

# Synthesis of Novel, Well-Defined, Soluble Polymers Containing Chiral Salen

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A new type of polyether containing chiral salens was synthesized through polycondensation of dialdehydes and *trans*-diaminocyclohexane and characterized by IR, NMR and GPC. The synthesized polymers were soluble in CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, and THF. The polymerization of propylene glycol-bis(4-salicylyl) ether yielded mainly cyclic oligomers while polymerization of diethylene glycol-bis(4-salicylyl) ether yielded a mixture of linear polymers and cyclic oligomers. However, the polymerization of the diketone, 1,6-bis(4-acetyl-3-hydroxyphenoxy)hexane, with diaminocyclohexane gave a more complicated mixture. The polycondensation of dialdehyde compounds with diamines thus has potential applications in the synthesis of linear polymers and macrocyclic compounds containing chiral salens.

**Key words:** salen, chiral, polymers.

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## การสังเคราะห์พอลิเมอร์ละลายได้ชนิดใหม่ที่มีไครัลซาเลนเป็นส่วนประกอบ

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พอลิเอเธอร์ชนิดใหม่ที่มีไครัลซาเลนเป็นส่วนประกอบสังเคราะห์ได้จากปฏิกิริยาพอลิคอนเดนเซชันของไดอัลคิลไฮด์และทรานส์ไดอะมิโนไซโคลเฮกเซน และพิสตุน์ทรานโครงสร้างโดย IR, NMR และ GPC พอลิเมอร์ที่สังเคราะห์ได้นี้ละลายได้ในตัวทำละลายเช่น  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$  และ THF ปฏิกิริยาพอลิเมอไรเซชันของ propylene glycol-bis(4-salicylyl) ether ให้ผลิตภัณฑ์เป็นวงแหวนออลิโกเมอร์ ส่วนปฏิกิริยาพอลิเมอไรเซชันของ diethylene glycol-bis(4-salicylyl) ether ให้ผลิตภัณฑ์เป็นของผสมของพอลิเมอร์เส้นตรงและวงแหวนออลิโกเมอร์ แต่พบว่าปฏิกิริยาพอลิเมอไรเซชันของไดคิโตนคือ 1,6-bis(4-acetyl-3-hydroxyphenoxy)hexane นั้นให้ผลิตภัณฑ์เป็นของผสมที่ซับซ้อนกว่า ดังนั้นปฏิกิริยาพอลิคอนเดนเซชันของไดอัลคิลไฮด์กับไดเอมีนจึงน่าจะสามารถนำมาประยุกต์ใช้ในการสังเคราะห์พอลิเมอร์และสารประกอบแมโครไซคลิกที่มีไครัลซาเลนเป็นส่วนประกอบ

