Polythioureas: Main Chain Chiral Polymers in Hydride Transfer Hydrogenation

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Chiral polythioureas have been synthesized and tested in asymmetric hydride transfer reduction of ketones with ruthenium. With polyurea **18**, 70% *ee* was attained for acetophenone reduction; after filtration, it can be reused at least four times without any detectable loss of activity and only a slight decrease in selectivity. Various aryl alkyl ketones were reduced with the same system and up to 84% *ee* was measured with isopropyl phenyl ketone.

Introduction

Hydride transfer hydrogenation of prochiral ketones is an attractive way to obtain chiral alcohols and an interesting alternative to the use of molecular hydrogen. Many nitrogen-containing ligands have been designed for this reaction. Among the best are the monosulfonamides of Noyori[1] and Knochel,[2] the bis(oxazolinylmethyl)amine of Zhang[3] and the thioureas developed in our own group.[4] In some cases, acetophenone has thus been reduced with *ee*s of up to 98%. But so far, no satisfying heterogeneous version has been proposed.

Heterogeneous catalysis is a method of choice for the large-scale synthesis of chiral molecules. Ideally, the catalyst can be easily recovered and reused without loss of activity or selectivity. However, many practical problems tend to arise in the design of an efficient catalytic system. Firstly, both activity and selectivity are often lower than those obtained with homogeneous catalysts. Then, the recycling often proceeds well only a limited number of times, because of metal leaching or system deactivation.

Noyori's ligand has been immobilized on polystyrene supports[5,6] but, although selective (acetophenone was reduced with *ee*s up to 99%), the polymeric catalysts cannot be reused several times without loss of both activity and selectivity. Similarly, dialdimine ligands have been polymerized with styrene and divinylbenzene.[7] The cross-linking ratio has been studied and the best polymer gives 1-phenylethanol with 70% *ee*. Nevertheless, it does not recycle efficiently. We have reported on the use of polyureas for the reduction of acetophenone.[8] These do recycle and have been used three times without loss of activity and selectivity, but the latter never exceeded 60%.

As thioureas are better ligands than ureas, we examined polythioureas as main chain chiral polymers in metal-catalysed hydride transfer hydrogenation. We first studied the reduction of acetophenone with several polythioureas and then tested the best structure with other substrates.

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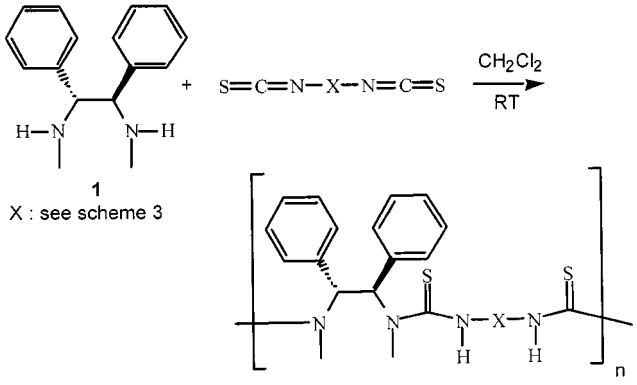
Results and Discussion

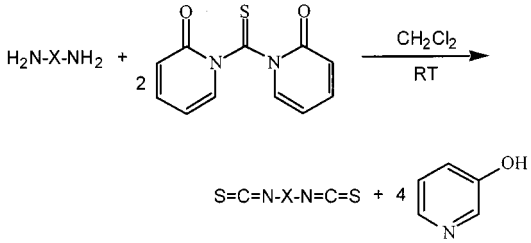
Polymer Synthesis and Characterisation

The polymers were synthesized from a chiral diamine, using one equivalent of diisothiocyanate. In homogeneous catalysis, the dithiourea derived from (1*R*,2*R*)-(+)-*N*,*N*′-dimethyl-1,2-diphenylethylenediamine **1** and phenyl isothiocyanate had led to the best results[4] (98% conversion, 89% *ee* with Ru), and so we chose this diamine as the chiral backbone (Scheme 1).



Scheme 1. Preparation of polythioureas from (1*R*,2*R*)-(+)-*N*,*N*′-dimethyl-1,2-diphenylethylenediamine and diisothiocyanates

Diisothiocyanates were synthesized according to the procedure of Kim et al., by using 1,1′-thiocarbonylbis(2,2′-pyridone)[9] (Scheme 23).



