Sodium iminoquinolates with cubic and hexagonal prismatic motifs: synthesis, characterization and their catalytic behavior toward the ROP of *rac*-lactide

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Qirui Zhang,^{a,d} Wenjuan Zhang,^{*,a,b} Shengdong Wang,^a Gregory A. Solan,^{a,c} Tongling Liang,^a Natesan Mannangatti Rajendran^a and Wen-Hua Sun^{*,a,d}

A series of sodium 2-arylimino-8-quinolates, **C1** - **C8**, differing in both the nature of the aryl and quinolate substituents, was prepared and characterized by ¹H / ¹³C NMR spectroscopy and elemental analysis. Their X-ray structures reveal multimetallic assemblies adopting a variety of structural cores all based on Na-O repeat units: cubic and tetrametallic for **C1**, **C2** and **C4**, hexagonal prismatic and hexametallic for **C3** and **C5**, and for tetrametallic **C7'** a core resembling a cyclooctatetraene-type tub-shape. In the presence of BnOH, **C1** - **C8** exhibit good activities towards the ring-opening polymerization (ROP) of *rac*-lactide, affording amorphous polylactides with broad molecular weight distributions. Furthermore, the substituent variation within the ligand frame of **C1** - **C8** affects the catalytic activities of the ROP with the least sterically hindered system, **C1**, yielding the highest conversion.

Introduction

Biodegradable polylactide (PLA) has been the focus of much attention in recent years due to its numerous applications in packaging, agricultural materials, drug delivery, medical devices, and so on.¹ Industrially, stannous octoate is used in its preparation, however, the presence of any trace amounts of toxic tin that may be incorporated into the polymer raises concerns as to its safe use in medical and food packaging applications.² To overcome this, complexes containing a variety of other metal centers have been identified as catalysts for the ring-opening polymerization (ROP) of lactide to give PLA including aluminum, rare earth metals, zinc as well as titanium.³ In addition, complexes based on environmentally-friendly alkali metals have also come to the fore as efficient initiators for the ROP of lactides.⁴ Indeed, the solid state structures of these group 1 compounds often reveal unusual multinuclear assemblies adopting a raft of geometrical forms including 6-membered rings (**A**, Chart 1) and cubic arrays (**B**, Chart 1),⁵ in addition to binuclear and mononuclear compounds^{6,7} such as crown ether stabilized sodium aryloxides (**C**, Chart 1).⁷

With regard to catalytic performance, sodium phenolates

can deliver high *iso*-selectivities (*P_m* up to 0.86) towards the ROP of *rac*-lactide under mild conditions.⁷ Elsewhere, the *tert*-butylphosphine-bridged bisphenolate complex [tBu-OPO]Na₂(DME)₂⁸ has shown to be efficient for the ROP of *L*-lactide as have sodium compounds bearing O,O,O-tridentate bis-phenolates.⁹ Likewise, sodium complexes of 2,2'-ethyldiene-*bis*(4,6-di-*tert*-butylphenol) (**D**, Chart 1), first reported in 2006 and later revisited, exhibit very good activities towards the ROP of *L*-lactide.¹⁰ Notably, sodium iminophenolates (**E**, Chart 1) display extremely high activities for the ROP of *rac*-lactide,¹¹ while sodium aminophenolates (**F**, Chart 1), which can aggregate to form dinuclear¹² and multinuclear compounds,¹³ display good activity in the controlled ROP of *rac*-lactide.

Chart 1 Some examples of the structural forms adopted by sodium aryloxide complexes

Recently we reported a series of metal-containing derivatives based on deprotonated 2-aryliminoquinolin-8-ols; their aluminum and yttrium complexes exhibited high activities toward the ROP of ϵ -caprolactone,^{14a,b} while their titanium

^a Key Laboratory of Engineering Plastics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China; *E-mail: whsun@iccas.ac.cn.

^b School of Materials Science and Engineering, Beijing Institute of Fashion Technology, Beijing 100029, China

^c Department of Chemistry, University of Leicester, University Road, Leicester LE1 7RH, UK

^d University of Chinese Academy of Sciences, Beijing 100049, China

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counterparts displayed high activities towards ethylene polymerization.^{14c-e} To further explore the use of 2-aryliminoquinolin-8-ols, we now disclose a series of sodium 2-arylimino-8-quinolates (**C1** – **C8**) that differ not only in the substitution patterns on the *N*-aryl group but also on the quinolate unit itself. Their solid state structures will be examined using single crystal X-ray diffraction and their role as catalysts for the ROP of *rac*-lactide thoroughly investigated.

Results and discussion

Synthesis and characterization of **C1** – **C8**

The 2-aryliminoquinolin-8-ols, 2-((2,6-*R*³₂-4-*R*⁴₂C₆H₂)N=CH)C₉H₅N-8-OH (**L1**: *R*³ = Me, *R*⁴ = H; **L2**: *R*³ = Et, *R*⁴ = H; **L3**: *R*³ = *i*-Pr, *R*⁴ = H; **L4**: *R*³ = CH(Ph)₂, *R*⁴ = Me) and 2-((2,6-*R*³₂-4-*R*⁴₂C₆H₂)N=CH)-5-*R*²-7-*R*¹₂C₉H₃N-8-OH (**L5**: *R*¹ = *R*⁴ = H, *R*² = Me, *R*³ = *i*-Pr; **L6**: *R*¹ = *R*⁴ = H, *R*² = *t*-Bu, *R*³ = *i*-Pr; **L7**: *R*¹ = H, *R*² = *R*³ = *R*⁴ = Me; **L8**: *R*¹ = *R*² = CH(Ph)₂, *R*³ = *i*-Pr, *R*⁴ = H), have been prepared using methods outlined in our previous work.¹⁴ Compound **L8** has not been reported before and hence full details for its synthesis are given in the experimental section. Reactions of **L1** – **L8** with an excess of NaH in THF at room temperature afforded, on work-up, sodium complexes **C1** – **C8**, respectively (as shown in Scheme 1), in moderate to good yield. All complexes have been characterized by ¹H / ¹³C NMR spectroscopy, elemental analysis and six examples by single crystal X-ray diffraction. The disappearance of the signal corresponding to phenolic proton in the ¹H NMR spectra of **C1** – **C8** confirms the successful deprotonation of the corresponding ligand **L1** – **L8**.

Scheme 1 Synthetic route to the sodium 2-arylimino-8-quinolates **C1** – **C8**

Single crystals of **C1** suitable for the X-ray determination were grown from a toluene/hexane solution of the complex that had been left to stand in the refrigerator compartment of a glove box. A view of **C1** is shown in Figure 1; selected bond distances and angles are collected in Table 1. **C1** is tetrametallic and adopts a distorted cubic form in which the edges of the cube are made up of Na–O bonds; such structural motifs are common to sodium compounds.^{5,11,12,15} All three donor atoms of the O,N,N ligand coordinate to a sodium and each sodium is coordinated by two nitrogen and three bridging oxygen atoms. The Na–O–Na bond

angles [range: 85.51(9) – 94.58(9) °] are close to 90 ° consistent with the cubic arrangement. In addition, the *N*-aryl planes of all four ligands are almost perpendicular to their corresponding Na–O–N–N coordination planes. The Na–O bond lengths range from 2.269(2) to 2.543(3) Å, which fall within the normal range found in sodium aryloxide compounds.^{5,11,12} The Na–N_{quino} bond lengths range from 2.352(3) to 2.408(3) Å, and are noticeably shorter than that

Fig. 1 (a) ORTEP drawing of **C1** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity; (b) Core structure with simplified ligand binding.

