

# Reaction of Phenol- and Thiophenol-Terminated Compounds with Bisoxazolines

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**ABSTRACT:** Bulk reactions of phenolic compounds (bisphenol-A and  $\alpha,\omega$ -diphenol oligosulfone) or thiols (thiophenol and bis(4-mercaptophenyl)sulfide) with bisoxazoline coupling agents, namely 2,2'-(1,3-phenylene)bis(2-oxazoline) (**mbox**), 2,2'-(1,4-phenylene)bis(2-oxazoline) (**pbox**), and 2,2'-(2,6-pyridylene)bis(2-oxazoline) (**pybox**), were carried out in the bulk at 140–240°C. The reactions were followed by viscosimetry, size exclusion chromatography, and <sup>1</sup>H- and <sup>13</sup>C-NMR spectroscopy. The phenol/bisoxazoline bulk reactions at 240°C required the presence of sodium methoxide catalyst. Bisoxazoline **pybox** gave the best results in this case. Thiol and dithiol/bisoxazoline reactions were faster and did not require any catalyst. High-molar-mass polymers were obtained within 5 min at 200°C while using

bis(4-mercaptophenyl)sulfide (BMPS) and any of the bisoxazolines. The NMR spectra of model compounds and polymers were fully assigned, showing that the oxazoline/phenol and oxazoline/thiophenol (tph) polyaddition reactions proceed in the expected way, without any noticeable side reaction. All polymers were amorphous and displayed good thermal stability. Bisoxazolines were also used as coupling agents for the preparation of copolymers of BMPS and  $\alpha,\omega$ -dicarboxy polyamide-12 and for the preparation of polysulfone-polyamide-12 block copolymers. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 628–636, 2009

**Key words:** bisoxazoline; poly(ether sulfone); thiophenol; block copolymers; polyamide

## INTRODUCTION

Cyclic imino ethers such as 2-oxazolines are highly useful compounds used in organic and polymer chemistry.<sup>1</sup> Oxazolines are known for many years to undergo cationic polymerization<sup>2,3</sup> and to react with many reagents such as carboxylic acids,<sup>4</sup> thiols,<sup>5</sup> epoxides,<sup>6</sup> or isocyanates.<sup>7</sup> Step-growth reactions between bisoxazolines and dicarboxylic acids<sup>8,9</sup> and diphenols<sup>10,11</sup> or dithiophenols<sup>12–14</sup> were used to prepare adhesives and coatings. The chain-coupling<sup>15,16</sup> or chain-extension<sup>17</sup> reactions of reactive oligomers is another application of bisoxazolines. In previous work, we reported kinetic and mechanistic studies on carboxylic acid–bisoxazoline reactions<sup>18</sup> and on the chain-coupling reactions of carboxy-terminated oligomers in the bulk.<sup>19</sup> We showed that this chemistry is much faster than the conventional reactions between oligomers bearing mutually reactive end groups to prepare high-molar-mass block copolymers.<sup>20</sup> Bisoxazoline **pybox**, namely 2,2'-(2,6-pyridylene)bis(2-oxazoline), presented a higher reac-

tivity than conventional 2,2'-(1,3-phenylene)bis(2-oxazoline) (**mbox**) and 2,2'-(1,4-phenylene)bis(2-oxazoline) (**pbox**)<sup>18</sup> for chain-coupling reactions of  $\alpha,\omega$ -dicarboxylic oligomers.

In this study, we were interested in using these bisoxazolines for bulk chain-coupling reactions of phenol and thiophenol (**tph**) oligomers. Only a few articles deal with polyaddition reactions of bisoxazolines and phenols or **tphs**. AB-type monomers such as 2-(4-hydroxyphenyl)-1,3-oxazoline<sup>21,22</sup> and *p*-((2-(2-oxazolin-2-yl)propyl)thio) phenol<sup>23</sup> or *m*-((2-(2-oxazolin-2-yl)propyl)thio)benzenethiol<sup>23</sup> are known to be thermally polymerized, neat or in solution, into low-molecular-weight polymers. Culbertson et al.<sup>10,11</sup> showed that bisphenol-A (**bpA**) and bisphenol-P<sup>22</sup> react with bisoxazolines to produce poly(ether amide)s. However, no detailed data were given on the synthesized polymers. Curing reactions of phenolics by bisoxazolines were claimed to yield high-performance thermosets.<sup>24</sup> The chain extension and curing reactions of phenolic resins and of poly(*p*-hydroxystyrene) were also reported.<sup>25–28</sup> More recently, Li and Wang<sup>29</sup> studied the curing behavior and properties of 4,4'-diaminodiphenyl methane-based benzoxazine oligomers/**pbox** copolymer resins, where the oxazoline reacted with OH phenolic groups generated by benzoxazine ring-opening reactions. Nishibuko et al.<sup>12–14</sup> obtained

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high-molecular-weight poly(amide-sulfide)s by solution reactions of bisoxazolines with dithiophenols in NMP or NMP/water, but no bulk reactions between such compounds have yet been reported in literature.

This article is devoted to a detailed study of the bulk reactions between 2,2'-arylene-bis(2-oxazolines) with **bpA**,  $\alpha,\omega$ -diphenol oligosulfone (**PSU**), **tph**, or bis(4-mercaptophenyl)sulfide (**BMPS**). Polyamide-polysulfone block copolymers and polyamide-sulfide copolymers were also synthesized by the bulk reactions of mixtures of dicarboxy polyamides (**PA12**) and **PSU** or **BMPS** with arylene bisoxazolines.

## EXPERIMENTAL PART

### Chemicals

Starting materials and reagents were commercially available (Aldrich, Fluka, Saint-Quentin Fallavier, France, or Acros, Halluin, France, purity grade 99%) and used as received unless otherwise indicated.  $\alpha,\omega$ -Dicarboxy polyamide-12 oligomer (**PA12-1**) ([COOH] = 1.915 mol/kg, chain limiter: adipic acid, free adipic acid: 0.43%) and (**PA12-2**) ([COOH] = 1.031 mol/kg, chain limiter: adipic acid) were obtained from Arkema (Serquigny, France).