Scheme 2. Synthesis of isothiocyanates from primary amines and 1,1′-thiocarbonylbis(2,2′-pyridone)

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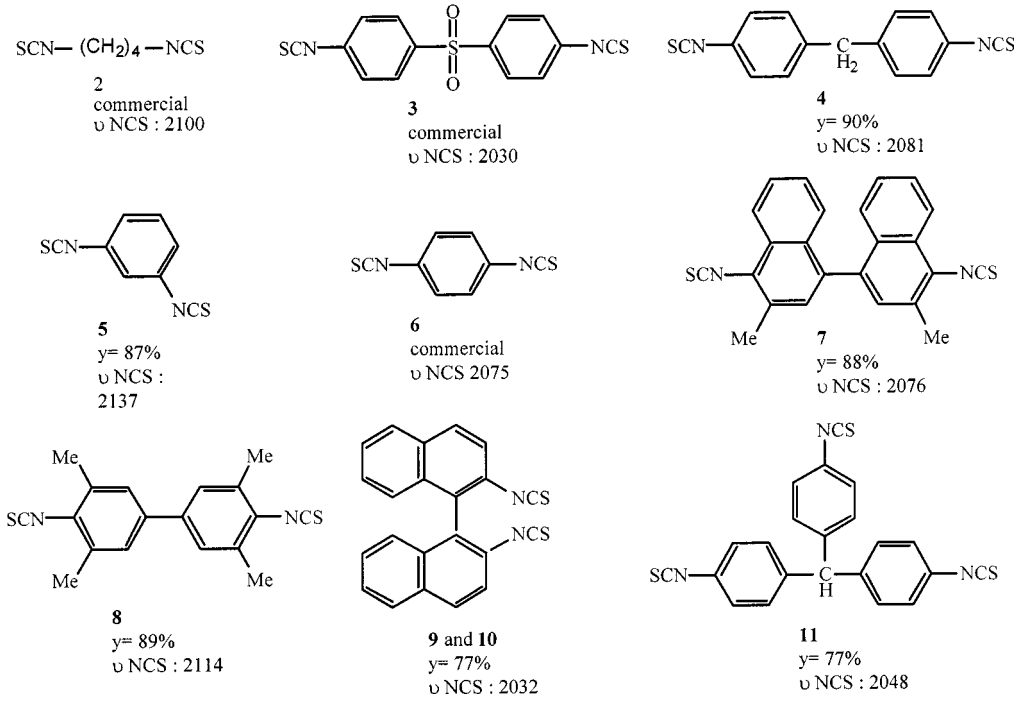


Scheme 3. Yields and NCS bands of the isothiocyanates synthesized

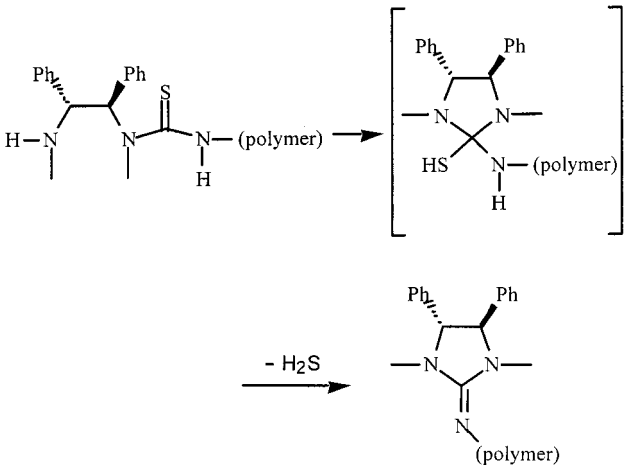
Anilines were readily transformed in a few minutes at room temperature in dichloromethane. As 2-hydroxypyridine is soluble in water, it was easily separated from the reaction mixture. As isothiocyanates are less polar than 1,1′-thiocarbonylbis(2,2′-pyridone), they could be isolated, in good yields, by chromatography on silica gel with dichloromethane as eluent (Scheme 3). They all possess a characteristic strong IR band slightly above 2000 cm^{-1} and were characterized fully (see Experimental Section).

Both rigid aromatic rings and flexible alkyl chains were tested as diisothiocyanate spacers. For aromatic structures, SO_2 and CH_2 were used as linkers between phenyl groups. The steric effect was tested using *meta*- and *para*-diisothiocyanates. The influence of the distance between two chiral sites was also tested, using phenyl and biphenyl spacers. Double induction effects were studied using the two enantiomers of 2,2′-diisothiocyanate-1,1′-binaphthalene with diamine **1** alternatively. Finally, we polymerized the diamine with a triisocyanate to evaluate the influence of cross-linking.

The polymers were obtained in good yields. They either precipitated during chain growth or after addition of 2-propanol. They were then filtered off, washed several times with *i*PrOH and dried under vacuum. All of them have been fully characterized by IR and elemental analysis, and also by NMR in DMSO for linear polymers and solid NMR for **21**. The degree of polymerisation (DP) has been determined for every structure.

Determination of the DP

The reaction of (1*R*,2*R*)-(+)-*N*,*N*′-dimethyl-1,2-diphenylethylenediamine with one equivalent of phenyl isothiocyanate led almost exclusively to the formation of guanidine.[4] This transformation can also occur during the polymer synthesis (Scheme 4).