คำสำคัญ ซาเลน, ไครัล, พอลิเมอร์

## INTRODUCTION

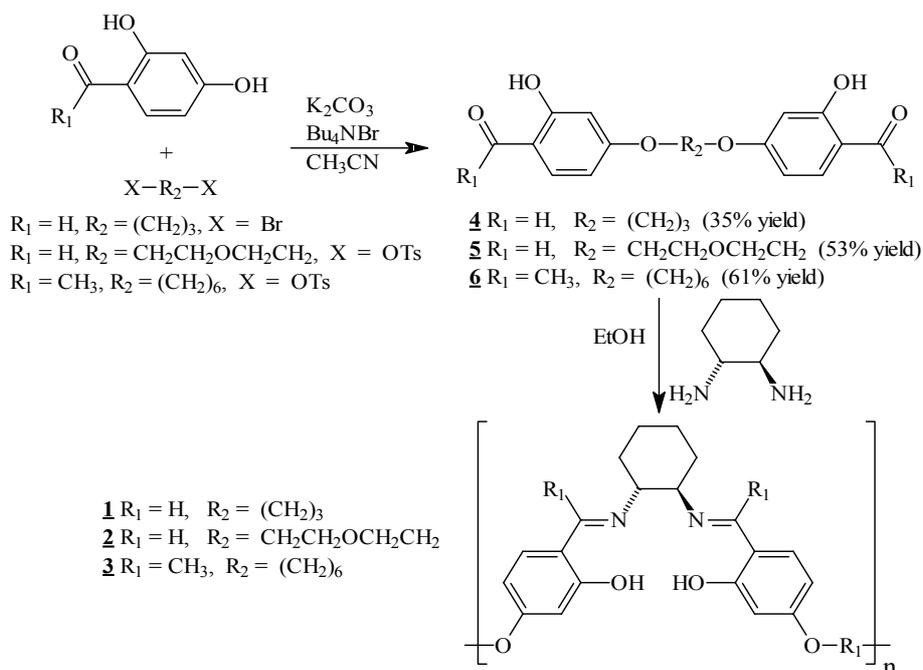
Salens have recently been demonstrated to be versatile functional building blocks in organic chemistry and related fields. Catalysts from metal-salen complexes have rapidly grasped attention in the area of asymmetric catalysis owing to their excellent enantioselectivity and applicability to a wide range of reaction types.<sup>(1)</sup> Polymer-supported catalysts containing chiral metal-salen complexes, have also been developed; however optimization for higher enantioselectivity remains necessary.<sup>(2)</sup> Polyesters incorporated with metal-salen complexes have been studied for their thermotropic and lyotropic liquid crystal properties.<sup>(3)</sup> Metal-salen complexes have also been known as good nonlinear optical chromophores.<sup>(4)</sup>

Characterization of polymers containing metal-salen complexes is often impossible by usual means because of their insolubility in common organic solvents and their paramagnetism. We have recently been particularly interested in the preparation of well-defined polymer precursors due to their ease of characterization and high feasibility of structural modification.<sup>(5)</sup> Soluble polymers containing chiral salen are potential

precursors for asymmetric polymeric catalysts, enantiotropic liquid crystals and second-order nonlinear optical materials. Despite their great potential for applications in catalysis and materials, only few soluble polymers containing salen have been synthesized to date<sup>(3b)</sup> and none of them are chiral. We report here the first synthesis of well-defined, soluble polymers containing chiral salens.

## RESULTS AND DISCUSSION

Our targeted polymers (**1**, **2** and **3**) were designed to have good solubilities in common organic solvents by incorporating flexible alkyl chains, through ether linkages, between rigid chiral salen units. The ether linkages were chosen due to their favorable chemical stability and convenient synthesis. The polymers **1**, **2** and **3** were synthesized in two steps from 2,4-dihydroxybenzaldehyde and 2,4-dihydroxyacetophenone (Scheme 1). In the first step, the preparations of monomers **4**, **5** and **6** were achieved in moderate yields by alkylation of 2,4-dihydroxybenzaldehyde or 2,4-dihydroxyacetophenone with appropriate alkylating agents, either dibromo or ditosylate



Scheme 1

compounds, using tetrabutylammonium bromide as a phase transfer catalyst. The second step is a condensation polymerization of the monomers with either racemic or (*R,R*)-*trans*-diaminocyclohexane, yielding the

polymers with satisfactory yields (Table 1). Each polymer was obtained as a yellow solid by a single precipitation in methanol from a methylene chloride solution.

**Table 1. Polymerization yields**

Monomer	Diamino cyclohexane	Polymer	% Yield
<b><u>4</u></b>	racemic	(±)- <b><u>1</u></b>	74
	( <i>R,R</i> )	( <i>R,R</i> )- <b><u>1</u></b>	56
<b><u>5</u></b>	racemic	(±)- <b><u>2</u></b>	52
	( <i>R,R</i> )	( <i>R,R</i> )- <b><u>2</u></b>	48
<b><u>6</u></b>	racemic	(±)- <b><u>3</u></b>	41