### Synthesis of bisoxazolines

**mbox**, 2,2'-(1,4-phenylene)bis-(2-oxazoline) (**pbox**), and 2,2'-(2,6-pyridine)bis-(2-oxazoline) (**pybox**) were prepared as previously described.<sup>18</sup>

### Synthesis of $\alpha,\omega$ -diphenol polysulfone

In a three-necked round-bottomed flask equipped with a nitrogen inlet and outlet and a distillation column fitted with a condenser, 225 mmol (51.36 g) of bpA, 115 g of dimethylsulfoxide, and 330 g of chlorobenzene were introduced. The mixture was heated between 60 and 80°C until a clear solution was obtained. Then, an aqueous solution of NaOH (18 g in 18 mL of water) was added, and then the mixture was refluxed until azeotropic distillation of water ceased. A solution of *p*-dichlorodisulfone (51.7 g; 0.180 mol) in chlorobenzene (103 g) was added, and then the mixture was heated at 160°C to eliminate the last traces of water and chlorobenzene. The mixture was then heated at 145°C for 6 h. After cooling down to room temperature, the crude product was acidified with 1.5 L of acetic acid, filtered, washed thoroughly with water and dried under vacuum. Seventy grams of  $\alpha,\omega$ -diphenol polysulfone ( $T_g = 157^\circ\text{C}$ ) were obtained.

### Polymerization reactions

The general procedure is described later with the **bpA-pybox** reaction: 16.5 mmol bisoxazoline **pybox** (3.58 g), 15.0 mmol **bpA** (3.42 g), and 21.0 mg (0.3 wt %) sodium methoxide were placed in a 50-mL glass reactor equipped with a nitrogen inlet and outlet and a central mechanical stirrer. The reactor was placed in an oil bath at the desired temperature, and the samples were withdrawn at intervals to monitor the reaction by size exclusion chromatography (SEC) and NMR.

### Analytical methods

#### NMR spectroscopy

<sup>13</sup>C- and <sup>1</sup>H-NMR were recorded on Bruker Avance 200, 250, or 300 MHz spectrometers using CDCl<sub>3</sub> [ $\delta = 7.26$  ppm (<sup>1</sup>H) and  $\delta = 76.9$  (<sup>13</sup>C) ppm] or DMSO-*d*<sub>6</sub> [ $\delta = 2.50$  (<sup>1</sup>H) and  $\delta = 39.6$  (<sup>13</sup>C) ppm] solutions.

#### Size exclusion chromatography

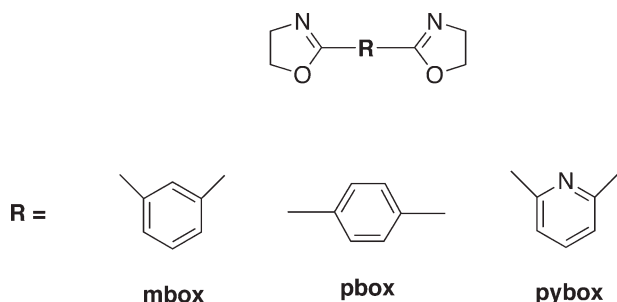
The SEC measurements were performed at room temperature on a Waters equipment consisting of a 410 refractive index detector, a 515 HPLC pump, and a set of Ultrastaygel columns (100 + 500 + 10<sup>3</sup> + 10<sup>4</sup> Å) at a THF flow rate of 1.0 mL/min. Polymers containing oligoamide blocs were trifluoroacetylated in CH<sub>2</sub>Cl<sub>2</sub>-trifluoroacetic anhydride mixture and eluted using CH<sub>2</sub>Cl<sub>2</sub> + 0.05 mol/L Bu<sub>4</sub>NBF<sub>4</sub>, at a flow rate of 1.3 mL/min. Polystyrene standards were used to calibrate all systems. Low-molar-mass oligomer (*n* = 1–6) internal calibration was also used for  $\alpha,\omega$ -diphenol polysulfone.

#### Differential scanning calorimetry

Differential scanning calorimetry (DSC) was performed on a TA Instruments DSC 2010 apparatus following heating/cooling cycle: (1) heating from 20 to 250°C at 20°C/min, (2) isotherm for 2 min, (3) cooling to 0°C at 10°C/min., (4) isotherm for 2 min, and (5) heating from 0 to 250°C at 20°C. Experiments were carried out under nitrogen atmosphere at low temperatures by means of a liquid nitrogen cooling accessory. The melting temperatures ( $T_m$ ) were taken as the minima of the melting endotherm. The glass transition temperatures ( $T_g$ ) were obtained from the second heating run at the inflection point.

#### Thermogravimetric analyses

Thermogravimetric analyses (TGA) were done on a TA Instruments Q50 TGA analyzer at a heating rate of 20°C/min in flowing nitrogen.



Scheme 1 Bisoxazolines used in this work.

### Reduced viscosities

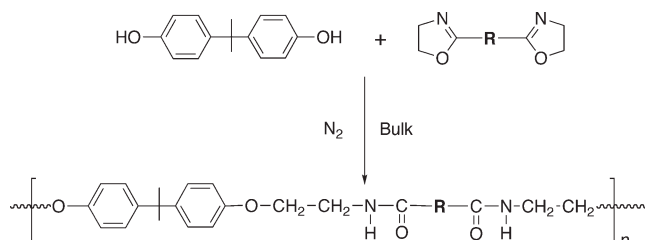
Reduced viscosities were measured from NMP solutions (0.5 g/dL) at 30°C, using a “Schott geräte” viscosimeter with a canon Ubbelohde AVS-400 microviscosimeter.

## RESULTS AND DISCUSSION

### Reaction between bisphenol-A (bpA) and bisoxazolines mbox, pbox and pybox

Culbertson et al.<sup>10,11</sup> studied the synthesis of poly(etheramide)s by reacting bpA with various bisoxazolines. However, to our best knowledge, bisoxazoline **pybox** (Scheme 1) has not yet been used for reactions with phenol and tph compounds, and no data are available on its reactivity with these reagents. All reactions shown in Scheme 2 were carried out using a 10 mol % excess of bisoxazoline to compensate for bisoxazoline loss by sublimation in our reaction conditions.<sup>18</sup>

The SEC curves corresponding to the reaction of bisoxazoline **mbox** with bpA carried out at 200°C with and without catalyst (0.3 wt % MeONa) at various reaction times are given in Figure 1. Without catalyst, the first oligomers, **bpA-mbox** and **bpA-mbox-bpA**, and large amounts of starting **mbox** and **bpA** are observed in the sample withdrawn after 20-min reaction. After 180 min, a low-molar-mass polymer was obtained ( $\bar{M}_n = 640$  g/mol) with traces of starting materials. A similar behavior was observed in the presence of 0.3 wt % of MeONa. However, a



Scheme 2 Reaction between bisphenol-A and bisoxazolines.

