temperature of the poly(binaphthoxy) homopolymer $[NP(O_2C_{20}H_{12})]_n$ (540 °C).[3] The polymer **4** has two further losses at 380 and 440 °C. On the other hand, polymer **6** shows a stepped and continuous loss of weight starting at ca. 150 °C (see Exp. Sect.), which is typical of the poly(phosphazene)s containing amino side groups.[17] The final residues at 800 °C, of the order of 50−65%, are comparable or higher than the 50% residue observed for $[NP(O_2C_{20}H_{12})]_n$ under the same experimental conditions.[3]

Experimental Section

General: All the reactions were carried out under nitrogen. Cs_2CO_3 (Aldrich) was dried at 140 °C prior to use. THF (VWR International) was treated with KOH and distilled twice from Na in the presence of benzophenone. Hexane (VWR intern), (*R*)-(+)-1,1′-bis(2-naphthol) [(*R*)-(+)-$C_{20}H_{10}(OH)_2$], HOC_5H_4N, and the phenols HOC_6H_4R (R = CN, COMe and CO_2nPr) were used as purchased (Aldrich); the amine H_2NnBu (Aldrich) was distilled from CaH_2. The starting polymer $[NPCl_2]_n$ was prepared as described by Magill et al.[18] The phosphane $HOC_6H_4PPh_2$ [12] and (*R*)-(+)-6,6′-dibromo-1,1′-binaphthalene-2,2′-diol [(*R*)-(+)-$C_{20}H_{10}Br_2(OH)_2$][19] were prepared as described previously. The IR spectra were recorded with a Perkin−Elmer FT Paragon 1000 spectrometer. NMR spectra were recorded with Bruker AC-200, AV-300 and DPX 300 instruments, using $CDCl_3$ as solvent unless otherwise stated. Chemical shifts (^1H and $^{13}C\{^1H\}$) are given in δ relative to TMS. $^{31}P\{^1H\}$ NMR values are given in δ relative to external 85% aqueous H_3PO_4. C, H, N analyses were performed with a Perkin−Elmer 2400 microanalyzer. Chlorine analyses were performed by Galbraith Laboratories. GPC were measured with a Perkin−Elmer equipment with a Model LC 250 pump, a Model LC 290 UV, and a Model LC 30 refractive index detector. The samples were eluted with a 0.1% by weight solution of tetra-*n*-butylammonium bromide in THF through 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. *Tg* values were measured with a Mettler 3000 differential scanning calorimeter DSC. Thermal gravimetric analyses were performed with a Mettler TA 4000 instrument. The polymer samples were heated at a rate of 10 °C/min from ambient temperature to 800 °C under a constant flow of nitrogen. The specific rotation [α] was measured with a Perkin−Elmer 343 or 241 in $CHCl_3$ at $c = 1$ at 20 °C using the Na-D or the 578-nm Hg lines, respectively. The colour, analytical, *Mw* (GPC), glass transition and specific rotation data for the polymers are given in Table 2. The IR spectra (KBr pellet) of all the copolymers **1**−**6** showed the expected bands of the $[NP(O_2C_{20}H_{12})]$ units. These were identical to those found in the homopolymer $[NP(O_2C_{20}H_{12})]_n$: $\tilde{\nu} = 3054\ cm^{-1}$ [w, ν_{CH} aromatic), 1622 w, 1590 m,1507 w, 1465 sh, 1433 sh,1403 w, 1362 m (aryl rings), 1318 (s, ν_{C-OP}), 1267 sh, 1220 vs (ν_{NP}), 1190 sh, 1155 w, 1072 (m, ν_{P-OC}), 964, 946 sh, (s, δ_{POC}), 896 w, 868 m, 812 (s, δ_{PNP}), 772 w, 746 m, 714 m, 695 w, 655 w, 571 (s, δ_{NPO}), 531 w, 487 w. The specific absorptions corresponding to the other repeating units present in the copolymers are given below. The ^{31}P NMR spectroscopic data are given in Table 3. The ^1H and ^{13}C NMR and TGA data for each compound are given below.