Scheme 4. Guanidine formation during polymerisation

During the formation of the polymer chain, an amino group can cyclise to form a guanidine. It thus stops the chain growing at that end of the chain. Polymerisation is thus a competition between addition of NHMe to NCS and cyclisation to a guanidine moiety. This process will be affected by the initial ratio of the two co-monomers. If amine is in excess, this will promote production of guanidine terminals. If isothiocyanate is in excess, it will favour isothiocyanate endings. The nature of the diisothiocyanate and the polymer structure are also important factors. So, we are likely to observe guanidine−guanidine, guanidine−isothiocyanate or isothiocyanate−isothiocyanate endings.

Using IR spectroscopy, the NCS bands appear above 2000 cm^{-1} and the guanidine C=N bands between 1630 and 1660 cm^{-1}. They are strong for monomers and still detectable in polymers. In their ^1H NMR and ^{13}C NMR spectra, methyl groups from guanidines and thioureas have different chemical shifts. Moreover, when using ^{13}C NMR, the benzylic CH also differs between monomers and the corresponding polymers. Finally, the ratio of the aromatic to the aliphatic protons observed by ^1H NMR permits a check that DP is correct. It is therefore possible to determine the number of guanidine moieties in a polymeric chain: 0, 1, or 2. As, in theory, a chain (Scheme 5) is composed of x diamines, $x+1$ diisothiocyanates and 0, 1, or 2 guanidines, C, H, N, and S contents can be calculated for every value of x and compared to the experimental values obtained by elemental analysis and ^1H NMR. Elemental analysis thus also gives a measure of the DP, and this is generally consistent with the value determined by NMR.

(guanidine) + [diisothiocyanate + diamine]$_x$ + diisothiocyanate + (guanidine)

Scheme 5. Composition of a polymeric chain

Table 1 reports estimated mean x. The error between experimental and calculated data is close to 0.4% for each element.

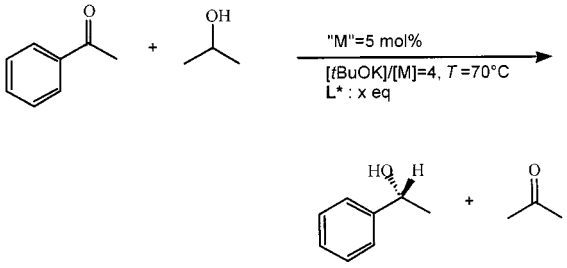
For **12**, **13**, and **17**, microanalyses and NMR spectroscopy do not permit any clear determination of the DP. The given value is the minimum DP number, and so it is then difficult to determine the chain length. As far as the other polymers are concerned, they are composed of about ten diamines and diisothiocyanates.

All the reported polymers are soluble in DMSO. Polymers **12**, **14**, **17**, and **18** are soluble in dichloromethane and precipitated only after addition of 2-propanol. They are all insoluble in this solvent; this is particularly relevant as the hydride transfer reduction of ketones is performed in 2-propanol. The polymers can thus be recovered by filtration and reused after catalytic testing (vide infra).

Hydride Transfer Reduction

Metallic Precursors

We first tested all the polymers by acetophenone reduction in standard conditions (Scheme 6).



Scheme 6. Hydrogen transfer reduction of acetophenone

In order to determine an appropriate metallic precursor, we tested **16** with $[Rh(COD)Cl]_2$, $[Ru(p\text{-cymene})Cl_2]_2$, and $[Ru(benzene)Cl_2]_2$. As $[Ir(COD)Cl]_2$ had previously given poor selectivities with dithioureas,[4] it was not tested here. In each case, we tested increasing L*/M ratios until the *ee* reached its highest value. Only the best results are reported in Table 2.

Table 2. Acetophenone reduction with **16** (conditions: [S] = $6\cdot10^{-2}$ (initial concentration); [S]/[M] = 20; [*t*BuOK]/[M] = 4; T = 70 °C)

Entry	Precursor	L*/M	time (h)	Conversion (%)	*ee*
1	$[Rh(COD)Cl]_2$	3	15	96	47
2	$[Ru(p\text{-cymene})Cl_2]_2$	2	15	93	63
3	$[Ru(benzene)Cl_2]_2$	2	15	98	63

Table 1. Structure, molecular weight, and elemental analyses of the synthesized polymers (see Table 3 for detailed structures)

Monomer	Polymer (yield, %)	Number of guanidines	x	Mol. wt.	C[a]	H[a]	N[a]	S[a]
2	**12** (45)	0	≥18	7416	64.08 (63.84)	6.79 (6.77)	13.59 (13.74)	15.53 (15.65)
3	**13** (81)	0	≥16	8546	63.19 (62.92)	4.89 (4.89)	9.83 (9.50)	16.48 (16.88)
4	**14** (87)	1	8±3	4670	71.82 (71.75)	5.78 (5.78)	10.81 (10.80)	11.59 (11.67)
5	**15** (72)	2	8±1	4066	68.56 (68.54)	5.59 (5.75)	13.31 (13.09)	12.54 (12.62)
6	**16** (80)	2	12±3	5800	68.00 (67.97)	5.76 (5.70)	12.96 (13.05)	13.28 (13.28)
7	**17** (87)	0	≥9	6128	75.52 (75.26)	5.71 (5.59)	8.67 (8.69)	10.10 (10.46)
8	**18** (60)	0	13±5	7667	72.11 (72.06)	6.33 (6.36)	9.76 (9.87)	11.80 (11.71)
9	**19** (80)	1	13±4	8489	75.48 (75.27)	5.11 (5.29)	9.07 (9.24)	10.33 (10.20)
10	**20** (87)	1	8±2	5445	75.58 (75.44)	5.19 (5.29)	9.18 (9.26)	10.05 (10.01)
11	**21** (85)	–	–	–	(72.68)	(5.73)	(10.73)	(10.86)