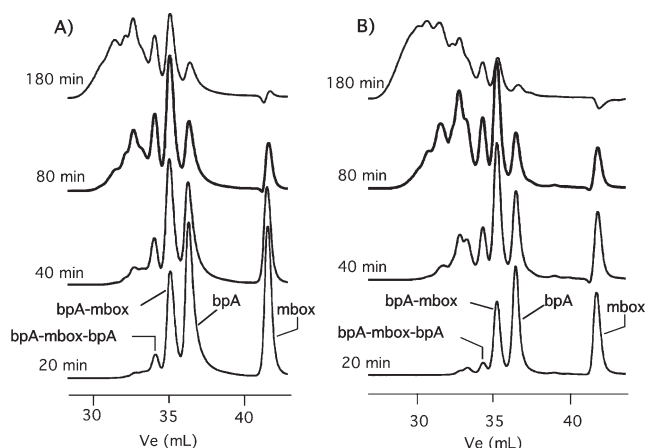


Figure 1 SEC chromatograms (THF, 1.0 mL/min) of the reaction product between bisoxazoline **mbox** and bisphenol-A (**bpA**) at 200°C after 20, 40, 80, and 180 min: (A) without catalyst and (B) with 0.3 wt % MeONa.

higher molar mass poly(etheramide) with lower content in residual starting compounds was obtained ( $\bar{M}_n = 1100$  g/mol).

The same experiment was carried out with bisoxazoline **pybox** at 200°C in the presence of the same catalyst for 180 min. The SEC curve of the resulting polymer is given in Figure 2. As found for bisoxazoline-carboxylic acid reactions,<sup>18,20</sup> **pybox** is more reactive and leads to higher molecular weight compounds in a shorter reaction time (40 min,  $\bar{M}_n = 2500$  g/mol). This was assigned to the higher basicity of the pyridine-containing coupling agent and to

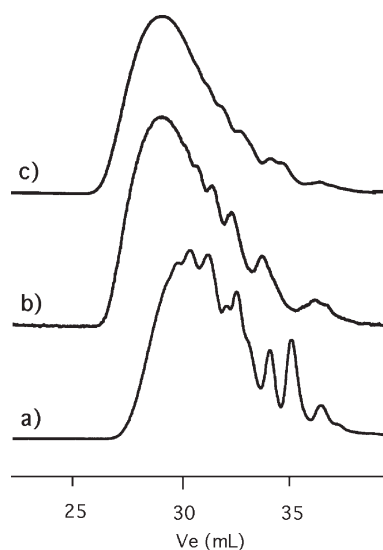
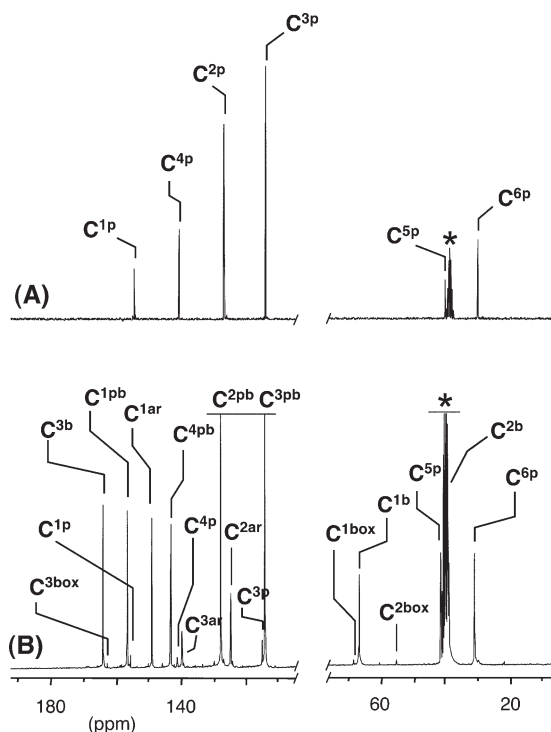
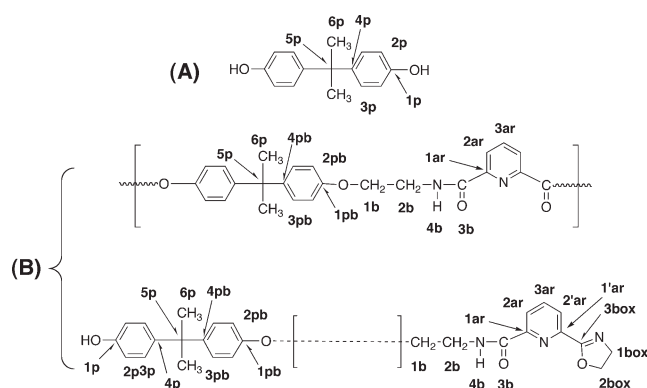


Figure 2 SEC chromatograms (THF, 1.0 mL/min) of the reaction product between bisoxazolines and bisphenol-A (**bpA**) with 0.3 wt % MeONa: (a) **mbox** (200°C, 180 min), (b) **pybox** (200°C, 180 min), and (c) **pybox** (240°C, 40 min).