Preparation of $\{[NP(OC_5H_4N)_2]_{0.1}[NP(O_2C_{20}H_{12})]_{0.9}\}_n$ (1): (*R*)-(+)-$(HO)_2(C_{20}H_{12})$ (8.16 g, 28.50 mmol) and Cs_2CO_3 (46.4 g, 142.5 mmol) were added to a solution of $[NPCl_2]_n$ (4.13 g, 35.65 mmol) in THF (440 mL) and the mixture was refluxed with vigorous mechanical stirring for 35 h. Then, the pyridone HOC_5H_4N (2.03 g, 21.34 mmol) was added and the refluxing was maintained for another 48 h. The resulting mixture was poured into water (1.5 L) to give a solid residue that was extracted at room temperature in THF (500 mL) for 4 h. The mixture was filtered and concentrated into a viscous liquid that was poured slowly into water (1.5 L). The product was reprecipitated in the same way from THF/IPA (isopropyl alcohol), and THF/hexane. Finally, the product was dried under vacuum at 70 °C for 7 d to give the polymer **1** as a white solid. Yield [5.41 g (47%)]. IR (KBr): $\tilde{\nu} = 1580$ w cm^{-1} (ν_{CC}-ν_{CN}, OC_5H_4N) (seen as a shoulder of the band at 1591 cm^{-1} of the binaphthoxy group). ^1H NMR ($CDCl_3$, 25 °C): $\delta = 5.5-8.0$ (very br. m, aromatic rings) ppm. ^1H NMR ($[D_6]$DMSO, 110 °C): $\delta = 6.7$, 6.8, 7.1, 7.6 (br. m, $O_2C_{20}H_{12}$), 6.9, 7.9 (br. m, OC_5H_4N-4) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta = 118$ (C-3 of OC_5H_4N), 153 (C-2 of OC_5H_4N), 159 (NPO*C*, OC_5H_4N), 124, 128−131, 133−135 (br. peaks, naphthalene rings), 150 (NPO$C_{\text{naphthalene ring}}$) ppm. TGA: −48% (500 °C); residue at 800 °C (52%).

Preparation of $\{[NP(OC_6H_4R)_2]_x[NP(O_2C_{20}H_{12})]_{1-x}\}_n$ [R = CN, $x = 0.15$ (2); R = COMe, $x = 0.20$ (3); R = CO_2nPr, $x = 0.20$ (4); R = PPh_2, $x = 0.10$ (5)]: The following procedure for **2** is representative for all the polymers using the data given in Table 1. (*R*)-(+)-$(HO)_2(C_{20}H_{12})$ (2.96 g, 10.34 mmol) and Cs_2CO_3 (16.87 g, 51.78 mmol) were added to a solution of $[NPCl_2]_n$ (PDCP) (1.5 g, 12.94 mmol) in THF (200 mL), and the mixture was refluxed for 4 h (t_1) with vigorous mechanical stirring. After that, the phenol HOC_6H_4CN (0.92 g, 7.72 mmol) was added and the refluxing was continued for another 18 h (t_2). The resulting mixture was poured into water (1.5 L) and the precipitate was washed with water (3 × 0.5 L), IPA (2 × 0.2 L) and diethyl ether (2 × 0.2 L). This crude product was purified from THF/H_2O, THF/IPA, and THF/hexane as explained for **1**. Finally, the product was dried under vacuum at 70 °C for 1 d (DT) to give the polymer as a pale creamy solid. Yield [3.2 g 77 (%)].

$\{[NP(OC_6H_4CN)_2]_{0.15}[NP(O_2C_{20}H_{12})]_{0.85}\}_n$ (2): IR (KBr): $\tilde{\nu} = 2227$ w cm^{-1} (ν_{CN}). ^1H NMR ($CDCl_3$, 25 °C): $\delta = 6.0-8.0$ (very br. m, aromatic rings) ppm. ^1H NMR ($[D_6]$DMSO, 110 °C): $\delta = 6.6$, 6.8, 7.1, 7.6 (br. m, $O_2C_{20}H_{12}$), 7.2, 7.8 (br. m, OC_6H_4CN) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta = 107$, 119 (OC_6H_4*C*N), 154 (NPO*C*, OC_6H_4CN), 122, 125−130, 132−133 (br. peaks, aromatic C), 148 (NPO$C_{\text{naphthalene ring}}$) ppm. TGA: −45.5% (530 °C); residue at 800 °C 54.5%.

