Electronic Supplementary Information

Enantiopure N,N,O-Scorpionate Zinc Amide and Chloride Complexes as Efficient Initiators for the Heteroselective ROP of Cyclic Esters.

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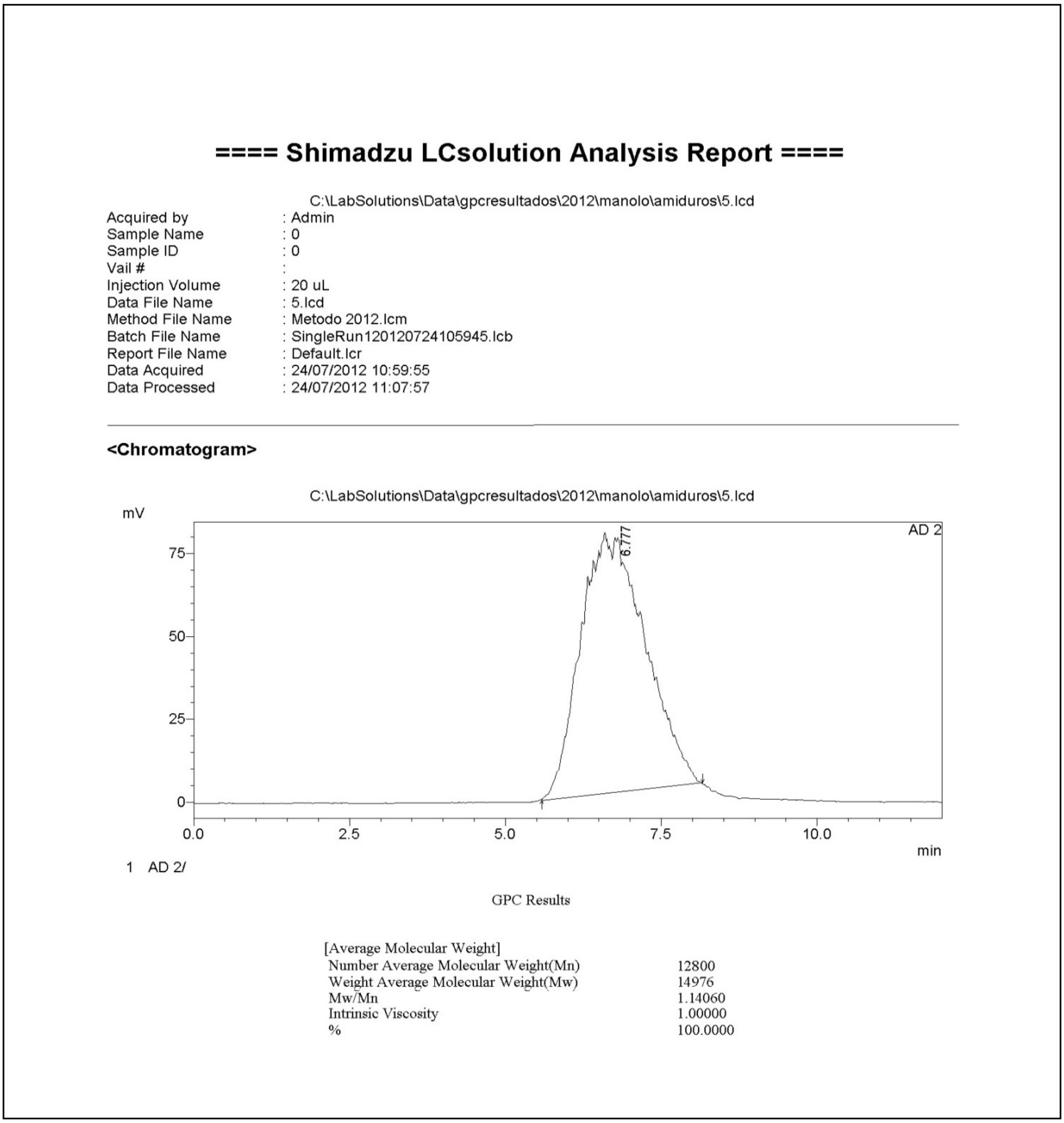
Table S1. Polymerization of ε-caprolactone catalyzed by **1–5**[a]