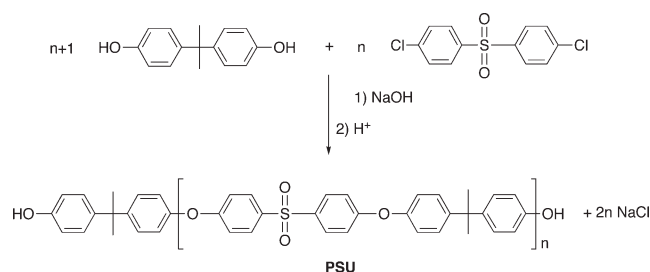


**Figure 3**  $^{13}\text{C}$ -NMR spectra (62.9 MHz,  $\text{DMSO-}d_6$ ) of (A) starting bisphenol-A (**bpA**) and (B) its reaction product with bisoxazoline **pybox** (240°C, 40 min, 0.3 wt % MeONa). See Scheme 3 for atom numbering.

the stabilization of reaction intermediates by intramolecular interaction between amide NH and pyridine nitrogen.<sup>18</sup> No side reactions between oxazoline groups and amide NH resulting in branching or even crosslinking<sup>9,30</sup> were detected even when using a large bisoxazoline excess. The  $^{13}\text{C}$ -NMR spectra of starting **bpA** and final polymer obtained after reaction with **pybox** at 240°C for 40 min with 0.3 wt % of MeONa are given in Figure 3. After reaction, the upperfield part of the spectra presents two new signals  $\text{C}^{1b}$  and  $\text{C}^{2b}$  at 66.13 and 38.81 ppm, respectively, which indicate that the phenol-oxazoline reaction occurred. The lower field part of the spec-



**Scheme 3** Atom numbering in (A) bisphenol-A (**bpA**) and (B) its reaction product with bisoxazoline **pybox**.



**Scheme 4** Synthesis of oligosulfone **PSU**.

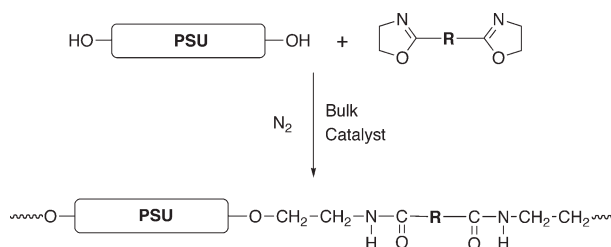
trum shows three new aromatic peaks ( $\text{C}^{1ar}$ ,  $\text{C}^{3ar}$ ,  $\text{C}^{2ar}$ ) at 148.59, 139.44, and 126.51 ppm arising from reacted pyridylene groups and a new carbonyl peak  $\text{C}^{3b}$  at 163.62 ppm assigned to the amide of the linking group. Small peaks assigned to phenol end groups ( $\text{C}^{1p}$ ,  $\text{C}^{4p}$ ,  $\text{C}^{3p}$ ) and new signals ( $\text{C}^{1pb}$ ,  $\text{C}^{4pb}$ ,  $\text{C}^{2pb}$ ,  $\text{C}^{3pb}$  at 156.16, 142.80, 129.55, and 113.95 ppm) assigned to reacted **bpa** units are also observed. The small peaks at 54.64, 67.94, and 162.31 ppm are assigned to oxazoline end group ( $\text{C}^{2box}$ ,  $\text{C}^{1box}$ ,  $\text{C}^{3box}$ ). No peaks coming from any side reaction are observed in the spectrum.

### Chain-coupling reaction of $\alpha,\omega$ -diphenol polysulfone by bisoxazolines

The preliminary results were used for the chain-coupling reaction of  $\alpha,\omega$ -diphenol poly(ethersulfone) (**PSU**). **PSU** was synthesized following a known procedure<sup>31</sup> (Scheme 4), and its number average molar mass was determined by  $^1\text{H}$ -NMR ( $\bar{M}_n = 1950$  g/mol) and by SEC using polystyrene standards ( $\bar{M}_n = 1990$  g/mol). The internal calibration using oligomer peaks ( $n = 1-6$ ) gave  $\bar{M}_n = 2020$  g/mol.

The chain-coupling reaction between bisoxazoline **pybox** and oligosulfone **PSU** were carried out at 240°C for 2 h (Scheme 5). In addition to sodium methoxide, various acids and bases, known to be catalysts for such reactions,<sup>10,11</sup> were tested, but the best results were obtained with sodium methoxide (Polymer 2, Table I). Increasing MeONa concentration did not yield significantly better results.

The influence of the coupling agent was studied by reacting **PSU** with bisoxazolines **mbox**, **pbox**,



**Scheme 5** Chain-coupling reaction between bisoxazoline **pybox** and oligosulfone **PSU**.

**TABLE I**  
Reaction Between  $\alpha,\omega$ -Diphenol polysulfone (PSU) and Bisoxazoline pybox (1/1.1 molar ratio)

Sample	Catalyst <sup>a</sup>	$\bar{M}_n$ <sup>a</sup> (g/mol)	$M_{\text{peak}}$ <sup>a</sup> (g/mol)	PDI <sup>a</sup>
PSU	–	1990 <sup>b</sup>	3400 <sup>b</sup>	2.0 <sup>b</sup>
1	no	5100	10200	1.9
2	MeONa	8500	26900	3.4
3	DMAP	6200	20000	3.3
4	PTSA	7800	18200	2.7
5	TPA	7300	19600	3.1

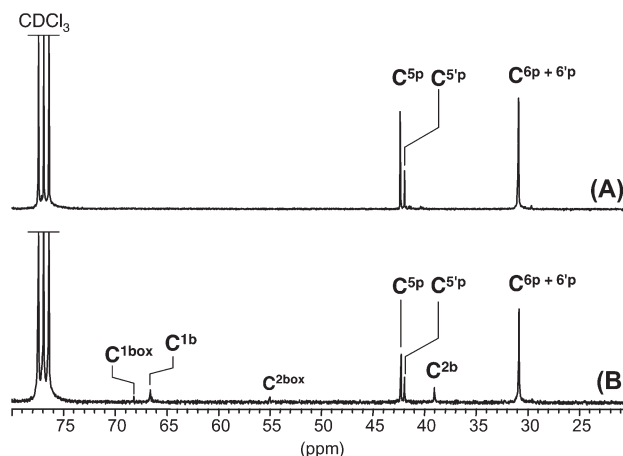
Reaction was carried out at 240°C for 120 min with 0.3 wt % of various catalysts (MeONa, sodium methoxide; DMAP, 4-(dimethylamino)pyridine; PTSA, 4-toluene sulfonic acid; TPA, 12-tungstophosphoric acid). Number-average molar mass ( $\bar{M}_n$ ), molar mass at the maximum of SEC curve ( $M_{\text{peak}}$ ), and polydispersity index (PDI) of starting oligomer and reaction products.

<sup>a</sup> Values from SEC in THF (PS calibration).