$\{[NP(OC_6H_4COMe)_2]_{0.2}[NP(O_2C_{20}H_{12})]_{0.8}\}_n$ (3): IR (KBr): $\tilde{\nu} = 1683$ m cm^{-1} (ν_{CO}), 1266 s, 1164 m. ^1H NMR ($CDCl_3$, 25 °C): $\delta = 1.9$ (3 H, $COCH_3$), 6.0−9.0 (very br. m, aromatic rings) ppm. ^1H NMR ($[D_6]$DMSO, 110 °C): $\delta = 2.1$ (3 H, $COCH_3$), 6.7, 6.8, 7.2, 7.6 (br. m, $O_2C_{20}H_{12}$) 7.4, 7.8 (br. m, $OC_6H_4COCH_3$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 29$ (CO*C*H_3), 157 (NOP*C*, OC_6H_4-$COCH_3$), 199 (*C*OMe), 125, 128−132, 133, 134, (br. peaks, aromatic rings), 150 (NPO$C_{\text{naphthalene ring}}$) ppm. TGA: −34.5% (485 °C); residue at 800 °C: 65.5%.

$\{[NP(OC_6H_4CO_2n\mathrm{Pr})_2]_{0.2}[NP(O_2C_{20}H_{12})]_{0.8}\}_n$ (4): IR (KBr): $\tilde{\nu} = 2964$ w cm^{-1}, 2877 w (ν_{CH} alkylic), 1717 (s, ν_{CO}), 1109 s. ^1H NMR ($CDCl_3$, 25 °C): $\delta = 0.8$ (3 H, $OCH_2CH_2CH_3$), 1.5 (2 H, $OCH_2CH_2CH_3$), 4.0 (2 H, $OCH_2CH_2CH_3$), 6.0−8.0 (very br. m, aromatic rings) ppm. ^1H NMR ($[D_6]$DMSO, 110 °C): $\delta = 0.8$ (3 H, $OCH_2CH_2CH_3$), 1.5 (2 H, $OCH_2CH_2CH_3$), 4.0 (2 H, $OCH_2CH_2CH_3$), 6.7, 6.8, 7.1, 7.5 (br. m, $O_2C_{20}H_{12}$), 7.3, 7.8 (br. m, OC_6H_4COO) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 11$ ($OCH_2CH_2CH_3$), 23 ($OCH_2CH_2CH_3$), 67 ($OCH_2CH_2CH_3$), 121 [$OC_6H_4C(O)OPr$], 155 (NPO*C*, $OC_6H_4C(O)OPr$], 166 (*C*OOPr), 122, 125−130, 132, 133 (br. peaks, aromatic rings), 148 (NPO$C_{\text{naphthalene ring}}$) ppm. TGA: −13.5% (380 °C), −11.5% (440 °C), −32% (516 °C); residue at 800 °C: 43%.

$\{[NP(OC_6H_4PPh_2)_2]_{0.1}[NP(O_2C_{20}H_{12})]_{0.9}\}_n$ (5): IR (KBr): $\tilde{\nu} = 1490$ cm^{-1} sh, 1434 m, 694 m. ^1H NMR ($CDCl_3$, 25 °C): $\delta = 5.5-8.5$ (very br. m, aromatic rings). ^1H NMR ($[D_6]$DMSO, 110 °C): $\delta =$ 6.4 (br. m, OC_6H_4P), 7.0 [br. m $P(C_6H_5)_2$], 6.6, 6.7, 7.0, 7.6 (br. m, $O_2C_{20}H_{12}$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 128$, 138 [$P(C_6H_5)_2$], 122, 127, 128, 131, 132, 134, (br. peaks, naphthalene and phosphane rings), 148 (NPO$C_{\text{naphthalene ring}}$) ppm. TGA: −42% (509 °C); residue at 800 °C: 58%.