Table 1 Selected bond lengths and angles in **C1**

Bond length (Å)			
O(2)–Na(4)	2.341(3)	O(2)–Na(2)	2.435(3)
O(1)–Na(4)	2.269(2)	O(1)–Na(3)	2.281(3)
O(4)–Na(4)	2.470(3)	O(4)–Na(2)	2.250(3)
O(3)–Na(2)	2.331(3)	O(3)–Na(3)	2.543(3)
N(4)–Na(2)	2.635(3)	N(6)–Na(3)	2.604(3)
N(2)–Na(1)	2.687(3)	N(1)–Na(1)	2.408(3)
N(5)–Na(3)	2.352(3)	N(7)–Na(4)	2.406(3)
O(2)–Na(1)	2.281(2)	O(1)–Na(1)	2.441(3)
O(4)–Na(3)	2.259(3)	O(3)–Na(1)	2.337(3)
N(8)–Na(4)	2.610(3)	N(3)–Na(2)	2.365(3)
Bond angle (°)			
Na(1)–O(2)–Na(4)	93.72(9)	Na(1)–O(2)–Na(2)	90.08(9)
Na(4)–O(1)–Na(3)	94.58(10)	Na(2)–O(4)–Na(4)	87.40(9)
Na(4)–O(1)–Na(1)	91.38(10)	Na(4)–O(2)–Na(2)	86.22(9)
Na(3)–O(1)–Na(1)	91.04(10)	Na(2)–O(3)–Na(1)	91.36(9)
Na(2)–O(4)–Na(3)	94.58(9)	Na(3)–O(4)–Na(4)	89.89(9)
Na(2)–O(3)–Na(3)	85.51(9)	Na(1)–O(3)–Na(3)	87.28(9)

for the Na-N_{imino} bonds [2.604(3) - 2.687(3) Å], indicative of the superior donor capacity of the quinolate nitrogen.

The molecular structure of **C2** is displayed in Figure 2, while selected bond lengths and angles are presented in Table 2. The structure is similar to **C1** with a cubic arrangement made up of Na-O bonds that form the framework of the cube with each of

Fig. 2 ORTEP drawing of **C2** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table 2 Selected bond lengths and angles for **C2**

Bond length (Å)			
Na1–O4	2.294(2)	Na2–O2	2.475(2)
Na1–O2	2.286(2)	Na2–O3	2.276(2)
Na1–O1	2.457(2)	Na2–O1	2.299(2)
Na1–N1	2.334(3)	Na4–N7	2.365(2)
Na2–N3	2.388(2)	Na3–N6	2.771(2)
Na3–N5	2.404(2)	Na1–N2	2.624(3)
Na3–O4	2.347(2)	Na3–O1	2.290(2)
Na3–O3	2.417(2)	Na4–N8	2.606(3)
Na2–N4	2.615(2)		
Bond angle (°)			
Na4–O4–Na1	86.02(7)	Na3–O3–Na4	92.04(7)
Na3–O4–Na1	92.66(7)	Na3–O3–Na2	89.74(7)
Na3–O4–Na4	88.63(7)	Na2–O1–Na1	88.47(7)
Na2–O3–Na4	93.41(7)	Na3–O1–Na1	89.94(7)
Na3–O1–Na2	92.39(7)	Na4–O2–Na1	92.50(7)
Na2–O2–Na1	88.32(7)	Na2–O2–Na4	89.39(7)

the four tridentate ligands N[^]N[^]O-chelating a single sodium atom with the O-donor additionally bridging two further sodium atoms. The Na-O-Na bond angles are close to 90 ° while the Na-O bond lengths [2.276(2) - 2.475(2) Å] fall in the same range as that seen **C1**. Likewise, the Na-N bond distances within a ligand show some disparity with the Na-N_{quino} lengths shorter than the Na-N_{imino} distances.

A perspective view of **C3** is shown in Figure 3; selected bond distances and angles are listed in Table 3. **C3** consists of six sodium atoms that assemble to form a hexagonal prismatic arrangement with the oxygen atoms filling the remaining six vertices. The two stacked six-membered Na₃O₃ rings adopt an S₆ symmetry. Such a structural motif is similar to that reported in some lithium species and a few sodium complexes,¹⁶ but to

Fig. 3 (a) ORTEP drawing of **C3** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity; (b) Core structure with simplified ligand binding.

Table 3 Selected bond lengths and angles for **C3**

Bond length (Å)			
Na1–O3	2.3063(16)	Na1–O2	2.335(18)
Na2–O2	2.265(2)	Na2–O3	2.265(19)
Na1–O1	2.403(2)	Na3–O3	2.361(19)
Na3–O1	2.2824(18)	Na1–N1	2.379(2)
Na2–O1	2.291(2)	Na3–O2	2.2548(17)
Na2–N3	2.414(2)	Na1–N2	2.711(2)
Na3–N5	2.415(2)		
Bond angle (°)			
O3–Na1–O2	88.18(7)	O2–Na1–O1	87.12(7)
Na2–O1–Na1	89.43(7)	Na3–O1–Na2	91.67(7)
Na2–O3–Na1	123.05(9)	Na3–O1–Na1	125.10(8)
Na1–O3–Na3	90.54(7)	Na2–O3–Na3	90.31(7)
O3–Na1–O1	105.49(7)		

the knowledge of the authors, represents the first example of a crystallographically characterized sodium complex without solvent coordination. With regard to the binding capacity of the N,N,O ligands, only two of the ligands coordinate through all three donor atoms while the other four bind through uniquely the O and N_{quino} atoms with the bulky N_{imino} group pendant and *trans*. In all cases the quinolate oxygen donor adopts a triply bridging bonding mode. With respect to the two fully chelated ligands the range in metal-ligand contacts, Na1–O1 2.402(2) Å, Na1–N_{quino} 2.378(2) Å, Na1–N_{imino} 2.712(2) Å, highlights the weakness of the imine interaction. Within the

four ligands adopting the bidentate mode, the Na-O bond distances represent the shortest [Na2-O3 2.266(2), Na3-O2 2.254(19) Å] of all the Na-O distances observed in **C3** with the Na-N_{quino} distances the longest [*ca.* 2.416(2) Å]. Furthermore, the average Na-O bond lengths [*ca.* 2.328(2) Å] are slightly shorter than those found in **C1** [*ca.* 2.353(3) Å] and **C2** [*ca.* 2.349(2) Å] in line with the improved donor properties of this ligand set.

Fig. 4 ORTEP drawing of **C4** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

As with **C1** and **C2**, **C4** is also tetrametallic forming a cubic-type structure in which the sodium and oxygen atoms fill the vertices of the cube. A view of **C4** is shown in Figure 4; selected bond distances and angles are given in Table 4. Unlike **C3** all the N,N,O donor atoms of the ligand in **C4** coordinate to sodium without any apparent dissociation of the imine donor (*vide infra*); this is somewhat surprising given the enhanced steric properties of the *ortho*-substituted benzhydryl groups on the *N*-aryl group in **C4**. All the Na-O-Na bond angles fall around 90° [87.97(8) - 93.41(8)°], supportive of the observed cubic arrangement. The Na-O bond lengths range from 2.277(2) to 2.428(2) Å, and are comparable with those seen in **C1**, **C2** and other sodium aryloxide species.^{5,11,12} Similarly, the Na-N_{quino} bond lengths [2.348(3), 2.360(3) Å] compare favourably to the corresponding distances in **C1** [2.352(3) - 2.408(3) Å] and **C2** [2.334(3) - 2.404(2) Å]. By contrast, the Na-N_{imino} distances [2.803(3), 2.853(3) Å] in **C4** are longer than the