<sup>b</sup> Values for starting oligomers.

and pybox in the same experimental conditions. As expected, bisoxazoline pybox gave the polymer of higher molar mass (Table II). The polymers were studied by DSC and TGA analyses. As can be seen in Table II, thermal stability increases after the coupling reaction. This can be explained by the molar mass increase and the parallel decrease of end-group concentration. All polymers are amorphous and display glass transition temperature in the 160–170°C range, higher than that of starting PSU, which can be assigned to the loss of chain mobility due to molar mass increase. On the other hand, this glass transition temperature range is lower than that of commercial bpA polysulfone (186°C<sup>32</sup>). This can be assigned to the introduction of aliphatic moieties into the aromatic backbone of polysulfone.

The <sup>13</sup>C-NMR spectrum of polymer 2 (Fig. 4) displays the expected features and confirms that reaction proceeded smoothly. The comparison of



**Figure 4** <sup>13</sup>C-NMR spectra (62.9 MHz, CDCl<sub>3</sub>) of the aliphatic region of (A) starting  $\alpha,\omega$ -diphenol polysulfone (PSU) and (B) its reaction product with bisoxazoline pybox at 240°C after 120 min (0.3 wt % MeONa). See Scheme 6 for atom numbering.

the upperfield parts of the spectrum with that of starting oligomer reveals the presence of two new peaks at 66.58 and 38.99 ppm, which correspond to the methylenes of coupling agent moieties after reaction with the phenol end groups of PSU ( $C^{1b}$  and  $C^{2b}$ ). Two small peaks at 68.16 and 54.99 ppm are assigned to  $C^{1\text{box}}$  and  $C^{2\text{box}}$  of oxazoline end groups. The other end-group signals  $C^{2'\text{ar}}$ ,  $C^{2''\text{ar}}$ ,  $C^{3'\text{ar}}$  (pyridine moieties) are detectable in the downfield part of the spectra (Fig. 5).  $C^{1'\text{ar}}$  cannot be observed because of overlapping with other signals. The signals of the phenol end groups of starting PSU at 153.73, 114.75, 127.66, and 141.99 ppm ( $C^{1\text{p}}\text{--}C^{4\text{p}}$ ) are shifted to 156.37, 113.92, 127.71, and 142.97 ppm ( $C^{1\text{pb}}\text{--}C^{4\text{pb}}$ ). The peaks corresponding to the opened oxazoline moieties  $C^{1\text{ar}}$ ,  $C^{3\text{ar}}$ , and  $C^{2\text{ar}}$  can easily be assigned at 148.53, 138.87, and

**TABLE II**  
Reaction Between  $\alpha,\omega$ -Diphenol polysulfone (PSU) and Various Bisoxazoline (1/1.1 molar ratio)

Sample	Box <sup>a</sup>	$\bar{M}_n$ <sup>b</sup> (g/mol)	$M_{\text{peak}}$ <sup>b</sup> (g/mol)	PDI <sup>b</sup>	$T_g$ <sup>d</sup> (°C)	$T_{10\%}$ <sup>e</sup> (°C)
PSU	–	1990 <sup>c</sup>	3400 <sup>c</sup>	2.0 <sup>c</sup>	157 <sup>c</sup>	424 <sup>c</sup>
2	pybox	8500	26900	3.4	171	433
9	pbox	3800	7300	2.1	160	433
10	mbox	3700	7900	2.1	163	451

Reaction was carried out at 240°C for 120 min with 0.3 wt % MeONa. Characterization of starting oligomer and reaction products: number-average molar mass ( $\bar{M}_n$ ), molar mass at the maximum of SEC curve ( $M_{\text{peak}}$ ), polydispersity index (PDI), glass temperature ( $T_g$ ), and 10% mass loss temperature ( $T_{10\%}$ ).

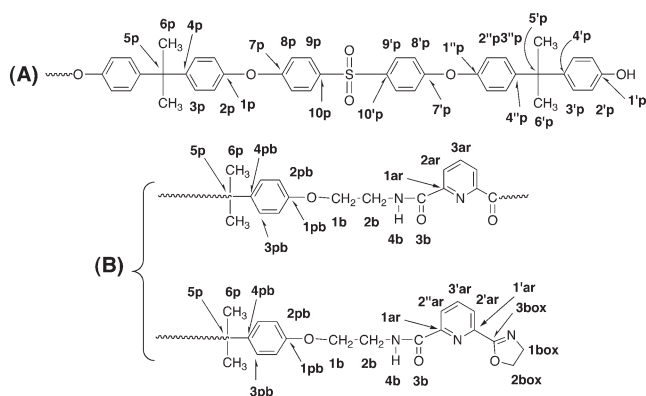
<sup>a</sup> Bisoxazoline used.

<sup>b</sup> Values from SEC in THF.

<sup>c</sup> Values for starting oligomer.

<sup>d</sup> Determined by DSC at 20°C/min (second heating curve).

<sup>e</sup> Determined by TGA at 20°C/min.

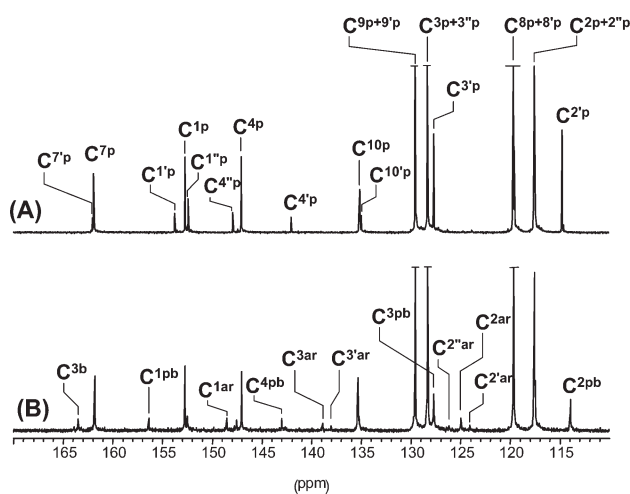


**Scheme 6** Atom numbering in (A) polysulfone PSU and (B) its reaction product with bisoxazoline **pybox**.

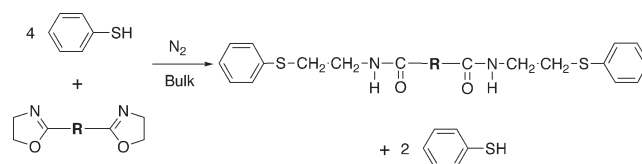
124.93 ppm. Again, no peaks coming from any side reaction can be observed.