As expected, all of the synthesized polymers were soluble in common organic solvents such as THF, methylene chloride and chloroform. The solubility of these polymers in common organic solvents allowed the characterization by <sup>1</sup>H-NMR and gel permeation chromatography (GPC). Structural elucidation of the polymers was thus accomplished by IR, <sup>1</sup>H-NMR and GPC. IR spectra of monomers **4** and **5** had a strong absorption peak inside the range of 1630-1642 cm<sup>-1</sup> corresponding to an aldehydic C=O stretching. Upon polymerization this peak totally disappeared and there was a new iminic C=N stretching peak at a lower energy (below 1630 cm<sup>-1</sup>), indicating a total conversion of the aldehyde to imine groups. This was also confirmed by <sup>1</sup>H-NMR. The <sup>1</sup>H-NMR spectra of polymers (±)-**1** and (±)-**2** (Figure 1) show a signal of an iminic proton (CH=N) at around 8.0 ppm in the absence of

the signal of the aldehydic proton (CH=O) at δ 9.7 ppm observed in the corresponding monomers (**4** and **5**).

Besides the strong signal of iminic protons at 8.04 ppm, the spectrum of (±)-**2** also has a very weak signal appearing at 8.23 ppm. This signal was assigned to the iminic protons at the termini of the polymer chain (**2L** in **Scheme 2**). To confirm this assignment, model compounds, salicylidene **7**<sup>(6)</sup> and bissalicylidene **8**, were prepared for spectral comparison. The <sup>1</sup>H-NMR spectra of **7** and **8** showed signals of the iminic protons at 8.22 and 8.05 ppm, respectively, in agreement with the previous assignment. The integration ratio of the signals at δ 8.04 to 8.23 ppm gave the average number of the repeating units of ~40 for polymer **2**. Polymers (*R,R*)-**1** and (*R,R*)-**2** gave virtually identical <sup>1</sup>H-NMR spectra to those of their racemic analogues.

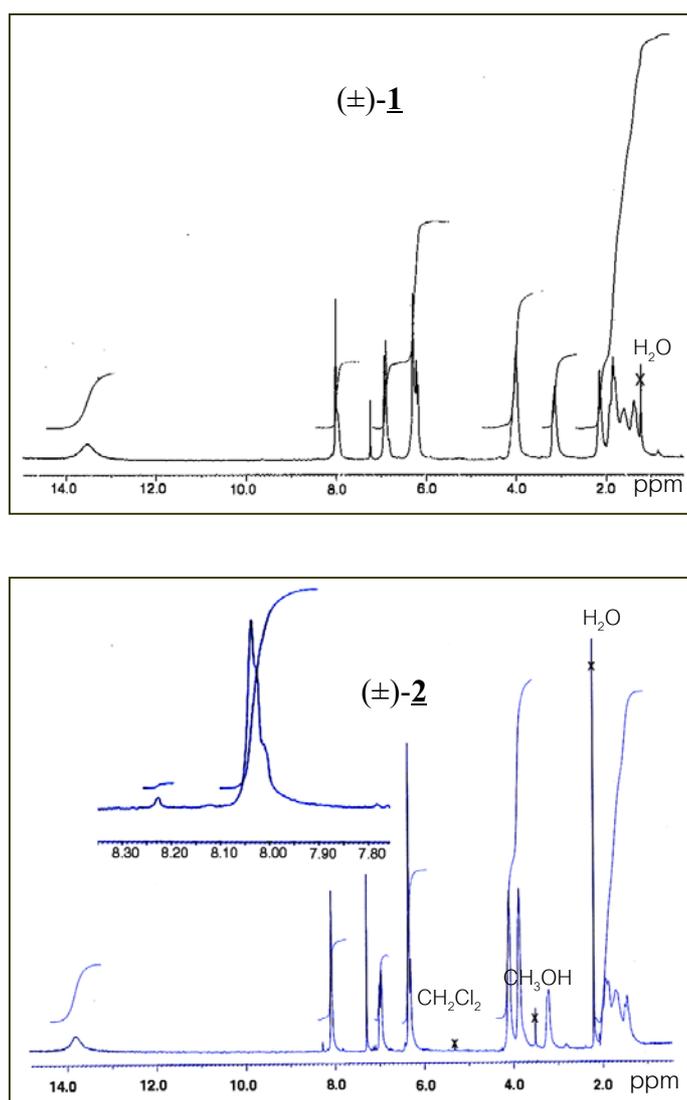


Figure 1.  $^1\text{H-NMR}$  spectra of polymers  $(\pm)\text{-1}$  and  $(\pm)\text{-2}$ .