Table 4 Selected bond lengths and angles for **C4**

Bond length (Å)			
O(2)–Na(1i)	2.287(3)	O(2)–Na(2)	2.428(2)
O(1)–Na(1)	2.426(2)	O(1)–Na(1i)	2.332(2)
O(1i)–Na(2)	2.277(2)	O(2i)–Na(1)	2.287(3)
O(1i)–Na(1)	2.332(2)	N(1)–Na(1)	2.360(3)
N(3)–Na(2)	2.348(3)	N(4)–Na(2)	2.803(3)
O(2)–Na(2i)	2.329(2)	O(1)–Na(2i)	2.277(2)
O(2i)–Na(2)	2.329(2)	N(2)–Na(1)	2.853(3)
Bond angle (°)			
Na(1i)–O(1)–Na(1)	91.81(8)	Na(1i)–O(2)–Na(2)	93.41(8)
Na(2i)–O(1)–Na(1)	93.72(8)	Na(2i)–O(1)–Na(1i)	88.13(8)
Na(1i)–O(2)–Na(2i)	87.97(8)	Na(2i)–O(2)–Na(2)	91.22(8)

The 'i' atoms have been generated by symmetry.

distances observed in either **C1** [2.604(3) - 2.687(3) Å], **C2** [2.606(3) - 2.771(2) Å] or **C3** [2.712(2) Å] highlighting the weakness of this interaction and consistent with the steric properties imparted by the *N*-substituted 4-methyl-2,6-dibenzhydrylphenyl group.

The molecular structure of **C5** is depicted in Figure 5; selected bond distances and angles are reported in Table 5. The structure resembles **C3** comprising a hexametallic array that takes the form of a hexagonal prism assembled through Na-O bonds. Two N,N,O ligands are fully chelated to sodium [Na3-O2 2.403(4) Å, Na3-N_{imino} 2.700(5) Å, Na3-N_{quino} 2.432(4)

Fig. 5 ORTEP drawing of **C5** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table 5 Selected bond lengths and angles for **C5**

Bond length (Å)			
O(2)–Na(3)	2.403(4)	O(1)–Na(3 ⁱ)	2.320(4)
O(2)–Na(2)	2.308(4)	O(1)–Na(2)	2.401(4)
O(2)–Na(1)	2.306(4)	O(1)–Na(1)	2.264(4)
O(3 ⁱ)–Na(2)	2.222(4)	O(3)–Na(2 ⁱ)	2.220(4)
N(5)–Na(2 ⁱ)	2.456(4)	N(1)–Na(1)	2.457(4)
N(5 ⁱ)–Na(2)	2.456(4)	N(3)–Na(3)	2.432(4)
N(4)–Na(3)	2.700(5)	O(1 ⁱ)–Na(3)	2.320(4)
O(3)–Na(3)	2.340(4)	O(3)–Na(1)	2.294(4)
Bond angle (°)			
Na(1)–O(1)–Na(2)	91.26(15)	Na(3 ⁱ)–O(1)–Na(2)	89.29(14)
Na(2 ⁱ)–O(3)–Na(3)	93.33(15)	Na(1)–O(1)–Na(3 ⁱ)	115.34(16)
Na(1)–O(3)–Na(3)	93.22(14)	Na(1)–O(2)–Na(3)	91.31(13)
Na(1)–O(2)–Na(2)	92.60(14)	Na(2)–O(2)–Na(3)	128.64(16)
Na(2 ⁱ)–O(3)–Na(1)	109.19(16)	Na(1)–O(1)–Na(3 ⁱ)	115.34(16)

The 'i' atoms have been generated by symmetry.

Å], while the other four acts as bidentate N⁺O ligands with the imine unit non-coordinated and *trans*. Similar trends in Na–O and Na–N_{quino} bond distances exist when compared to **C3** with the bidentate Na–O distances [Na1–O1 2.264(4), Na2–O3 2.219 Å], much shorter than those involving the tridentate ligand [Na3–O2 2.403(4) Å], while the corresponding Na–N_{quino} bond length of 2.456(4) Å shows some modest lengthening when compared to that of Na3–N_{quino} [2.432(4) Å]. In addition, the average Na–O bond length in **C5** [*ca.* 2.312(4) Å] is, in general, shorter than structurally related **C3** [*ca.* 2.328(2) Å] and also the cubic-type structures **C1** [*ca.* 2.353(3) Å], **C2** [*ca.* 2.349(2) Å] and **C4** [*ca.* 2.331(3) Å], underlining the effect of the *p*-methyl group on the electron donor ability of the quinolate unit.

Single crystals of **C7'** were grown by prolonged standing of a toluene/hexane solution of **C7** stored in the refrigerator compartment of a glovebox. During crystallization it is evident that partial decomposition of **C7** occurred generating **C7'**. Multiple attempts were made to grow crystals of **C7** itself from different solvents or over shorter time periods; in each case the crystals formed were not of suitable quality for an X-ray determination. A view of the molecular structure of **C7'** is shown in Figure 6; selected bond distances and angles are given in Table 6. The structure reveals an unusual tetrametallic species, distinct from **C1**, **C2** and **C4**, in which four sodium atoms are coordinated by four deprotonated **L7** ligands and four neutral **L7** ligands to form a core reminiscent of a cyclooctatetraene tub-shape. The sodium atoms display a variety of coordination numbers and geometries. Na1 is coordinated by N1 and three bridging oxygen atoms, O1, O2, O7, to form a tetrahedral geometry. At Na2 a distorted octahedral geometry is adopted in which three ligands N_{quino}⁺O-chelate, with O2, O4, N5, N7 forming the equatorial belt and N3 and O3 the axial sites [N3–Na2–O3 is 158.47(9)°]. Na3 is coordinated by O5, N9, N10 from the same ligand and two other bridging oxygen atoms (O6, O3) to give a geometry best described as distorted pyramidal with O3 occupying the apex and O5, N9, N10, O6 the basal plane. A distorted

Fig. 6 (a) ORTEP drawing of **C7'** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity; (b) Core structure with simplified ligand binding.

Table 6 Selected bond lengths and angles for **C7'**

Bond length (Å)			
O(1)–Na(1)	2.251(3)	O(2)–Na(2)	2.408(2)
O(2)–Na(1)	2.233(2)	O(3)–Na(3)	2.515(3)
O(5)–Na(3)	2.362(3)	O(6)–Na(4)	2.406(2)
O(7)–Na(4)	2.314(2)	O(7)–Na(1)	2.327(2)
N(5)–Na(2)	2.493(3)	N(9)–Na(3)	2.440(3)
N(7)–Na(2)	2.736(3)	N(10)–Na(3)	2.873(3)
N(13)–Na(4)	2.694(3)	N(11)–Na(4)	2.550(3)
O(3)–Na(2)	2.301(2)	O(4)–Na(2)	2.316(2)
O(6)–Na(3)	2.368(3)	O(8)–Na(4)	2.335(3)
N(1)–Na(1)	2.446(3)	N(3)–Na(2)	2.566(3)
N(15)–Na(4)	2.706(3)		
Bond angle (°)			
Na(2)–O(3)–Na(3)	125.47(10)	Na(3)–O(6)–Na(4)	112.43(10)
Na(1)–O(2)–Na(2)	98.76(9)	O(1)–Na(1)–N(1)	70.03(9)
O(5)–Na(3)–N(10)	127.02(10)	O(5)–Na(3)–N(9)	67.21(9)
O(3)–Na(2)–N(5)	70.82(9)	O(4)–Na(2)–N(7)	64.49(9)
O(8)–Na(4)–N(15)	64.33(8)	Na(4)–O(7)–Na(1)	114.86(10)
O(2)–Na(2)–N(3)	65.87(8)	O(6)–Na(4)–N(11)	67.15(8)
O(7)–Na(4)–N(13)	66.74(8)		

octahedral geometry, similar to that at Na2, is observed at Na4 with three N_{quino}⁺O ligands chelating. To promote the tub-shape core it is apparent that an intramolecular network of OH⁺–O_{quino} hydrogen bonding interactions is involved making use of the four neutral ligands and the four anionic ligands.