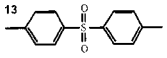
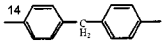
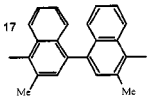
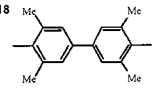
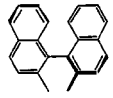
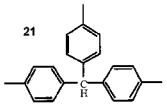
[a] % calculated (found).

As observed in the homogeneous phase, rhodium gave lower selectivities. However, [Ru(*p*-cymene)Cl_2]$_2$ and [Ru(benzene)Cl_2]$_2$ showed approximately the same behaviour. We thus retained [Ru(benzene)Cl_2]$_2$ for the following studies.

Polymer Structure

Results concerning acetophenone reduction with all the polymers are given in Table 3.

Table 3. Acetophenone reduction with polythioureas (**12**−**21**) and [$RuCl_2(C_6H_6)$]$_2$ (conditions: [S] = $6\cdot10^{-2}$ (initial concentration); [S]/[M] = 20; [*t*BuOK]/[Ru] = 4; T = 70 °C)

Entry	Polymer n° / Linker	L*/M	Time (d)	Conversion (%)	e.e. (%)
1	12 — $(CH_2)_4$ —	2	2	94	31 (S)
2	13 	2	3	34	39 (S)
3	14 	1.5	1	98	43 (S)
4	15 	2	1	40	56 (S)
5	16 	2	1	98	63 (S)
6	17 	1.5	1	96	70 (S)
7	18 	1.5	1	92	70 (S)
8	19 	10	1	71	48 (S)
9	20 	1.5	1	80	64 (S)
10	21 	8	1	47	65 (S)

With the flexible alkyl linker, the transformation proceeded with low selectivity; 31% *ee* and 94% conversion were observed after two days (Table 3, entry 1). The flexibility of the polymer may explain this poor *ee*. With **13** and **14** (Table 3, entries 2−3), the selectivity was only slightly improved; close to 40% for both structures. Introduction of sp^3 geometry between the two aromatic groups results in a different polymer chain conformation and so modifies the catalytic environment. The electron-withdrawing effect of SO_2 slowed down the reaction. Changing to purely aromatic linkers improved the catalytic properties. Thus, polymers **15** and **16** (Table 3, entries 4−5) gave selectivities close to 60%. With the *meta* isomer, we had thought that a helix might be formed, leading to macrochirality in the polymeric chain. In fact, phenylethanol was obtained with approximately the same *ee* with both **15** and **16**. Moreover, the *meta* isomer induced steric hindrance in the polymer chain and the system was less active. Increasing the spacer length (biphenyl) improved selectivity, which reached 70% *ee* (polymers **17** and **18**, Table 3, entries 6−7). Introduction of a second chiral source onto the diisocyanate component induced important modifications to the physical properties of the resulting material. Polymeric chains did not have the same length nor, above all, the same solubility. Polymer **20** is soluble in DMSO at room temperature, as are all the other linear polymers. Heating to around 50 °C was required to dissolve **19**. Moreover, it precipitated again as soon as the temperature decreased. We observed only weakly enhanced or diminished effects on selectivity. Both alcohols were obtained with *S* configuration and similar *ee*s (Table 3, entries 8−9). Enantiomeric recognition is thus largely controlled by the 1,2-diphenylethylene moiety. Polymer **21** is fully cross-linked. Site accessibility was thus decreased, and a ligand/metal ratio of 8 had to be used, but only 47% conversion was then observed. Selectivity increased from 43% with polymer **14** to 65% *ee* with **21**. Though catalytic site access is more difficult, it is more selective thanks to the stiffness of the polymer.

Catalyst Recycling

The recycling of polymer **18** was studied. Results concerning acetophenone reduction with **18** and [Ru(benzene)Cl_2]$_2$ are given in Table 4.

Table 4. Acetophenone reduction with the recycled catalyst: **18** and [Ru(benzene)Cl_2]$_2$ (initial conditions: [S] = $6\cdot10^{-2;}$ [S]/[M] = 20; [*t*BuOK]/[Ru] = 4; T = 70 °C; no additional Ru was used.)

Use number	Time (days)	Conversion (%)	*ee* (%)
1	1	92	70 (*S*)
2	1	98	67 (*S*)
3	1	99	66 (*S*)
4	1	99	63 (*S*)
5	1	98	61 (*S*)

The first experiment was performed according to the standard procedure. The polymer was then filtered and reused without addition of supplementary metal.