entry	**initiator**	**temp. (°C)**	**yield (g)**	**conv (%)**[b]	**$M_{n(theor)}$ (Da)**[c]	**M_n (Da)**[d]	**M_w/M_n**[d]
1	**1**	20	0.22	11	2 500	3 800	1.28
2	**1**[e]	20	traces	-			
3	**1**	50	1.11	54	12 300	11 700	1.26
4	**1**[e]	50	0.45	22	5 000	4 500	1.24
5	**2**	20	traces	-			
6	**2**	50	0.53	26	5 900	5 500	1.23
7	**3**	20	0.60	29	6 600	6 900	1.17
8	**3**	50	1.15	56	12 800	11 900	1.15
9	**4**	20	0.24	12	2 700	3 700	1.07
10	**4**	50	0.98	48	10 900	11 600	1.12
11	**5**	20	1.21	59	13 500	13 200	1.11
12	**5**	50	1.25	61	13 900	14 900	1.12

[a] Polymerization conditions: 90 μmol of Zn, 10 mL of toluene as solvent, 3 h of reaction time, $[\varepsilon\text{-CL}]_0/[\text{Zn}]_0 = 200$. [b] Percentage conversion of the monomer [(weight of polymer recovered/weight of monomer) × 100]. [c] Theoretical M_n = [(monomer/catalyst) × (% conversion) × (M_w of CL)]/100. [d] Determined by size exclusion chromatography relative to polystyrene standards in tetrahydrofuran. Experimental M_n was calculated considering Mark–Houwink's corrections[1] for M_n [M_n(obsd) = 0.56 × M_n(GPC)]. [e] 10 mL of tetrahydrofuran as solvent.



==== Shimadzu LCsolution Analysis Report ====

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Sample ID : 0
Vail # :
Injection Volume : 20 uL
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Method File Name : Metodo 2012.lcm
Batch File Name : SingleRun120120724105945.lcb
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<Chromatogram>

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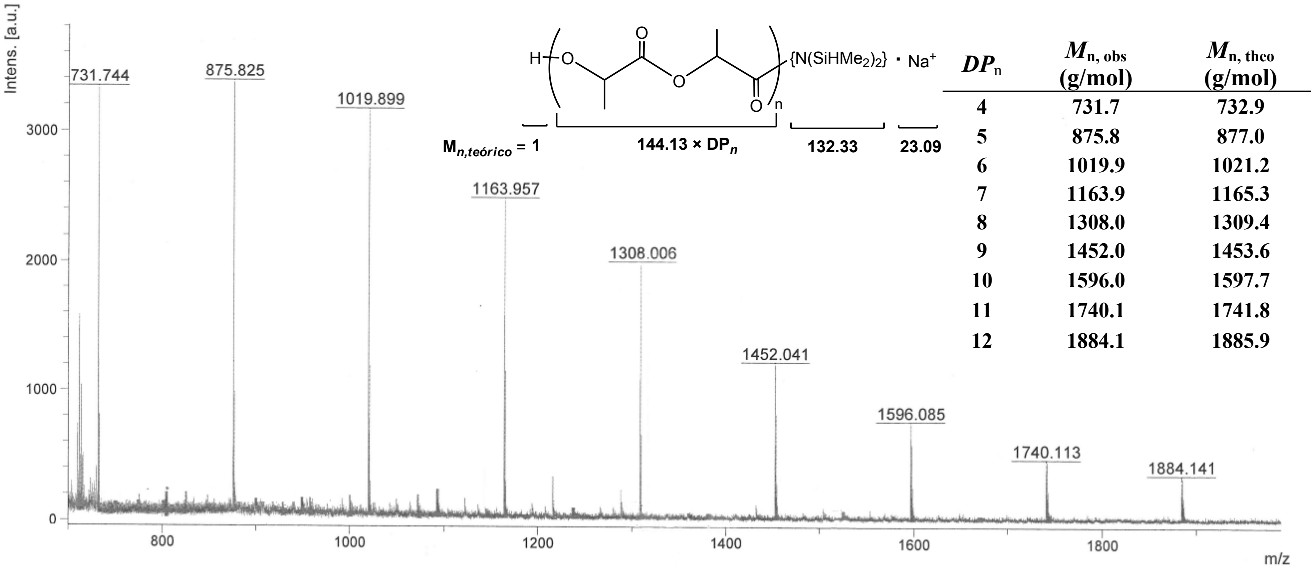
GPC Results