ROP of *rac*-LA using **C1** – **C8**

Complex **C7** was used, in the first instance, as the test (pro-) initiator to allow an investigation of the optimal conditions for the ring opening polymerization conditions of *rac*-lactide; the results are compiled in Table 7.

Firstly, we investigated the effect of temperature on the polymerization as it has been reported that the efficiencies of polymerization are affected by the reaction temperature.¹⁷ The polymerization runs, using benzyl alcohol as the activator, were performed over the 20 to 100 °C temperature range (runs 1 - 6, Table 7), and it was found that optimal temperature occurred at 80 °C with a conversion to PLA of 91% (run 4, Table 7). Analysis of the polymers obtained at 60 °C, 80 °C and 100 °C (runs 3, 4, and 6, Table 7) revealed the molecular weights and molecular weight distributions to be similar. With regard to the duration of the polymerization (runs 4, 7 - 11, Table 7), the conversion steadily increases from 0.5 hours to 3 hours at which point it appears to plateau between 3 and 6 hours. These trends are generally reproduced in the molecular weights and molecular weight distributions which increase and level out after 3 hours; the exception being for the slightly

lower molecular weight for the polymer obtained after 6 hours (run 11, Table 7). It is unclear as the origin of this drop in molecular weight but it would seem plausible that it is due to re-initiation of the active species occurring at this point.

Secondly, we explored the use of **C7** as the initiator itself (*i.e.*, without the benzyl alcohol activator) as some sodium complexes have shown high efficiencies toward the ROP of lactide in the absence of activator.^{6,11a} However, using **C7** alone only showed low conversions (run 12, Table 7) with low molecular polymer obtained. By contrast **C7** in the presence of one equivalent of benzyl alcohol, under comparable conditions, gave 91% conversion (run 4, Table 7). On further increasing the amount of benzyl alcohol from two to four equivalents resulted in a lowering of the conversion (runs 13, 14, Table 7). Notably, the PLA obtained showed a narrower molecular distribution, indicating a more controlled active species under these conditions.^{11a} On increasing the amount of *rac*-lactide, the conversion was found to decrease to 25% (runs 15, Table 7) from 91% (runs 4, Table 7) which can be attributed to a lower concentration of the catalytic species.

Table 7 ROP of *rac*-LA using **C7** in the presence and absence of BnOH ^a

Run	[<i>rac</i> -LA]:[Na]:[BnOH]	T/°C	Time/h	Solvent	Conversion ^b (%)	<i>M_n</i> (×10 ⁴) ^c	PDI ^c
1	250: 1: 1	20	2	toluene	29		
2	250: 1: 1	40	2	toluene	70		
3	250: 1: 1	60	2	toluene	88	1.41	1.54
4	250: 1: 1	80	2	toluene	91	1.46	1.59
5	250: 1: 1	90	2	toluene	89		
6	250: 1: 1	100	2	toluene	86	1.45	1.56
7	250: 1: 1	80	0.5	toluene	36		
8	250: 1: 1	80	1	toluene	71	0.98	1.29
9	250: 1: 1	80	3	toluene	91		
10	250: 1: 1	80	4	toluene	91	1.65	1.61
11	250: 1: 1	80	6	toluene	91	1.54	1.64
12	250: 1: 0	80	2	toluene	7.2	1.00	1.27
13	250: 1: 2	80	2	toluene	66	0.97	1.30
14	250: 1: 4	80	2	toluene	54	0.95	1.34
15	500: 1: 1	80	2	toluene	25	1.07	1.27
16	250: 1: 1	69	2	hexane	65	1.52	1.65
17	250: 1: 1	66	2	THF	Trace	-	-
18	250: 1: 1	40	2	DCM	97	1.32	1.37
19	250: 1: 1	120	2	no solvent	90	1.64	1.57

^a Conditions: 20 μmol Na; 3.0 ml toluene. ^b Determined by ¹H NMR spectroscopy. ^c GPC data were recorded in CHCl₃ vs. polystyrene standards, using a correcting factor of 0.58.¹⁹

Thirdly, the effect of solvent on the polymerization was probed (runs 16-18, Table 7). In tetrahydrofuran, **C7**/BnOH was essentially inactive, in hexane reasonable conversion could be achieved (65%) while in dichloromethane the highest conversion of the all the runs was obtained (97%). It would seem likely that detrimental coordination of THF to sodium^{13, 18} is responsible for the poor catalytic activity while the low solubility of **C7** in hexane may account for its performance characteristics. In addition, the bulk polymerization (without solvent) also showed a good activity (run 19, Table 7), demonstrating the general applicability of this sodium species.

Table 8 ROP of *rac*-LA using **C1** - **C8** in the presence of BnOH^a

Run	Na complex	R ¹	R ²	R ³	R ⁴	Conv. (%) ^b	M _n (×10 ⁴) ^c	PDI ^c	Pr
1	C1	H	H	Me	H	96	1.73	1.76	0.46
2	C2	H	H	Et	H	83	1.18	1.66	0.46
3	C3	H	H	<i>i</i> Pr	H	76	1.41	1.67	0.44
4	C4	H	H	Θ	Me	83	1.77	1.66	0.45
5	C5	H	Me	<i>i</i> Pr	H	91	1.96	1.73	0.45
6	C6	H	<i>t</i> Bu	<i>i</i> Pr	H	69	1.46	1.47	0.47
7	C7	Me	Me	Me	Me	92	1.46	1.59	0.48
8	C8	Θ	Θ	<i>i</i> Pr	H	75	1.60	1.61	0.45

^a Conditions: 20 μmol Na, [*rac*-LA]:[Na]:[BnOH] = 250:1:1; toluene 3 ml, 80 °C, 2 h.^b Determined by ¹H NMR spectroscopy. Θ: CH(Ph)₂ ^c GPC data were recorded in CHCl₃ vs. polystyrene standards, using a correcting factor of 0.58. ¹⁹

Under the optimised conditions established for **C7** (*viz.*, [*rac*-LA]:[Na]:[BnOH] = 250:1:1; 80 °C, 2 h), **C1** - **C8** were all investigated; the results are collected in Table 8. The data clearly show that substituents present on the ligand backbone greatly affect the catalytic conversions in the order: **C1** (96%) > **C5** (91%) ~ **C7** (92%) > **C2** (83%) ~ **C4** (83%) > **C3** (76%) ~ **C8** (75%) > **C6** (69%). Indeed, the least sterically protected system **C1** (R³ = Me, R¹ = R² = R⁴ = H) leads to the highest conversion while more bulky systems *e.g.*, **C3** (R³ = *i*Pr, R¹ = R² = R⁴ = H), **C6** (R³ = *i*Pr, R² = *t*Bu, R¹ = R⁴ = H) and **C8** (R³ = *i*Pr, R¹ = R² = CH(Ph)₂, R⁴ = H), give noticeably lower conversions. With regard to electronic effects it would appear that the activities generally increase as the electron-donating properties of the R substituents (on both the quinolate and *N*-aryl groups) decrease (runs 1 - 3; 5 and 6, Table 8). Hence, **C1** (R³ = Me) > **C2** (R³ = Et) > **C3** (R³ = *i*Pr) as well as **C5** (R² = Me) > **C6** (R² = *t*Bu). This would suggest that higher net charges on the active species are favourable for the catalysis. However, the inconsistent observation that a higher conversion is achieved for **C5** (R² = Me) over **C3** (R² = H) (runs 3 and 5, Table 8) would imply other effects (*e.g.*, solubility) are also influential.