### Reaction between thiophenol and bisoxazolines

Although thiol reactions with several bisoxazolines have already been described in solution,<sup>12–14</sup> we did not find any data on reactions in the bulk at high temperature. Model bulk reactions between **tph** and bisoxazolines **mbox**, **pbox**, and **pybox** were first studied (Scheme 7). To compensate **tph** ( $T_{\text{eb}} = 169^\circ\text{C}$ ) loss by evaporation during the reactions, they were carried out using a fourfold excess of this reagent. Figure 6 presents the SEC chromatograms of the reaction mixture after heating for 1, 2, 5, and 10 min at  $140^\circ\text{C}$ . The reaction is much faster than with phenolic compounds. After 1-min reaction, two new peaks appear, which were identified as monothioe-



**Figure 5**  $^{13}\text{C}$ -NMR spectra (62.9 MHz,  $\text{CDCl}_3$ ) of the aromatic region of (A) starting  $\alpha,\omega$ -diphenol polysulfone (PSU) and (B) its reaction product with bisoxazoline **pybox** at  $240^\circ\text{C}$  after 120 min (0.3 wt % MeONa). See Scheme 6 for atom numbering.



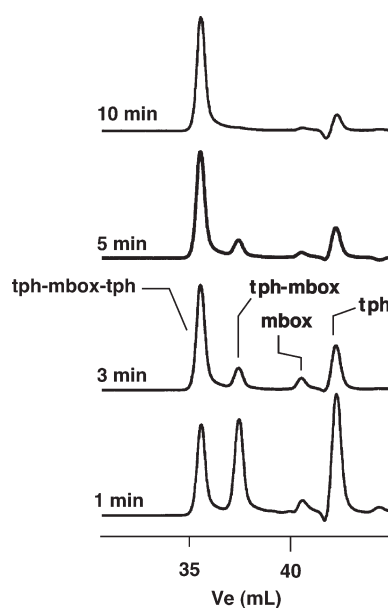
**Scheme 7** Reaction between thiophenol and bisoxazolines.

theramide **tph-mbox** and dithioetheramide **tph-mbox-tph**. After only 10 min, the reaction is complete, and the SEC curve shows only the peaks of bisadduct **tph-mbox-tph** and residual **tph**. No catalysis is, therefore, required for **tph**-oxazoline reaction.

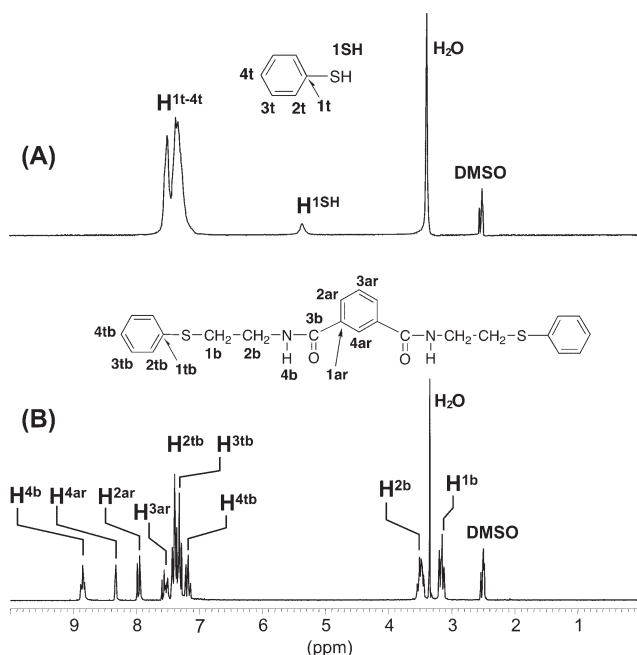
The  $^1\text{H}$ -NMR spectra of **tph** and its reaction product with **mbox** are given as an example in Figure 7. The following features evidence the oxazoline-SH reaction: (i) disappearance of the SH proton at 5.36 ppm, (ii) appearance of new signals assigned to the opened oxazoline ring: CONH resonances at 8.87 ppm ( $\text{H}^{4b}$ ), aromatic signals at 8.34, 7.95, and 7.56 ppm, and  $-\text{S}-\text{CH}_2-\text{CH}_2-\text{NH}$ , and  $-\text{S}-\text{CH}_2-\text{CH}_2-\text{NH}$  signals at 3.16 and 3.48 ppm, respectively ( $\text{H}^{1b}$  and  $\text{H}^{2b}$ ), and (iii) absence of signals arising from starting bisoxazolines or from side reaction. Similar results were obtained with all bisoxazolines.

### Reaction between bis(4-mercaptophenyl)sulfide and bisoxazolines

Based on the model reaction, bulk reactions were carried out between bisoxazolines **mbox** and **pybox**



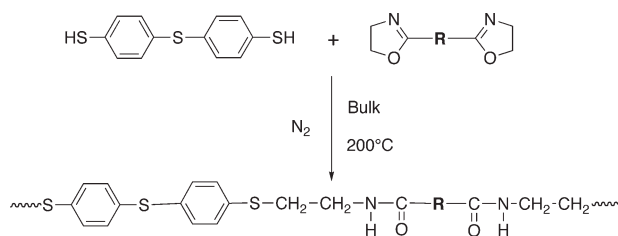
**Figure 6** SEC chromatograms (THF, 1.0 mL/min) of the reaction product between bisoxazoline **mbox** and thiophenol (**tph**) at  $140^\circ\text{C}$  after 1, 2, 5, and 10 min. Mole ratio of **tph/mbox** = 4/1.



**Figure 7**  $^1\text{H-NMR}$  spectra (300 MHz,  $\text{DMSO-}d_6$ , ref. TMS) of (A) thiophenol (**tph**) and (B) its reaction product with bisoxazoline **mbox** ( $140^\circ\text{C}$ , 10 min).

with **BMPS** at  $200^\circ\text{C}$  for 5 min (Scheme 8). The results of viscosity measurements of resulting polymers indicate that polymers were obtained (Table III). Viscosities are higher than those obtained by Nishikubo et al.<sup>14</sup> in NMP at  $90^\circ\text{C}$  and shorter times are required, 5 min instead of 48 h. The final polymers are amorphous with  $T_g = 114\text{--}117^\circ\text{C}$ , close to those of Nishikubo et al.,<sup>14</sup> and present good thermal stability ( $T_{10\%} = 360$  and  $367^\circ\text{C}$ ).