[Average Molecular Weight]

Number Average Molecular Weight(Mn)	12800
Weight Average Molecular Weight(Mw)	14976
Mw/Mn	1.14060
Intrinsic Viscosity	1.00000
%	100.0000

Figure S1. GPC trace corresponding to a poly(L-lactide) prepared from catalyst **5** (Table 2, entry 10).



DP_n	$M_{n,\text{obs}}$ (g/mol)	$M_{n,\text{theo}}$ (g/mol)
4	731.7	732.9
5	875.8	877.0
6	1019.9	1021.2
7	1163.9	1165.3
8	1308.0	1309.4
9	1452.0	1453.6
10	1596.0	1597.7
11	1740.1	1741.8
12	1884.1	1885.9

Figure S2. Selected area of MALDI–ToF mass spectrum of PLA sample obtained with [L-LA]$_0$/[**2**]$_0$ = 15, 83% conversion; theoretical molecular weights calculated according to the equation: $M_n = (DP_n \times M_{wLA}) + M_{wHN(SiHMe2)2} + M_{wNa}$, where DP_n is the degree of polymerization, $M_{wLA} = 144.13$, $M_{wHN(SiHMe2)2} = 133.34$ and $M_{wNa} = 23.09$ g·mol^{-1}.

The distribution in the spectrum (Figure S2) indicates the existence of a single family of polymer chains capped by –CH(CH$_3$)OH and N(SiHMe$_2$)$_2$– *termini*, corresponding to oligomers of formula H(OCHMeCO)$_{2n}$ N(SiHMe$_2$)$_2$)·Na$^+$ (n = 4 to 12) with consecutive peaks separated by increments of 144 Da. Moreover, neither intermolecular ester-exchange (transesterification) reactions nor cyclic oligomers were detected.

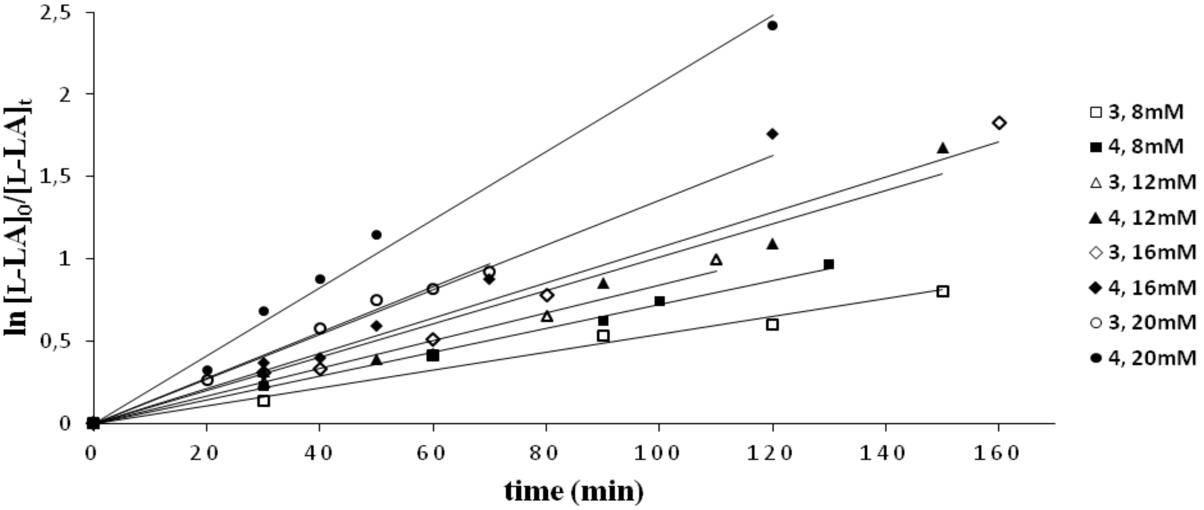


Figure S3. Pseudo-first-order kinetic plots for the polymerization of L-LA in toluene at 50ºC employing [Zn{N($SiMe_3$)$_2$}(bpzte)]$_2$ (**3**) and [Zn{N($SiHMe_2$)$_2$}(bpzte)]$_2$] (**4**) as catalysts ([L-LA]$_0$ = 0.72 M).