Table 2.  $M_n$  and  $M_w$  obtained from GPC and the inferred numbers of repeating units of polymers  $\underline{1}$  and  $\underline{2}$ .

Polymer	Formula Weight of Repeating Unit	Molecular Weight from GPC		Inferred Number of Repeating Units Obtained from		
		$M_n$	$M_w$	$M_n$	$M_w$	$^1\text{H-NMR}$
<u>1</u>	394.46	1440	2730	4	7	$\infty$
<u>2</u>	424.48	2640	10340	6	24	40

To confirm the degree of polymerization, the molecular weight of polymer ( $\pm$ )-2 was determined by GPC using THF as a solvent. The number-averaged and weight-averaged molecular weights ( $M_n$  and  $M_w$ ) of polymer ( $\pm$ )-2 obtained from GPC gave a much lower average number of repeating units than that obtained from the  $^1\text{H-NMR}$

spectrum (Table 2). This difference was even greater for polymer ( $\pm$ )-1 for which the  $^1\text{H-NMR}$  spectrum showed no signal of the iminic protons at the chain termini which should imply a very high molecular weight, but the  $M_n$  and  $M_w$  obtained from GPC were very low.

## Scheme 2

Cyclic structures can be a possible explanation for the difference in the numbers of repeating units obtained from NMR and GPC. Polymer ( $\pm$ )-**2** should contain both the linear structure **2L** and cyclic oligomer **2C**, while polymer **1** should contain only the cyclic oligomer, **1C**, which possesses a low molecular weight but has no chain terminus.

The  $^1\text{H-NMR}$  spectrum of ( $\pm$ )-**3** consisted of all signals from both the diketone and diamino monomers with some shifts in their signals indicating the polymerization between these two monomers. However, the spectrum was a little more complex than those of polymers ( $\pm$ )-**1** and ( $\pm$ )-**2**. The observed signals appeared to indicate that polymer ( $\pm$ )-**3** contained both ketone and amino termini. This is reasonable as the methyl ketone is much less reactive than the aldehyde. The low reactivity of the diketone monomer was also observed experimentally during the polymerization. Polymerization of diketone **6** with *trans*-diaminocyclohexane for two days at  $75^\circ\text{C}$  only showed nearly complete consumption of **6** on TLC while the complete consumption of dialdehydes **3** and **4** was observed within five hours under similar conditions of polymerization.

## CONCLUSIONS

Synthesis of a new class of soluble polymers containing salen derivatives was accomplished by polycondensation of *trans*-diaminocyclohexane with dicarbonyl compounds. The polymers had good solubility in common organic solvents, which allowed structural elucidation by  $^1\text{H-NMR}$  and GPC. The polymers obtained from the condensation of *trans*-diaminocyclohexane with bisalicylaldehyde derivatives can be either linear chains or cyclic oligomers, depending strongly on the structures of the bisalicylaldehyde monomers. Further studies of the polycondensation to selectively obtain the linear or cyclic polymers are now in progress.

## EXPERIMENTAL

The  $^1\text{H-NMR}$  spectra were collected on a Bruker ACF 200 MHz FT-NMR spectrometer in deuterated chloroform solution. The IR spectra were acquired on a Nicolet Impact 410 FT-IR spectrometer from neat samples prepared on a NaCl window. The average molecular weights of the polymers were determined in THF by Waters GPC-150 CB, with a RI detector calibrated with polystyrene standards. The elemental analyses were performed on a Perkin 2400 CHN elemental analyzer. All chemicals were purchased from Fluka and used as received.