The  $^1\text{H-NMR}$  spectra of starting **BMPS** and its reaction product with bisoxazoline **mbox** after 5-min reaction at  $200^\circ\text{C}$  are given in Figure 8. The methylenes of reacted oxazoline moieties are detected at 3.15 and 3.47 ppm ( $\text{H}^{1b}$  and  $\text{H}^{2b}$ ,



**Scheme 8** Reaction of bis(4-mercaptophenyl)sulfide with bisoxazolines.

respectively), and no resonances of nonreacted oxazoline can be found. The reaction is also evidenced by the disappearance of the [sbondSH peak ( $\text{H}^{1\text{SH}}$  at 5.63 ppm) and the presence of new aromatic signals at 8.31, 7.97, and 7.53 ppm ( $\text{H}^{4\text{ar}}$ ,  $\text{H}^{2\text{ar}}$ , and  $\text{H}^{3\text{ar}}$ , respectively) and of the amide signal at 8.84 ppm ( $\text{H}^{4b}$ ). The modification of the two new doublets at 7.25 and 7.37 ppm of **BMPS** ( $\text{H}^{2\text{tb-}3\text{tb}}$ ) also reflects the coupling reaction. Again, no side reaction is detected in the spectrum.

#### Coupling reactions of $\alpha,\omega$ -dicarboxy-polyamide-12 (PA12) and PSU or BMPS by bisoxazolines

The chain-coupling reaction of a mixture of PSU or **BMPS** and polyamide-12 (**PA12-1** or **PA12-2**,  $\bar{M}_n = 1040$  and  $1940$ , respectively) were carried out with a 10 mol % excess of bisoxazoline and 0.3 wt % MeONa for the reaction with PSU (Scheme 9).

The reactions were studied by SEC to follow the progress of the reaction and to determine the average molar masses. Figure 9 shows that the coupling reaction of dicarboxy-terminated **PA12-2** and diphenol-terminated PSU by bisoxazoline **pybox** yielded copolymers of higher molar mass. The values of  $\bar{M}_n$  (10,000–11,000) reported in Table IV are comparable with that of obtained for the chain-coupling

**TABLE III**  
Reaction Between Bis(2-mercaptophenyl) Sulfide (**BMPS**) and Bisoxazolines **mbox** and **pybox** (1/1.1 molar ratio)

Sample	box <sup>a</sup>	$\eta^b$ (dL.g <sup>-1</sup> )	$\eta^b$ (dL.g <sup>-1</sup> )	$T_g^d$ ( $^\circ\text{C}$ )	$T_m^d$ ( $^\circ\text{C}$ )	$\Delta H_m^d$ (J/g)	$T_{10\%}^e$ ( $^\circ\text{C}$ )
<b>BMPS</b>	–	–	–	–	119	105	245
<b>11</b>	<b>pybox</b>	0.35	–	117	–	–	360
<b>12</b>	<b>mbox</b>	0.49	0.34 <sup>c</sup>	114	–	–	367

Reaction was carried out at  $200^\circ\text{C}$  for 5 min; reduced viscosity ( $\eta$ ), melting temperature, melting enthalpy, and glass temperature ( $T_m$ ,  $\Delta H_m$ , and  $T_g$ ), 10% mass loss temperature ( $T_{10\%}$ ).

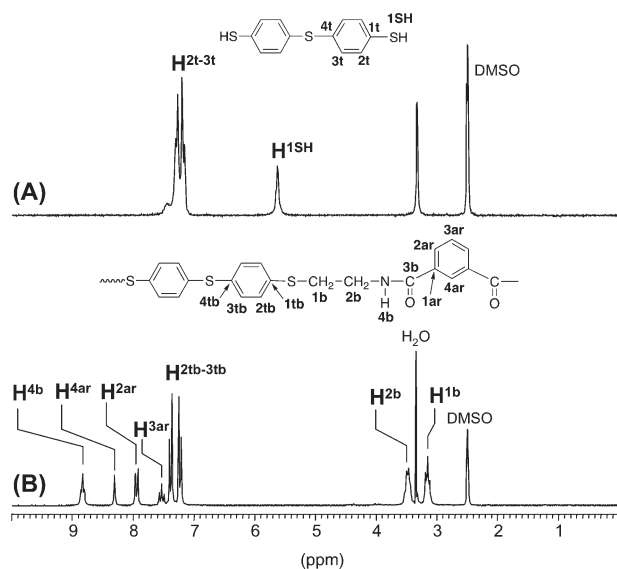
<sup>a</sup> Bisoxazoline.

<sup>b</sup> Reduced viscosity measured at 0.5 g/dL in NMP at  $30^\circ\text{C}$ .

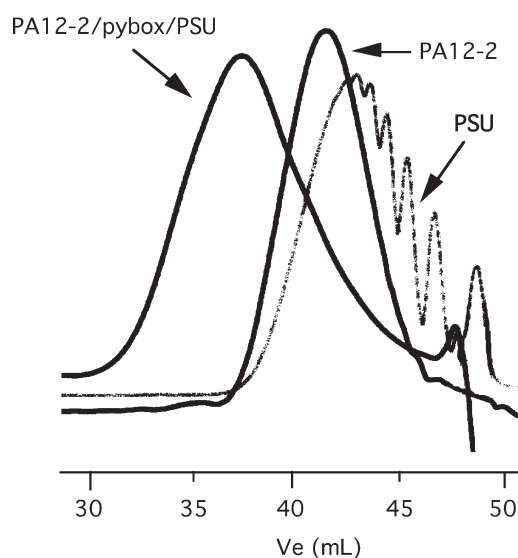
<sup>c</sup> Synthesis carried out in NMP at  $90^\circ\text{C}$  for 48 h.<sup>13</sup>

<sup>d</sup> Determined by DSC at  $20^\circ\text{C}/\text{min}$  (second heating curve).

<sup>e</sup> Determined by TGA at  $20^\circ\text{C}/\text{min}$ .