We have also explored the probability of racemic enchainment (*i.e.*, the probability of a forming a new racemic diad) for the PLA's obtained using **C1** - **C8**. These were calculated from their deconvoluted homodecoupled ¹H NMR spectra; the values obtained are collected in Table 8.²⁰ For each run the values are close to 0.5 (range: 0.44 - 0.48) consistent with atactic structures for all the PLA's.

Characterization of PLA

A coordination-insertion mechanism is generally considered to be operative for the ring opening polymerization involving sodium complexes, as has been reported for a variety of other metal species.^{18b,21} The ¹H NMR spectrum for the polymer obtained in the absence of BnOH (run 12, Table 7) suggests cyclic structures which is further supported by the MALDI-TOF spectrum (Figure 7). In the MALDI spectrum peaks separated by 144 mass units along with two major repeating masses are evident (*viz.*, A and B). Within the A series the two most intense peaks at *m/z* = 6364.2 (A) and 6380.3 (A') are assigned as cyclic polymers based on [C₆H₈O₄]₄₄·Na⁺ and [C₆H₈O₄]₄₄·K⁺, which can be explained by an intra-chain

transesterification mechanism. In addition, a less intense B series of peaks corresponds to cyclic polymers of the type [C₆H₈O₄]_n+ [C₃H₄O₂]₂·Na⁺/K⁺ (*e.g.*, [C₆H₈O₄]₄₄+ [C₃H₄O₂]₂·Na⁺/K⁺, *m/z* = 6148.1 (B) and 6165.7 (B')), the result of inter- and intra-chain transesterification side reactions; similar processes having been identified for other sodium complexes.^{6,13} Unlike some literature reports,^{13,22} there is no evidence for CH₃O terminal groups that can derive from methanol.

Figure 7 The MALDI-TOF spectrum of PLA obtained without BnOH (run 12, Table 7)

For the PLA obtained in the presence of benzyl alcohol, the ¹H NMR spectra show signals at *ca.* 5.1 ppm corresponding to a benzyl alkoxide group which would suggest an active species involving Na-OCH₂Ph. The MALDI-TOF spectra of the PLA obtained with one equivalent of benzyl alcohol show peaks separated by 72 mass units (see Fig. 8a), suggesting intra-chain transesterification side reactions in the polymerization. Closer inspection reveals two (*i.e.*, A and B) major repeating masses and another less intense peak. The major intense peaks (A and B) are assigned as cyclic polymers of general composition [C₆H₈O₄]_n+ [C₃H₄O₂]₂·M⁺ (M = Na (A) or K (A')) and [C₆H₈O₄]_n·M⁺ (M = Na (B) or K (B')), indicating the presence of both intra- and inter-chain transesterification side reactions.^{6,13} On the other hand, the less intense peaks for example at *m/z* = 1712.9 and 1729.3 are assigned as linear polymers corresponding to PhCH₂O+[C₆H₈O₄]₁₂·Na (C)/K⁺ (C') with benzyl end-groups, in accordance with the ¹H NMR spectra. The MALDI-TOF spectrum of the PLA obtained using two equivalents of BnOH gave slightly different results for the polymer fractions. In this case, it is now composed of four types of polymer (see Fig. 8b). The most intense peaks were assigned as [C₆H₈O₄]_n+ [C₃H₄O₂]₂·M⁺ (M = Na (A)/K (A')) and [C₆H₈O₄]_n·M⁺ (M = Na (B)/K (B')) and they are attributed to cyclic polymers; the less intense peaks were assigned as PhCH₂O+[C₆H₈O₄]_n·Na⁺ (C)/K⁺ (C') along with PhCH₂O+[C₆H₈O₄]_n+ [C₃H₄O₂]₂·Na⁺ (D)/K⁺ (D'). On comparison of the two spectra in Figure 8, the ratio of polymer containing the PhCH₂O end-groups increased, suggesting that more BnOH introduced the faster initiation of the active NaOCH₂Ph species.

Figure 8 MALDI-TOF spectra of the PLA's obtained in the presence of (a) 1 eq. of BnOH (run 4, Table 7) and (b) 2 eq. of BnOH (run 13, Table 7)

The above results demonstrate that the cyclic polymers are the main structural types obtained using sodium-based **C1** - **C8** in either the presence or absence of BnOH, consistent with inter- and intra-chain transesterification as the major mechanisms. Notably different to that reported elsewhere, inter-chain transesterification side reactions play a key role in these polymerizations. In common to all, the polymers display quite broad molecular weight distributions which can be attributed to undesirable back-biting and intra-chain and transesterification reactions occurring, leading to macrocycles. Alternatively, catalyst inhomogeneity may also contribute to broad or multimodal polymer molecular weight distributions.

Conclusions

Eight examples of sodium 2-arylimino-8-quinolates, **C1** - **C8**, have been synthesized and fully characterized. The crystal structures of **C1** - **C5** and **C7'** reveal a diversity of structural types with **C1**, **C2** and **C4** adopting tetrametallic cubic cores, **C3** and **C5** hexametallic hexagonal prismatic cores and **C7'**, a decomposition product of **C7**, a tetrametallic structure with a core best described as a cyclooctatetraene-type tub-shape. In the absence of benzyl alcohol, **C7** showed low activity for the ROP of *rac*-lactide while in its presence, **C7** exhibited very good activity. By varying the substituents of the *N*-aryl group and quinolate moiety, the polymerization of *rac*-LA was influenced; indeed the steric (and electronic properties) of the substituents appended to the iminoquinolate greatly affected

their catalytic activity. All the resultant PLA display high molecular weight and broad molecular weight distributions. Microstructural analysis of the PLA's generated showed that without benzyl alcohol, the polymers were cyclic in nature and contained some inter-chain by-product. With benzyl alcohol, the major component of the polymers was again based on cyclic structures and inter-chain polymer by-product along with a minor component based on a linear polymer with OCH₂Ph end-groups.

Experimental

General considerations

All reactions were performed using standard Schlenk techniques in an atmosphere of high-purity nitrogen or using glovebox techniques. Toluene and THF were dried by refluxing over sodium and benzophenone, and then distilled under nitrogen and stored over activated molecular sieves (4 Å) for 24 h in a glovebox prior to use. CDCl₃, C₆D₆ and C₂D₂Cl₄ were dried over activated 4 Å molecular sieves. CH₂Cl₂ and *n*-hexane were dried over CaH₂ for 48 h, distilled under nitrogen and stored over activated molecular sieves (4 Å) in a glovebox prior to use. The ligands (**L1** - **L7**) were prepared by the condensation reaction of 8-hydroxyquinoline-2-carbaldehyde with the corresponding substituted aniline as described in our previous work.¹⁴ Elemental analyses were performed using a PE2400II Series analyser (Perkin-Elmer Co.). ¹H and ¹³C NMR spectra were recorded on a BrukerDMX-400 (400 MHz for ¹H, 100 MHz for ¹³C) or Bruker Frontier-300 (300 MHz for ¹H, 75 MHz for ¹³C) spectrometer. All spectra were obtained in the solvent indicated at 25 °C unless otherwise stated and chemical shifts are given in ppm and are referenced to SiMe₄ (δ 0.00, ¹H, ¹³C). IR spectra were recorded on a Perkin-Elmer System 2000 FT-IR spectrometer. The GPC measurements were performed using an instrument composed of a Waters-1515 HPLC pump, a Waters 2414 refractive index detector and a combination of Styragel HT- 2, HT-3 and HT-4 columns, the effective molar mass ranges of which are 100–10000, 500–30 000 and 5000–600 000, respectively. CHCl₃ was used as the eluent (flow rate: 1 mL min⁻¹, at 35 °C). Molecular weights and molecular weight distributions were calculated using polystyrene as standard.