### *propyleneglycol bis(4-salicylyl)ether, 4*

A mixture of 2,4-dihydroxybenzaldehyde (4.61 g, 33 mmol), 1,3-dibromopropane (3.38 g, 17 mmol), tetrabutylammonium bromide (1.06 g, 3 mmol), and  $\text{K}_2\text{CO}_3$  (4.56 g, 33 mmol) in acetonitrile (40 mL) was stirred at  $75^\circ\text{C}$  for 48 h. The mixture was allowed to cool to room temperature and 2M HCl solution (30 mL) was then added. The resulting brownish slurry was extracted with methylene chloride (3 x 30 mL). The combined organic layer was dried over  $\text{NaSO}_4$  and the solvent was removed by a rotary evaporator. The residue was eluted through a silica gel column by hexane/ethyl acetate (85/15). The product was collected and the solvent was removed to give propyleneglycol bis(4-salicylyl)ether, **4**, as a white solid (1.82 g, 35%).  $^1\text{H-NMR}$ :  $\delta$  2.29 (2H, m), 4.19 (4H, t,  $J$  6.0), 6.42 (2H, d,  $J$  2.5), 6.52 (2H, dd,  $J$  8.5, 2.5), 7.41 (2H, d,  $J$  8.5), 9.70 (2H, s), 11.45 (2H, s). IR ( $\text{cm}^{-1}$ ): 1568, 1634, 2843, 2945.

### *diethyleneglycol bis(4-salicylyl) ether, 5*

The monomer **5** was synthesized in the same manner as **4** by using diethylene glycol ditosylate instead of 1,3-dibromopropane. Compound **5** was obtained as a white solid in 53% yield after purification by silica gel column chromatography using hexane/ethylacetate (70:30) as an eluent.  $^1\text{H-NMR}$ :  $\delta$  3.92 (4H, t,  $J$  4.5), 4.17 (4H, t,  $J$  4.5), 6.40

(2H, d,  $J$  2.5), 6.55 (2H, dd,  $J$  8.5, 2.5), 7.40 (2H, d,  $J$  8.5), 9.69 (2H, s), 11.44 (2H, s). **IR** ( $\text{cm}^{-1}$ ): 1506, 1633, 2865, 2934.

**bis-1,6-(3-hydroxy-4-acetylphenoxy) hexane, 6**

The monomer 6 was synthesized in the same manner as 4 by using 1,6-dibromohexane and 2, 4-dihydroxyacetophenone instead of 1, 3-dibromopropane and 2, 4-dihydroxybenzaldehyde, respectively. Compound 6 was obtained as a white solid in 61% yield after recrystallization in hexane.  **$^1\text{H-NMR}$** :  $\delta$  1.50 (8H, m), 2.53 (6H, s), 3.97 (4H, t,  $J$  6.5), 6.37 (2H, s), 6.41 (2H, d,  $J$  8.5), 7.59 (2H, d,  $J$  8.5), 12.73 (2H, s), **IR** ( $\text{cm}^{-1}$ ): 1567, 1607, 2897, 2933, 3400 (broad).

**polymers ( $\pm$ )-1, ( $\pm$ )-2 and ( $\pm$ )-3**

A typical procedure for the polymerization: A mixture of 4 (1.22 g, 3.86 mmol) and ( $\pm$ )-*trans*-1,2-diaminocyclohexane (0.44 g, 3.85 mmol) in THF (15 mL) was stirred at 75 °C for 24 h. The mixture was allowed to cool to room temperature and the solvent was removed by a rotary evaporator. The residue was redissolved in methylene chloride (10 mL). The resulting solution was added dropwise into methanol (100 mL) and stirred vigorously to precipitate the polymer product. The precipitate was collected by suction filtration and dried under vacuum to give polymer 1 as a yellow solid (1.12 g, 74%).

**polymer ( $\pm$ )-1**:  **$^1\text{H-NMR}$** :  $\delta$  1.2-2.3 (10H, m), 3.1-3.2 (2H, broad), 3.9-4.1 (4H, broad), 6.20 (2H, d,  $J$  8.5), 6.26 (2H, broad), 6.92 (2H, d,  $J$  8.5), 8.02 (2H, s), 13.6 (2H, broad). **IR** ( $\text{cm}^{-1}$ ): 1512, 1624, 2854, 2934 **Elem. Anal.**: calcd for  $\text{C}_{23}\text{H}_{26}\text{N}_2\text{O}_4$  70.03% C, 6.64% H, 7.10% N; measured 67.22 % C, 6.84% H, 6.63% N.