Polymer **18** can be reused at least four times without any detectable loss of activity. The selectivity decreased slightly during the recyclings though. Some catalyst leaching might be supposed, but could not be detected by titration. Moreover, the filtrate did not catalyse the reduction. The formation of heterogeneous metallic ruthenium could also explain this feature. Transformation of the terminals of the polymer into guanidine moieties might also occur.

Reduction of Prochiral Alkyl Aryl Ketones

Other ketones were reduced with polymer **18** (Table 5).

Whatever the ketone, the reduction proceeded with high activity and good selectivity, even though this latter still remained lower than with the homogeneous system.[8]

Table 5. Aryl alkyl ketones (RCOR′) reduced with **18** and [Ru(benzene)Cl_2]$_2$ (conditions: polymer **18**; [L]/[M] = 1.5; [S] = $6\cdot10^{-2}$ (initial concentration); [S]/[M] = 20; [*t*BuOK]/[Ru] = 4; T = 70 °C)

R	R′	Time (day)	Conversion (%)	*ee* (%)
Ph	Me	1	92	70
Ph	Et	1	95	80
Ph	*n*Pr	1	90	76
Ph	*i*Pr	1	87	84
Ph	*t*Bu	1	85	78
1-Naphth	Me	1	90	74

Conclusion

A series of polythioureas was synthesized by easy polyaddition of diisothiocyanates with (1*R*,2*R*)-(+)-*N*,*N*′-dimethyl-1,2-diphenyl-1,2-ethylenediamine. The polymers, which are insoluble in 2-propanol, were used for heterogeneous asymmetric hydrogen transfer reduction of acetophenone. The best structure resulted in the production in a few hours of phenylethanol with 96% conversion and 70% *ee*. It was, moreover, reused 4 times without loss of activity and only slight loss of selectivity. The *ee*s obtained with other aryl alkyl ketones ranged from 74 to 84%.

Even though selectivities are not as high as in some homogeneous counterparts, we have developed an efficient heterogeneous system for the transfer hydrogenation of prochiral ketones.

Further testing of this system with other asymmetric transformations seems worth recommending.

Experimental Section

General Remarks: ^{1}H NMR: Bruker AC 200 (200 MHz), δ = 0 (tetramethylsilane) and 7.24 ($CHCl_3$). − ^{13}C NMR: Bruker AC 200 (50 MHz), δ = 77.0 ($CDCl_3$). − Optical rotation was measured on a Perkin−Elmer 241 polarimeter. − IR analyses (in KBr) were performed on a Perkin−Elmer 1720X apparatus.

General Procedure for the Synthesis of Diisothiocyanates: To a suspension of 1,1′-thiocarbonylbis(2,2′-pyridone) (8.63 mmol) in dichloromethane (50 mL) was added the diamine (2.88 mmol). Dissolution was instantaneous. After evaporation of solvent, the crude mixture was filtered over SiO_2 (eluent CH_2Cl_2) to obtain the pure product.

General Procedure for the Hydride Transfer Reduction of Ketones: The appropriate amount of ligand was added to the catalyst precursor (M: $6\cdot10^{-3}$ mmol) in 2 mL of a solution of potassium *tert*-butoxide in 2-propanol (0.012 mol/L) and stirred for 1 h 30 min under an inert atmosphere ([*t*BuOK]/[M] = 4). After addition of the ketone (0.12 mmol), the mixture was kept overnight at room temperature. The solution was then heated (70 °C) in order for the reaction to proceed. All the reduction products were identified by GC by comparison with the commercial optically pure products or with literature data.

General Procedure for Polymer Recycling: After centrifugation, solvent was eliminated and only the solid was kept. Base and substrate were then added and the classical procedure for the hydride transfer reaction was followed.

Compound 4: This compound was prepared following the general procedure described above, starting from 4,4′-methylenedianiline. Yield: 90%; mp: 138−140 °C. − IR: ṽ = 3029, 2926, 2081, 1574, 1498, 1441, 1107, 929, 866, 818, 785. − ^{1}H NMR ($CDCl_3$): δ = 3.93 (s, 2 H, CH_2), 7.12 (s, 8 H_{aro}). − ^{13}C NMR ($CDCl_3$): δ = 41.1 (CH_2), 125.9−139.8 (C_{aro}), 135.4 (NCS). − $C_{15}H_{10}N_2S_2$ (282.4): calcd. C 63.80, H 3.57, N 9.92, S 22.71; found C 63.66, H 3.54, N 9.79, S 23.01.