Preparation of 3,5-diphenylmethyl-2-[(2,6-diisopropylphenyl imino)methyl]quinolin-8-ol (**L8**).

A mixture of 8-hydroxyquinoline-2-aldehyde (1.06 g, 2.0 mmol), 2,6-diisopropylaniline (0.36 g, 2.0 mmol) and a few drops of acetic acid was stirred and heated to reflux in ethanol (20 mL) for 3 h. The resulting precipitate was collected by filtration and dried under reduced pressure to give **L8** as a yellow solid (0.47 g, 34%). ¹H NMR (400 MHz, CDCl₃, TMS): δ 8.40 (s, 2H, N=CH and quino-H), 8.34 (d, *J* = 8.8 Hz, 1H, OH), 8.28 (d, *J* = 8.8 Hz, 1H, quino-H), 7.22-7.19 (m, 15H, quino-CH(C₆H₅)₂), 7.04–6.99 (m, 8H, quino-CH(C₆H₅)₂ and Ar-H), 6.73 (s, 1H, Ar-H), 6.09 (s, 1H, quino-CH(C₆H₅)₂), 6.06 (s, 1H, quino-CH(C₆H₅)₂), 2.96–2.91 (m, 2H, Ar-CH(CH₃)₂), 1.16 (d, *J* = 6.8 Hz, 12H, -CH(CH₃)₂). ¹³C-NMR (100 MHz, CDCl₃, TMS): δ 162.9,

151.7, 148.7, 148.6, 148.4, 143.2, 143.1, 138.2, 137.3, 133.9, 132.5, 130.0, 129.4, 129.3, 128.6, 128.4, 126.6, 126.3, 125.2, 124.8, 123.2, 118.5, 52.6, 49.8, 28.2, 23.6. Anal. Calcd for $C_{48}H_{44}N_2O$: C, 86.71; H, 6.67; N, 4.21. Found: C, 86.98; H, 6.83; N, 4.28%.

Preparation of sodium imino-quinolates **C1** – **C8**

Synthesis of C1. To a stirred solution of 2-((2,6-dimethylphenylimino)methyl)quinolin-8-ol (**L1**) (0.28 g, 1.0 mmol) in tetrahydrofuran (15 mL) was added NaH (0.024 g, 1.0 mmol) at room temperature. The color of the mixture turned dark red immediately. The stirring was maintained for 3 h and the reaction mixture filtered to remove excess NaH. All volatiles were removed under reduced pressure and the resulting residue washed with *n*-hexane to afford a red powder (0.238 g, 80%). 1H NMR (400 MHz, $CDCl_3$, TMS): δ 8.07 (s, 1H, N=CH), 8.02 (d, J = 8.0 Hz, 1H, quino-*H*), 7.29 (d, J = 8.0 Hz, 1H, quino-*H*), 6.96–7.02 (m, 4H, quino-*H* and Ar-*H*), 6.64 (d, J = 8.0 Hz, 1H, Ar-*H*), 6.24 (d, J = 8.0 Hz, 1H, Ar-*H*), 1.73 (s, 6H, Ar- CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.8, 151.0, 145.7, 145.3, 136.7, 131.7, 128.2, 127.9, 127.6, 123.8, 121.2, 115.3, 115.0, 107.8, 68.1, 18.3. FT-IR (cm^{-1}): 3036 (m), 2956 (m), 2917 (m), 1630 (s), 1581 (m), 1545 (m), 1499 (m), 1448 (m), 1344 (m), 1283 (m), 1188 (m), 1130 (m), 1092 (m), 1052 (m), 968 (m), 918 (w), 896 (m), 834 (m), 804 (m), 761 (m), 732 (m). Anal. Calcd for $C_{18}H_{15}N_2NaO \cdot 0.5THF$: C, 71.33; H, 6.26; N, 7.56%. Found: C, 71.17; H, 6.19; N, 7.51%.

Synthesis of C2. The synthesis of **C2** was carried out by the same procedure as described for **C1**, except that 2-((2,6-diethylphenylimino)methyl)quinolin-8-ol (**L2**) was used. Yield: 96%. 1H NMR (400 MHz, $CDCl_3$, TMS): δ 8.10 (s, 1H, N=CH), 8.05 (d, J = 8.0 Hz, 1H, quino-*H*), 7.34 (d, J = 8.0 Hz, 1H, quino-*H*), 7.08–7.00 (m, 4H, quino-*H* and Ar-*H*), 6.65 (d, J = 8.0 Hz, 1H, Ar-*H*), 6.33 (d, J = 8.0 Hz, 1H, Ar-*H*), 2.13–2.08 (m, 4H, Ar- CH_2CH_3), 0.85 (t, J = 3.0 Hz, 6H, Ar- CH_2CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.0, 163.8, 150.5, 145.3, 144.6, 136.7, 133.4, 132.0, 131.8, 125.4, 124.1, 121.4, 115.3, 107.4, 24.2, 14.4. FT-IR (cm^{-1}): 3152 (m), 3152 (m), 2962 (m), 2868 (m), 1627 (s), 1584 (m), 1544 (m), 1500 (m), 1445 (m), 1361 (m), 1342 (m), 1299 (m), 1221 (m), 1179 (m), 1132 (m), 1096 (m), 1056 (m), 967 (m), 918 (w), 898 (m), 853 (m), 833 (m), 804 (m), 738 (m), 701 (m). Anal. Calcd for $C_{20}H_{19}N_2NaO$: C, 73.60; H, 5.87; N, 8.58%. Found: C, 73.46; H, 5.77; N, 8.47%.

Synthesis of C3. The synthesis of **C3** was carried out by the same procedure as that described for **C1**, except that 2-((2,6-diisopropylphenylimino)methyl)quinolin-8-ol (**L3**) was used. Yield: 82%. 1H NMR (400 MHz, $CDCl_3$, TMS): δ 8.05 (t, J = 8.0 Hz, 2H, N=CH and quino-*H*), 7.51 (d, J = 4.0 Hz, 1H, quino-*H*), 7.07 (s, 3H, quino-*H*), 6.84 (s, 1H, Ar-*H*), 6.61 (s, 1H, Ar-*H*), 6.34 (s, 1H, Ar-*H*), 2.68 (d, J = 4.0 Hz, 2H, Ar- $CH(CH_3)_2$), 0.83 (d, J = 4.0 Hz, 12H, Ar- $CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$): δ 163.6, 149.2, 146.8, 144.0, 137.9, 137.0, 131.7, 129.0, 128.2, 125.4, 124.4, 122.9, 120.6, 114.5, 27.8, 23.3. FT-IR (cm^{-1}): 2959 (m), 2926 (m), 2867 (m), 2361 (m), 2336 (m), 1632 (s), 1582 (m), 1544 (m), 1500 (m), 1451 (m), 1345 (s), 1286 (m), 1251 (w), 1178 (m), 1132 (m), 1097 (m), 1057 (m), 970 (m), 929 (m), 896 (m), 834 (m), 801 (m), 775 (m), 740 (m), 676 (m). Anal. Calcd for

$C_{22}H_{23}N_2NaO \cdot 1.5THF$: C, 72.70; H, 7.63; N, 6.07. Found: C, 72.44; H, 7.23; N, 6.56%.