**polymer ( $\pm$ )-2**:  **$^1\text{H-NMR}$** :  $\delta$  1.4-2.2 (8H, m), 3.16 (2H, broad), 3.83 (4H, broad), 4.05 (4H, broad), 6.2-6.3 (4H, m), 6.93 (2H, d,  $J$  8.5), 8.04 (2H, s), 13.77 (2H, broad). **IR** ( $\text{cm}^{-1}$ ): 1514, 1624, 2848, 2934. **Elem. Anal.**: calcd for  $\text{C}_{24}\text{H}_{28}\text{N}_2\text{O}_5$  67.90% C,

6.65% H, 6.60% N; measured 67.22 % C, 6.44% H, 6.72% N.

**polymer ( $\pm$ )-3**:  **$^1\text{H-NMR}$** :  $\delta$  1.4-2.0 (14H, m), 2.22 (2H, s), 3.79 (4H, broad), 3.90 (3H, m), 6.20 (2H, d,  $J$  9.0), 6.26 (2H, s), 7.20 (2H, d,  $J$  9.0), 13.16 (2H, broad). **IR** ( $\text{cm}^{-1}$ ): 1606, 2863, 2936, 3458.

**polymers (*R,R*)-1 and (*R,R*)-2**

A typical procedure for the preparation of the single (*R,R*) enantiomer of polymers: A mixture of 4 (0.80 g, 2.53 mmol), (*R,R*)-*trans*-1, 2-diaminocyclohexane mono-(+)-tartrate salt(0.67 g, 2.54 mmol) and  $\text{K}_2\text{CO}_3$  (0.35 g, 2.53 mmol) in THF (15 mL) was stirred at 75 °C for 24 h. The mixture was allowed to cool to room temperature and filtered. The solvent was removed by a rotary evaporator and the residue was redissolved in methylene chloride (10 mL). The resulting solution was added dropwise into methanol (100 mL) and stirred vigorously to precipitate the polymer product. The precipitate was filtered and dried under vacuum to give polymer (*R,R*)-1 as a yellow solid (0.55 g, 56%). Polymers (*R,R*)-1 and (*R,R*)-2 gave virtually identical  $^1\text{H-NMR}$  spectra to those of their racemic analogues (( $\pm$ )-1 and ( $\pm$ )-2).

**( $\pm$ )-*N,N'*-(4-ethoxysalicylidene)-*trans*-1,2-cyclohexanediamine, 7**

Compound 7 was prepared according to a method reported in the literature.<sup>(6)</sup>  **$^1\text{H-NMR}$** :  $\delta$  1.1-2.3 (11 H, m), 2.7-2.8 (3 H, m), 3.1-3.2 (1 H, broad), 3.98 (2 H, q,  $J$  7.0), 6.2-6.3 (2 H, m), 7.07 (1 H, d,  $J$  8.5), 8.22 (1 H, s), 13.80 (1 H, broad).

**( $\pm$ )-*N,N'*-bis(4-ethoxysalicylidene)-*trans*-1,2-cyclohexanediamine, 8**

A mixture of 3 (1.00 g, 6.02 mmol) and ( $\pm$ )-*trans*-1,2-diaminocyclohexane (0.43 g, 3.77 mmol) in ethanol (10 mL) was stirred at 75 °C for 2 h. The mixture was allowed to cool to room temperature and methylenechloride (20 mL) was added. The

solution was extracted with water (2 x 15 mL). The organic layer was dried over sodium sulfate and the solvent was removed by rotary evaporator to give the desired product **8** as a yellow solid (0.98 g, 64%). m.p. 105-107 °C. <sup>1</sup>H-NMR: δ 1.36 (6 H, t, *J* 7.0), 2.0 – 1.4 (8 H, m), 3.19 (2 H, m), 3.94 (4 H, q, *J* 7.0), 6.2 – 6.3 (4 H, m), 6.96 (2 H, d, *J* 8.5), 8.05 (2 H, s), 13.73 (2 H, broad). IR (cm<sup>-1</sup>): 1514, 1626, 2854, 2929, 2980.

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