Compound 5: This compound was prepared following the general procedure described above, starting from 1,3-phenylenediamine. Yield: 87%; mp: 52−54 °C. − IR: ṽ = 3062, 2137, 1576, 1476, 998, 873, 784, 726, 672. − ^{1}H NMR ($CDCl_3$) : δ = 7.10 (m, 3 H_{aro}), 7.34 (m, 1 H_{aro}). − ^{13}C NMR ($CDCl_3$): δ = 122−132.9 (C_{aro}), 138.1 (NCS). − $C_8H_4N_2S_2$ (192.3): calcd. C 49.98, H 2.10, N 14.57, S 33.35; found C 50.16, H 2.21, N 14.41, S 33.22.

Compound 7: This compound was prepared following the general procedure described above, starting from 3,3′-dimethylnaphthidine. Yield: 88%; mp: 194−196 °C. − IR: ṽ = 3073, 2930, 2076, 1620, 1595, 1570, 1504, 1440, 1367, 1504, 1440, 1367, 894, 801, 757, 644. − ^{1}H NMR ($CDCl_3$): δ = 2.65 (s, 6 H, 2 CH_3), 7.33 (m, 6 H_{aro}), 7.61 (m, 2 H_{aro}), 8.20 (d, J = 8.4 Hz, 2 H_{aro}). − ^{13}C NMR ($CDCl_3$): δ = 18.9 (CH_3), 122.8−136.9 (C_{aro}). − $C_{24}H_{16}N_2S_2$ (396.5): calcd. C 72.70, H 4.07, N 7.06, S 16.17; found C 72.92, H 4.12, N 6.95, S 16.01.

Compound 8: This compound was prepared following the general procedure described above, starting from 3,3′,5,5′-tetramethylbenzidine. Yield: 89%; mp: 194−196 °C. − IR: ṽ = 3044, 2929, 2114, 1600, 1577, 1469, 1441, 1385, 925, 867, 752, 719. − ^{1}H NMR ($CDCl_3$): δ = 2.43 (s, 12 H, CH_3), 7.22 (s, 4 H_{aro}). − ^{13}C NMR ($CDCl_3$): δ = 18.9 (CH_3), 126.5−138.6 (C_{aro}), 136.1 (NCS). − $C_{18}H_{16}N_2S_2$ (324.5) calcd. C 66.63, H 4.97, N 8.63, S 19.76; found C 66.81, H 4.70, N 8.69, S 19.80.

Compound 9: This compound was prepared following the general procedure described above, starting from (*R*)-(+)-1,1′-binaphthyl-2,2′-diamine. Yield: 77%; mp: 145−147 °C; $[\alpha]_D^{20}$ = −170 (c = 1.01, acetone). − ^{1}H NMR ($CDCl_3$): δ = 7.18 (d, J = 8.4 Hz, 2 H_{aro}), 7.38 (td, J = 7.7 Hz, J = 1.2 Hz, 2 H_{aro}), 7.52 (m, 4 H_{aro}), 7.98 (d, J = 8.3 Hz, 2 H_{aro}), 8.04 (d, J = 8.8 Hz, 2 H_{aro}). − ^{13}C NMR ($CDCl_3$): δ = 123.4−133 (C_{aro}), 138.5 (NCS).

Compound 10: This compound was prepared following the general procedure described above, starting from (*S*)-(−)-1,1′-binaphthyl-2,2′-diamine. Yield: 90%; mp: 145−147 °C; $[\alpha]_D^{20}$ = +169 (c = 1.01 acetone).

Compound 11: This compound was prepared following the general procedure described above, starting from 4,4′,4"-methanetriyltris-(aniline) that was synthesized from pararosaniline base [COH(*p*-$C_6H_5NH_2)_3$]: This compound (2 g, 6.55 mmol) was added to a mixture of Pd/C (10%, 0.7 g, 0.66 mmol) in THF (20 mL) and stirred under 1 atm of H_2 for 12 h. After filtration and recrystallisation (ethanol/toluene 2:1), 1.49 g (5.15 mmol) of 4,4′,4"-methylenetrianiline was obtained. Yield: 79%; mp: 208−210 °C. − ^{1}H NMR ([D_6]DMSO): δ = 4.84 (s, 6 H, 3 NH_2), 4.99 (s, 1 H, CH), 6.47 (d, J = 8.5 Hz, 6 H_{aro}), 6.72 (d, J = 8.5 Hz, 6 H_{aro}). − ^{13}C NMR ([D_6]DMSO): δ = 53.9 (CH), 113.6−146.3 (C_{aro}). − **11:** Yield: 77% (oil). − IR: ṽ = 3031, 2924, 2048, 1654, 1600, 1577, 1504, 995, 873, 821, 787. − ^{1}H NMR ($CDCl_3$): δ = 5.51 (s, CH), 7.03 (d, J = 8.5 Hz, 6 H_{aro}), 7.18 (d, J = 8.5 Hz, 6 H_{aro}). − ^{13}C NMR: δ =

55.5 (CH), 126−141.9 (C_{aro}), 135.9 (NCS). − $C_{22}H_{13}N_3S_3$ (415.5) calcd. C 63.59, H 3.15, N 10.11, S 23.15; found C 63.77, H 3.02, N 10.08, S 23.13.