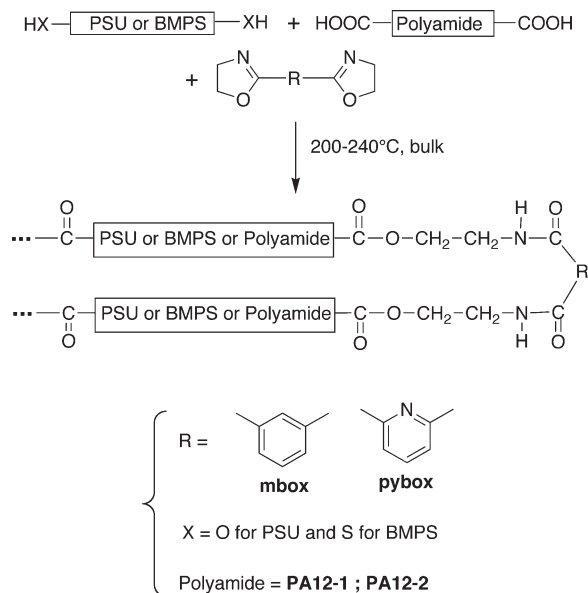
**Figure 8**  $^1\text{H-NMR}$  spectra (300 MHz,  $\text{DMSO-}d_6$ , ref. TMS) of (A) starting bis(4-mercaptophenyl)sulfide (**BMPS**) and (B) its reaction product with bisoxazoline **mbox** ( $200^\circ\text{C}$ , 5 min).



**Figure 9** SEC chromatograms ( $\text{CH}_2\text{Cl}_2$ , 1.3 mL/min) of starting  $\alpha,\omega$ -diphenol polysulfone (**PSU**),  $\alpha,\omega$ -dicarboxy polyamide-12 (**PA12-2**), and their reaction product with bisoxazoline **pybox** at  $240^\circ\text{C}$  after 120 min (0.3 wt % MeONa).

reaction of **PSU** alone but are lower than those of obtained for  $\alpha,\omega$ -dicarboxy oligoamide (**PA12-1** or **PA12-2**).<sup>20</sup>

The results of the thermal characterizations are summarized in Table IV. The DSC curves of **PSU/PA12-2** copolymer exhibit a high-temperature melting point ( $166^\circ\text{C}$ ) assigned to the polyamide phase. Such multiblock copolymers have not yet been



**Scheme 9** Chain-coupling reaction between bisoxazolines, carboxy-terminated oligoamide, and phenol- or thio-phenol-terminated compounds.

described. Some polysulfone–polyamide blends were obtained by the reactive blending of polysulfone and PA6 in the presence of polysulfone oligomers bearing anhydride end groups or side groups,<sup>33–35</sup> but these compounds are difficult to compare with the present copolymers. It should be underlined, however, that PA6-polysulfone-PA6 triblock copolymers were prepared by initiating lactam-6 polymerization on amine-terminated polysulfones.<sup>36</sup> The resulting copolymers exhibited the thermal transitions of PA6 ( $T_m = 194\text{--}210^\circ\text{C}$ ) and polysulfone ( $T_g = 144\text{--}157^\circ\text{C}$ ). In this case, the  $T_g$  of **PSU/PA12-2** polysulfone phase cannot be observed, because it appears in the same temperature range as the melting point of the PA phase.

The **BMPS/PA12-1** copolymer is amorphous and exhibits only one glass transition temperature at  $72^\circ\text{C}$ , intermediate between those of **BMPS-pybox** copolymer ( $117^\circ\text{C}$ ) and starting polyamide ( $57^\circ\text{C}$ ), indicating the presence of only one polymer phase. Table IV also illustrates the higher thermal stability of final copolymer with respect to starting polyamide.

## CONCLUSION

Phenol- and tph-terminated compounds or oligomers and bisoxazolines **mbox**, **pbox**, and **pybox** react efficiently in the bulk at  $140\text{--}240^\circ\text{C}$ . tph groups react very rapidly (5 min at  $200^\circ\text{C}$ ) and give high-molar-mass polymers, whereas phenol groups react more



TABLE IV  
Coupling Reaction of Dicarboxy polyamide PA12-1 and  $\alpha,\omega$ -Diphenol polysulfone (PSU) by Bisoxazoline pybox(10% mol excess of bisoxazoline, 240°C, 120 min)

Sample	Box <sup>b</sup>	$\bar{M}_n^c$ (g/mol)	$M_{peak}^c$ (g/mol)	PDI <sup>c</sup>	$T_g^e$ (°C)	$T_m^e$ (°C)	$\Delta H_m^e$ (J/g)	$T_{10\%}^f$ (°C)
PA12-1	–	2300 <sup>d</sup>	3000 <sup>d</sup>	1.5 <sup>d</sup>	–	150 <sup>d</sup>	59 <sup>d</sup>	362 <sup>d</sup>
PA12-2	–	5000 <sup>d</sup>	6700 <sup>d</sup>	1.4 <sup>d</sup>	–	173 <sup>d</sup>	57 <sup>d</sup>	394 <sup>d</sup>
PA12-2/PSU <sup>a</sup>	pybox	11000	19400	2.6	–	166	19	414
PA12-1/BMPS <sup>a</sup>	mbox	10600	18600	1.8	72	–	–	393

Reaction was carried out with 0.3 wt % of MeONa and coupling reaction of dicarboxy polyamide PA12-1 and BMPS by bisoxazoline mbox (10 mol % excess of bisoxazoline, 200°C, 180 min); characterization of starting oligoamides and reaction products: number-average molar mass ( $\bar{M}_n$ ), molar mass at the maximum of SEC curve ( $M_{peak}$ ), polydispersity index (PDI), glass transition temperature ( $T_g$ ), melting temperature, and melting enthalpy ( $T_m$  and  $\Delta H_m$ ), and 10% mass loss temperature ( $T_{10\%}$ ).

<sup>a</sup> Starting oligomer mass ratio 1/1.

<sup>b</sup> Bisoxazoline.

<sup>c</sup> Values from SEC in CH<sub>2</sub>Cl<sub>2</sub> after sample trifluoroacetylation.

<sup>d</sup> Values for starting oligomer.

<sup>e</sup> Determined by DSC at 20°C/min (second heating curve).

<sup>f</sup> Determined by TGA at 20°C/min.

slowly in the same temperature range and require the addition of a catalyst. The NMR analyses indicate that the reactions take place without detectable side reactions. These reactions were easily applied to the preparation of block copolymers from phenol- and tph-terminated compounds with  $\alpha,\omega$ -dicarboxy oligoamides.

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