Synthesis of C4. The synthesis of **C4** was carried out by the same procedure as that described for **C1**, except that 2-((2,6-dibenzhydryl-4-methylphenylimino)methyl)quinolin-8-ol (**L4**) was used. Yield: 21%. 1H NMR (CD_2Cl_2 , 400 MHz): δ 7.86 (d, J = 8.4 Hz, 1H, N=CH), 7.71 (d, J = 8.0 Hz, 1H, quino-*H*), 7.26–7.24 (m, 4H, quino-*H*), 7.03–7.02 (m, 4H, Ar- $CH(C_6H_5)_2$), 6.97–6.95 (m, 5H, Ar- $CH(C_6H_5)_2$), 6.76–6.70 (m, 4H, Ar- $CH(C_6H_5)_2$), 6.54–6.52 (m, 4H, Ar- $CH(C_6H_5)_2$), 6.49–6.27 (m, 5H, Ar- $CH(C_6H_5)_2$ and Ar-*H*), 5.82 (s, 2H, Ar- $CH(C_6H_5)_2$), 2.30 (s, 3H, Ar- CH_3). ^{13}C NMR (100 MHz, C_6D_6): δ 162.7, 143.2, 137.2, 133.2, 132.1, 129.2, 129.1, 128.4, 128.2, 126.5, 124.5, 123.0, 49.7, 31.6, 27.9, 23.2, 22.6, 13.9. FT-IR (cm^{-1}): 3729 (w), 3056 (m), 3025 (m), 2361 (m), 2336 (m), 1630 (s), 1581 (m), 1539 (m), 1494 (m), 1450 (m), 1346 (s), 1296 (m), 1244 (m), 1195 (m), 1161 (w), 1124 (m), 1098 (m), 1077 (w), 1057 (m), 1030 (m), 967 (m), 900 (m), 829 (m), 697 (m). Anal. Calcd for $C_{47}H_{41}N_2NaO \cdot 2/3THF$: C, 82.50; H, 5.81; N, 4.21. Found: C, 82.78; H, 5.87; N, 4.13%.

Synthesis of C5. The synthesis of **C5** was carried out by the same procedure as that described for **C1**, except that 5-methyl-2-((2,6-diisopropylphenylimino)methyl)quinolin-8-ol (**L5**) was used. Yield: 71%. 1H NMR (400 MHz, $C_2D_2Cl_4$, TMS): δ 8.36 (d, J = 4.4 Hz, 3H, N=CH and quino-*H*), 8.03 (s, 1H, quino-*H*), 7.28 (d, J = 8.0 Hz, 1H, quino-*H*), 7.11 (d, J = 6.8 Hz, 1H, Ar-*H*), 7.06 (t, J = 7.6 Hz, 2H, Ar-*H*), 2.92–2.87 (m, 2H, Ar- $CH(CH_3)_2$), 2.56 (s, 3H, quino- CH_3), 1.11 (d, J = 6.7 Hz, 12H, Ar- $CH(CH_3)_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.4, 148.3, 136.9, 133.7, 129.0, 128.1, 125.2, 124.7, 124.4, 122.9, 118.3, 53.6, 31.4, 29.1, 27.8, 23.3, 22.5, 17.7, 14.1. FT-IR (cm^{-1}): 2959 (m), 2924 (m), 2866 (m), 2361 (s), 2336 (m), 1630 (s), 1572 (m), 1546 (m), 1513 (w), 1451 (s), 1399 (m), 1343 (m), 1298 (m), 1248 (m), 1179 (w), 1143 (w), 1089 (m), 1051 (m), 976 (m), 832 (m), 683 (m). Anal. Calcd for $C_{23}H_{25}N_2NaO$: C, 74.98; H, 6.84; N, 7.60. Found: C, 74.56; H, 6.83; N, 7.48%.

Synthesis of C6. The synthesis of **C6** was carried out by the same procedure as that described for **C1**, except that 5-tert-butyl-2-((2,6-diisopropylphenylimino)methyl)quinolin-8-ol (**L6**) was used. Yield: 72%. 1H NMR (400 MHz, $CDCl_3$, TMS): δ 8.80 (s, 1H, N=CH), 8.31 (s, 2H, quino-*H*), 7.24 (d, J = 6.0 Hz, 2H, quino-*H*), 7.15 (d, J = 23.2 Hz, 3H, Ar-*H*), 2.86 (s, 2H, Ar- $CH(CH_3)_2$), 1.52 (s, 9H, quino- $CH(CH_3)_3$), 1.01 (s, 12H, Ar- $CH(CH_3)_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.9, 148.6, 137.4, 135.7, 128.8, 128.0, 125.1, 124.3, 122.8, 117.9, 31.7, 31.4, 27.8, 23.2. FT-IR (cm^{-1}): 2959 (m), 2869 (m), 2361 (s), 2336 (m), 1630 (s), 1590 (m), 1569 (m), 1510 (w), 1456 (s), 1386 (w), 1361 (m), 1318 (m), 1279 (w), 1244 (m), 1179 (m), 1136 (m), 1081 (w), 1054 (m), 978 (m), 927 (m), 690 (m). Anal. Calcd for $C_{26}H_{31}N_2NaO$: C, 76.07; H, 7.61; N, 6.82. Found: C, 76.22; H, 7.78; N, 6.69%.

Synthesis of C7. The synthesis of **C7** was carried out by the same procedure as that described for **C1**, except that 2-((2,4,6-trimethylphenylimino)methyl)-5-methyl-quinolin-8-ol (**L7**) was used. Yield: 77%. 1H NMR (400 MHz, $CDCl_3$): δ 7.84 (s, 1H, N=CH), 7.67 (d, J = 8.4, 1H, quino-*H*), 7.56 (s, 1H, quino-*H*), 6.79 (s, 1H, quino-*H*), 6.65 (s, 3H, quino-*H* and Ar-*H*), 2.17 (s, 6H,

Ar-CH₃ and quino-CH₃), 1.90 (s, 6H, Ar-CH₃). ¹³C NMR (100 MHz, C₆D₆): δ 163.5, 148.3, 141.8, 132.8, 132.5, 130.3, 129.1, 129.0, 125.3, 118.8, 112.7, 31.6, 22.7, 20.6, 18.1, 17.5, 14.0. FT-IR (cm⁻¹): 2917 (m), 2856 (m), 1628 (s), 1567 (m), 1513 (m), 1475 (w), 1442 (w), 1359 (m), 1335 (w), 1292 (m), 1238 (m), 1201 (m), 1143 (m), 1076 (m), 1030 (m), 974 (w), 918 (m), 832 (s), 793 (m), 752 (m), 726 (m), 701 (m), 655 (w). Anal. Calcd for C₂₀H₁₉N₂NaO: C, 73.60; H, 5.87; N, 8.58. Found: C, 73.29; H, 5.77; N, 8.24%.