Preparation of $\{[NP(NHn\mathrm{Bu})_2]_{0.2}[NP(O_2C_{20}H_{12})]_{0.8}\}_n$ (6): (*R*)-(+)-$(HO)_2(C_{20}H_{12})$ (2.73 g, 9.54 mmol) and Cs_2CO_3 (29.24 g, 24.86 mmol) were added to a solution of $[NPCl_2]_n$ (1.38 g, 11.91 mmol) in THF (150 mL), and the mixture was refluxed with vigorous mechanical stirring for 21 h. After that, *n*-butylamine (H_2NnBu) (3.28 mL, 2.43 g, 33.22 mmol) was added at 0 °C and stirring was continued at room temp. for 54 h. The mixture was then poured into water (1.5 L) giving a white solid which was purified by re-precipitating it from THF/H_2O, THF/IPA, and THF/hexane. The resulting white polymer was dried under vacuum at 70 °C for 1 d and later at 90 °C for 2 d. Yield 3 g, 84%. IR (KBr): $\tilde{\nu} = 3396$ w cm^{-1} (ν_{NH} amine), 2952 m, 2927 m, 2868w (ν_{CH} alkyl), 1508 m, 1094 w. ^1H NMR ($[D_8]$THF, 25 °C): $\delta = 0.36$, 0.58 (br., $NHCH_2CH_2CH_2CH_3$), 2.2 (very br., $NHCH_2CH_2CH_2CH_3$), 2.6 (br., N*H*Bu), 7.3, 7.8 (very br. m, aromatic rings) ppm. ^1H NMR ($[D_6]$DMSO, 120 °C): $\delta = 0.4$ (br., $NHCH_2CH_2CH_2CH_3$), 0.7 (br., $NHCH_2CH_2CH_2CH_3$), 2.3 (very br., $NHCH_2CH_2CH_2CH_3$), 2.9 (br., N*H*Bu), 7.2, 7.3, 7.6, 7.7 (br. m, aromatic rings) ppm. $^{13}C\{^1H\}$ NMR ($[D_8]$THF, 25 °C): $\delta = 15$ (br., $NHCH_2CH_2CH_2CH_3$), 21 (br., $NHCH_2CH_2CH_2CH_3$), 35 (br., $NHCH_2CH_2CH_2CH_3$), 42 (br., $NHCH_2CH_2CH_2CH_3$), 123, 126, 127, 128, 130, 132, 133, 134 (br. peaks, naphthalene rings) 150 (NPO$C_{\text{naphthalene ring}}$) ppm. TGA: −4% (210 °C), −12% (370 °C), 28% (507 °C); residue at 800 °C: 56%.

Preparation of $\{[NP(OC_6H_4PPh_2)_2]_{0.2}[NP(O_2C_{20}H_{10}Br_2)]_{0.8}\}_n$ (7): (*R*)-(+)-$(HO)_2(C_{20}H_{10}Br_2)$ (6.4 g, 14.41 mmol) and Cs_2CO_3 (23.5 g, 72.13 mmol) were added to a solution of $[NPCl_2]_n$ (2.09 g, 18.03 mmol) in THF (300 mL), and the mixture was refluxed with vigorous mechanical stirring for 14 h. After that, the phenol ($HOC_6H_4PPh_2$) (3 g, 10.78 mmol) was added and refluxing was continued for 30 h. The mixture was then poured into water (1.5 L) giving a yellow solid which was washed with water (2 × 1 L) and then purified by re-precipitating it from THF/H_2O, THF/IPA, and THF/hexane. The resulting yellow polymer was dried under vacuum at 70 °C for 1 d. Yield 6.86 g, 74%. IR (KBr): $\tilde{\nu} = 3052$ (w, ν_{CH} aromatic) cm^{-1}, 1585 m, 1493 m, 1434 w, 1396 w, 1354 w (aryl rings), 1317 (m, ν_{C-OP}), 1255 sh, 1217 (vs, ν_{NP}**)** 1186 sh, 1170 sh, 1066 (m, ν_{P-OC}), 960 (s, δ_{POC}), 942 s, 874 m, 826 m, 807 (m, δ_{PNP}), 778 w, 742 w, 728 w, 692 w, 655 w, 601 w, 570 (m, δ_{NPO}), 533 w, 493 w, 472 w. ^1H NMR ($CDCl_3$, 25 °C): $\delta = 5.5-9.5$ (very br. m, aromatic rings). ^1H NMR ($[D_6]$DMSO, 110 °C): $\delta = 6.4$ (br. m, OC_6H_4P), 7.0 (br. m, $P(C_6H_5)_2$], 6.4, 6.8, 7.4, 7.7 (br. m, $O_2C_{20}H_{10}Br_2$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta = 120$ (br., Br*C*), 121−122, 129−134 (br. peaks, naphthalene and phosphane rings), 148 (NPO$C_{\text{naphthalene ring}}$), 129, 138 [$P(C_6H_5)_2$], 152 [NPO*C*, $P(C_6H_5)_2$] ppm. TGA: −48% (477 °C); residue at 800 °C: 52%.

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