Polymer Synthesis: Diisothiocyanate (2.06 mmol) was dissolved in the minimum possible volume of CH_2Cl_2. Diamine (2.09 mmol) in CH_2Cl_2 (1 mL) was then added. The reaction mixture was stirred for 12 h under Ar. *i*PrOH (50 mL) was added and the reaction mixture was allowed to stir for 12 h. The polymer precipitated and was recovered by filtration. After washing with *i*PrOH, it was dried under vacuum for two days.

Polymer 12: This polymer was obtained according to the procedure described above, starting from diisocyanate **2**. Yield 45%; mp: 202−204 °C; $[\alpha]_D^{20} = -470$ (c = 0.5, DMSO). − IR: $\tilde{\nu}$ = 3346, 3051, 2936, 1531, 1455, 1391, 1341, 1233, 1186, 1071, 788, 705. − ^{1}H NMR ([D$_6$]DMSO): δ = 1.56 (s, CH_2), 2.81 (s, NMe), 3.59 (s, CH_2), 7.25 (d, J = 8 Hz, CH_{aro}), 7.52 (d, J = 7 Hz, CH_{aro}), 7.83 (CH_{aro}). − ^{13}C NMR: δ = 26.2 (CH_2), 32.6 (CH_2), 45.5 (CH_2), 59.9 (CH), 127.6−137.9 (C_{aro}), 181.5 (CS). − $(C_{22}H_{28}N_4S_2)_n$ calcd. C 64.08, H 6.79, N 13.59, S 15.53; found C 63.84, H 6.77, N 13.74, S 15.65.

Polymer 13: This polymer was obtained according to the procedure described above, starting from diisocyanate **3**. Yield: 81%; mp: 207−209 °C; $[\alpha]_D^{20} = -355$ (c = 0.51, DMSO); IR: $\tilde{\nu}$ = 3346, 3050, 2944, 2030, 1628, 1596, 1527, 1319, 1153, 1110, 1075, 837, 702. − ^{1}H NMR ([D$_6$]DMSO): δ = 2.47 (s, NMe), 3.11 (s, NMe), 7.27 (m, CH), 7.59 (m, CH), 7.86 (br. s, CH), 9.51 (NH). − ^{13}C NMR: δ = 33.4 (NMe), 34.1 (NMe), 60.2 (CH), 71.7 (CH), 125.7−145.6 (C_{aro}), 181.9 (NCS). − $C_{450}H_{418}N_{60}O_{30}S_{44}$ (8546) calcd. C 63.19, H 4.89, N 9.83, S 16.48; found C 62.92, H 4.89, N 9.50, S 16.88.

Polymer 14: This polymer was obtained according to the procedure described above, starting from diisocyanate **4**. Yield: 87%; mp: 207−209 °C; $[\alpha]_D^{20} = -339$ (c = 0.51, DMSO). − IR: $\tilde{\nu}$ = 3367, 3027, 2921, 2080, 1599, 1515, 1332, 1230, 1073, 760, 700. − ^{1}H NMR ([D$_6$]DMSO): δ = 3.09 (s, NMe), 3.95 (s, CH_2), 7.27 (m, CH), 7.57 (m, CH), 7.96 (s, CH), 9.19 (s, 1 H, NH). − ^{13}C NMR: δ = 33.5 (NMe), 40.0 (CH_2), 60.2 (CH), 72.1 (CH), 123.7−138.8 (C_{aro}), 182 (NCS). − $C_{279}H_{268}N_{36}S_{17}$ (4670) calcd. C 71.82, H 5.78, N 10.81, S 11.59; found C 71.75, H 5.78, N 10.80, S 11.67.

Polymer 15: This polymer was obtained according to the procedure described above, starting from diisocyanate **5**. Yield: 72%; mp: 202−204 °C; $[\alpha]_D^{20} = -367$ (c = 0.51, DMSO). − IR: $\tilde{\nu}$ = 3369, 3029, 2934, 1598, 1520, 1480, 1328, 1223, 1075, 757, 700. − ^{1}H NMR ([D$_6$]DMSO): δ = 2.57 (s, NMe), 3.13 (s, NMe), 7.28 (m, CH), 7.58 (m, CH), 7.98 (m, CH), 9.31 (s, NH). − ^{13}C NMR: δ = 33.7 (NMe), 60.4 (CH), 72.1 (CH), 124.1−141.4 (C_{aro}), 182.1 (NCS). − $C_{232}H_{232}N_{38}S_{16}$ (4066) calcd. C 68.56, H 5.59, N 13.31, S 12.54; found C 68.54, H 5.75, N 13.09, S 12.62.