Synthesis of C8. The synthesis of **C8** was carried out by the same procedure as that described for **C1**, except that 5,7-dibenzyl-2-[(2,6-diisopropylphenylimino)methyl]quinolin-8-ol (**L8**) was used. Yield: 34%. ¹H NMR (CD₂Cl₂, 400 MHz): δ 8.44-8.26 (m, 4H, N=CH and quino-H), 7.24-7.13 (m, 14H, quino-CH(C₆H₅)₂), 7.00 (d, J = 6.4 Hz, 8H, quino-CH(C₆H₅)₂), 6.73 (s, 1H, Ar-H), 6.07 (d, J = 9.2 Hz, 2H, quino-CH(C₆H₅)₂), 2.97-2.90 (m, 2H, Ar-CH(CH₃)₂), 1.13 (d, J = 6.8 Hz, 12H, Ar-CH(CH₃)₂). ¹³C NMR (100 MHz, C₆D₆): δ 162.9, 149.0, 148.7, 143.4, 143.3, 136.9, 133.7, 132.7, 129.3, 126.3, 126.1, 125.3, 124.8, 123.1, 117.9, 52.3, 49.7, 31.5, 28.1, 23.1, 22.6, 13.9. FT-IR (cm⁻¹): 3057 (m), 3023 (m), 2960 (s), 2926 (m), 2867 (m), 2362 (m), 2336 (m), 1627 (s), 1594 (m), 1560 (m), 1532 (w), 1492 (s), 1428 (m), 1349 (m), 1314 (m), 1258 (m), 1175 (m), 1097 (w), 1075 (m), 1027 (m), 728 (m), 696 (m). Anal. Calcd for C₅₅H₅₁N₂NaO: C, 84.80; H, 6.60; N, 3.62. Found: C, 84.96; H, 6.74; N, 3.77%.

Ring opening polymerization of *rac*-lactide

A representative polymerization procedure, in the presence of one equivalent of benzyl alcohol (Table 7, run 4), is as follows: a toluene solution of **C7** (0.020 mmol, 1.0 mL toluene) and BnOH (0.020 mmol) were added to a Schlenk tube in the glovebox at room temperature. The solution was stirred for 2

min, and then *rac*-lactide (5.0 mmol) along with toluene (2.0 mL) introduced. The reaction mixture was then placed into an oil bath preheated at 80 °C, and the solution stirred for the prescribed time (2 h). The polymerization mixture was then quenched by the addition of an excess of glacial acetic acid (0.2 mL), and the contents poured into methanol (200 mL). The resultant polymer was collected on filter paper and dried under reduced pressure.

The bulk polymerization process (run 19, Table 7) is as follows: **C7** (0.020 mmol), BnOH (0.020 mmol) and *rac*-lactide (5.0 mmol) were added to a Schlenk tube in the glovebox at room temperature. The tube was then placed in an oil bath preheated to 120 °C, and the contents stirred for 2 hours at this temperature. The reaction mixture was then quenched by the addition of an excess of glacial acetic acid (0.2 mL) and methanol (200 mL) added to precipitate the polymer. The polymer was collected on filter paper and dried under reduced pressure.

Crystal structure determinations

Single crystals of **C1** – **C5** and **C7'** suitable for X-ray diffraction determinations were obtained from chilled toluene/hexane or tetrahydrofuran/hexane solutions. With graphite monochromated Mo-K_α radiation (λ = 0.71073 Å), cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least squares on *F*². All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXTL-97 package.²⁴ Details of the X-ray structure determinations and refinements are provided in Table 9.

Table 9 Crystal data and refinement details for **C1** – **C5** and **C7'**

	C1	C2	C3	C4	C5	C7'
Empirical formula	C ₇₂ H ₆₀ N ₈ Na ₄ O ₄	C ₈₇ H ₈₄ N ₈ O ₄ Na ₄	C ₁₄₆ H ₁₅₂ N ₁₂ Na ₆ O ₆	C ₁₈₆ H ₁₄₈ N ₈ Na ₄ O ₄	C ₁₅₂ H ₁₆₆ N ₁₂ Na ₆ O ₆	C ₁₆₀ H ₁₅₆ N ₁₆ Na ₄ O ₈
Formula weight	1193.24	1397.58	2308.74	2651.08	2394.91	2522.96
Crystal color	red	red	red	red	red	red
Temperature (K)	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	triclinic	triclinic	Monoclinic	Triclinic	triclinic
space group	P-1	P-1	P-1	C2/c	P-1	P-1
a (Å)	14.787(3)	15.570(3)	14.507(3)	31.790(6)	14.410(3)	16.0814(14)
b (Å)	15.067(3)	17.110(3)	16.694(3)	18.998(4)	17.255(3)	19.4781(16)
c (Å)	18.853(4)	18.140(4)	17.000(3)	30.209(6)	17.335(3)	25.689(2)
α (°)	81.79	93.88(3)	100.84	90	110.08	70.678(3)
β (°)	71.41	93.24(3)	105.10	109.39	104.88	89.763(4)
γ (°)	89.01	116.22(3)	115.30	90	109.92	79.664(4)
Volume (Å ³)	3938.6(14)	4305.2(15)	3375.9(12)	17210(6)	3448.3(11)	7457.0(11)
Z	2	2	1	4	1	2
D _{calc} (Mg m ⁻³)	1.006	1.078	1.136	1.023	1.153	1.124
μ (mm ⁻¹)	0.082	0.084	0.086	0.069	0.086	0.080
F(000)	1248	1476.0	1226	5584	1276	2672
Crystal size (mm)	0.32 × 0.26 × 0.20	0.2 × 0.2 × 0.2	0.18 × 0.11 × 0.09	0.419 × 0.265 × 0.122	0.19 × 0.12 × 0.02	0.327 × 0.144 × 0.037
θ range (°)	1.15 - 27.48	2.66 - 55	3.14 - 54.96	1.27 - 27.48	1.60 - 25.20	3.09 - 50.398
	-17 ≤ h ≤ 19	-20 ≤ h ≤ 20	-18 ≤ h ≤ 18	-41 ≤ h ≤ 41	-17 ≤ h ≤ 17	-17 ≤ h ≤ 19
Limiting indices	-17 ≤ k ≤ 19	-21 ≤ k ≤ 22	-21 ≤ k ≤ 21	-24 ≤ k ≤ 24	-20 ≤ k ≤ 20	-23 ≤ k ≤ 23
	-24 ≤ l ≤ 24	-23 ≤ l ≤ 23	-22 ≤ l ≤ 22	-39 ≤ l ≤ 39	-20 ≤ l ≤ 20	-30 ≤ l ≤ 30
No. of rflns collected	33902	34204	47372	120753	41307	59409
No. of unique rflns R _{int}	17616(0.0605)	19319(0.0432)	15399(0.0455)	19726(0.0882)	12384(0.1162)	26701(0.0569)
Completeness to θ (%)	97.4	97.5	99.6	99.9	99.7	99.3
Goodness-of-fit on F ²	0.972	1.034	1.114	1.177	1.260	1.130
Final R indices	R ₁ = 0.0882	R ₁ = 0.0808	R ₁ = 0.0781	R ₁ = 0.1047	R ₁ = 0.1390	R ₁ = 0.0898
[I > 2σ (I)]	wR ₂ = 0.2332	wR ₂ = 0.2118	wR ₂ = 0.1801	wR ₂ = 0.2165	wR ₂ = 0.2372	wR ₂ = 0.2424
R indices (all data)	R ₁ = 0.1438	R ₁ = 0.1138	R ₁ = 0.0953	R ₁ = 0.1340	R ₁ = 0.1771	R ₁ = 0.1065
	wR ₂ = 0.2652	wR ₂ = 0.2341	wR ₂ = 0.0924	wR ₂ = 0.2327	wR ₂ = 0.2549	wR ₂ = 0.2578
Largest diff peak and hole(eÅ ⁻³)	0.345/-0.367	0.81/-0.28	0.55/-0.38	0.536/-0.214	0.465/-0.447	0.45/-0.39

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