Polymer 16: This polymer was obtained according to the procedure described above, starting from diisocyanate **6**. Yield: 80%; mp: 219−221 °C; $[\alpha]_D^{20} = -367$ (c = 0.51, DMSO). − IR: $\tilde{\nu}$ = 3369, 3037, 2951, 1631, 1603, 1519, 1478, 1332, 1227, 1075, 700. − ^{1}H NMR ([D$_6$]DMSO): δ = 2.63 (s, NMe), 3.13 (s, NMe), 7.34 (m, CH), 7.59 (m, CH), 7.98 (br. s, CH), 9.29 (br. s, NH). − ^{13}C NMR: δ = 33.7 (NMe), 60.3 (CH), 72.3 (CH), 126.4−140 (C_{aro}), 182.1 (NCS). − $C_{328}H_{328}N_{54}S_{22}$ (5800) calcd. C 68.00, H 5.76, N 12.96, S 13.28; found C 67.97, H 5.70, N 13.05, S 13.28.

Polymer 17: This polymer was obtained according to the procedure described above, starting from diisocyanate **7**. Yield: 87%; mp: 233−235; $[\alpha]_D^{20} = -182$ (c = 0.5, DMSO). − IR: $\tilde{\nu}$ = 3391, 3063, 2947, 2080, 1600, 1495, 1326, 1077, 766, 701. − ^{1}H NMR ([D$_6$]DMSO): δ = 2.67 (br. s, CH_3), 3.37 (br. s, NMe), 7.41 (br. s, CH), 7.71 (br. s, CH), 8.23 (br. s, CH), 9.66 (s, NH). − ^{13}C NMR: δ = 18.4 (CH_3), 33.8 (NMe), 60.3 (CH), 125.7−137.8 (C_{aro}), 182.4 (NCS). − $C_{384}H_{340}N_{38}S_{20}$ (6128) calcd. C 75.52, H 5.71, N 8.67, S 10.10; found C 75.26, H 5.59, N 8.69, S 10.46.

Polymer 18: This polymer was obtained according to the procedure described above, starting from diisocyanate **8**. Yield: 56%; mp: 215−217 °C; $[\alpha]_D^{20} = 200$ (c = 0.5, DMSO). − IR: $\tilde{\nu}$ = 3388, 3029, 2917, 2086, 1602, 1499, 1332, 1227, 1077, 862, 700. − ^{1}H NMR ([D$_6$]DMSO): δ = 2.23 (s, CH_3), 2.35 (s, CH_3), 2.42 (s, CH_3), 3.13 (s, NMe), 7.23−7.6 (m, CH), 8.07 (br. s, CH), 9.01 (br. s, NH). − ^{13}C NMR: δ = 18.1−18.4 ($3CH_3$), 33.4 (NMe), 60.2 (CH), 125.7−138 (C_{aro}), 181.4 (NCS). − $C_{460}H_{484}N_{54}S_{28}$ (7667) calcd. C 72.11, H 6.33, N 9.76, S 11.80; found C 72.06, H 6.36, N 9.87, S 11.71.

Polymer 19: This polymer was obtained according to the procedure described above, starting from diisocyanate **9**. Yield: 81%; mp: 213−215 °C; insoluble in every tested solvent. − IR: $\tilde{\nu}$ = 3387, 3235, 3057, 2938, 2037, 1619, 1596, 1499, 1320, 1075, 817, 754, 700. − ^{1}H NMR ([D$_6$]DMSO. − 100 °C): δ = 2−2.5 (m, NMe), 3.00 (m, NMe), 6.66−8 (m, CH). − ^{13}C NMR: δ = 33.9 (NMe), 61.1 (CH), 122.7−138.5 (C_{aro}), 182.6 (NCS). − $C_{532}H_{446}N_{56}S_{27}$ (8489) calcd. C 75.48, H 5.11, N 9.07, S 10.33; found C 75.27, H 5.29, N 9.24, S 10.20.

Polymer 20: This polymer was obtained according to the procedure described above, starting from diisocyanate **10**. Yield: 87%; mp: 208−210 °C; $[\alpha]_D^{20} = -412$ (c = 0.5, DMSO). − IR: $\tilde{\nu}$ = 3391, 3058, 2932, 1618, 1593, 1500, 1320, 1081, 817, 754, 700. − ^{1}H NMR ([D$_6$]DMSO): δ = 2−2.8 (m, NMe), 6.3−8.4 (m, CH). − ^{13}C NMR: δ = 33.1−37.1 (NMe), 60.4−60.9 (CH), 73.1 (CH), 126.8−138.4 (C_{aro}), 183.1 (NCS). − $C_{342}H_{286}N_{36}S_{17}$ (5445) calcd. C 75.58, H 5.19, N 9.18, S 10.05; found C 75.44, H 5.29, N 9.26, S 10.01.

Polymer 21: This polymer was obtained according to the procedure described above, starting from diisocyanate **11**. Yield: 85%. − IR: $\tilde{\nu}$ = 3367, 3029, 2927, 2048, 1631, 1598, 1510, 1319, 1227, 1066, 698; solid state ^{13}C NMR: δ = 34.9 (NMe), 55.3 (CH), 61.9 (CH), 72.5 (CH), 129.1−138.5 (C_{aro}), 183.7 (NCS); elemental analysis: found C 72.68, H 5.73, N 10.73, S 10.86.

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