In all cases, the linearity of the semi-logarithmic plots of ln ([**L**-LA]$_0$/[**L**-LA]$_t$) versus reaction time for catalysts **3** and **4** at 50ºC, employing different initial catalyst concentrations, shows that the propagations were first order with respect to **L**-LA monomer (Figure S3) (square correlation coefficients ≥ 0.97).

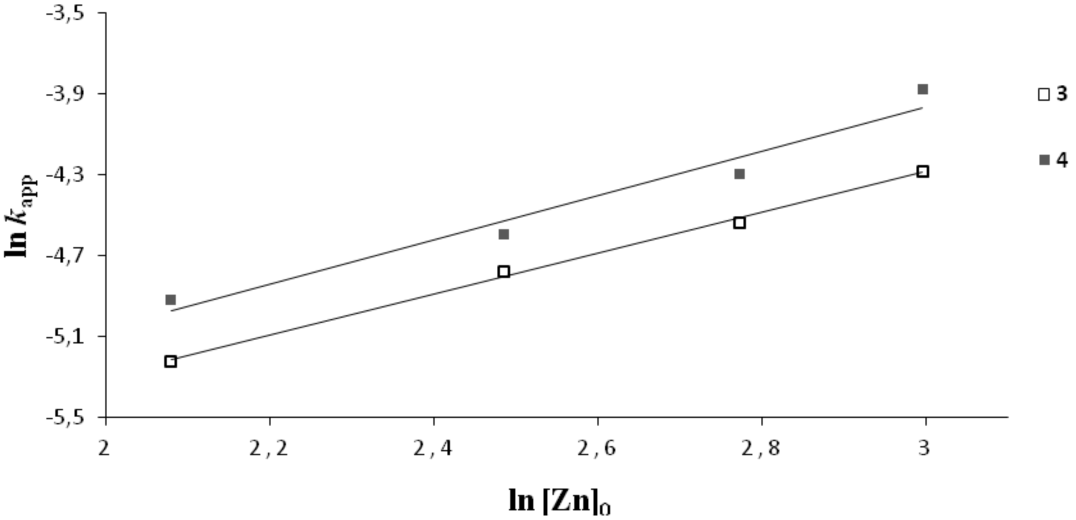


Figure S4. Plots of ln k_{app} versus ln $[catalyst]_0$ for the polymerization of L-LA employing initiators $[Zn\{N(SiMe_3)_2\}(bpzte)]_2$ (**3**) and $[Zn\{N(SiHMe_2)_2\}(bpzte)]_2]$ (**4**) in toluene at 50ºC, with $[LA]_0$ = 0.72 mol/L.

The kinetic dependence on the catalyst concentration (*n*) and the propagation rate constant (k_p) confirms that the reaction is also first order in catalysts **3** and **4** at 50ºC (Figure S4). These values prove that the polymerization of L-LA mediated by these initiators obeys an overall second-order rate kinetic law of the form:

$$-\,\mathrm{d}[LA]/\mathrm{d}t = k_p[\text{catalyst}]^1[\text{LA}]^1$$

Table S2. Rate constants dependence on the initial catalyst concentration for L-LA polymerization at 50ºC for **3** and **4**.

Catalyst	**[catalyst]$_0$ × 10^3 (M)**	**k_{app} × 10^4 (s^{-1})**	**k_p × 10^2 (M^{-1}·s^{-1})**	***n***
3	8	6.0 ± 0.1	5.3 ± 0.4	1.03 ± 0.02
	12	7.2 ± 0.1		
	16	11.3 ± 0.4		
	20	13.8 ± 0.2		
4	8	4.2 ± 0.1	4.6 ± 0.9	1.05 ± 0.04
	12	5.1 ± 0.4		
	16	7.3 ± 0.3		
	20	10.8 ± 0.3		

$P_s = 0.79$

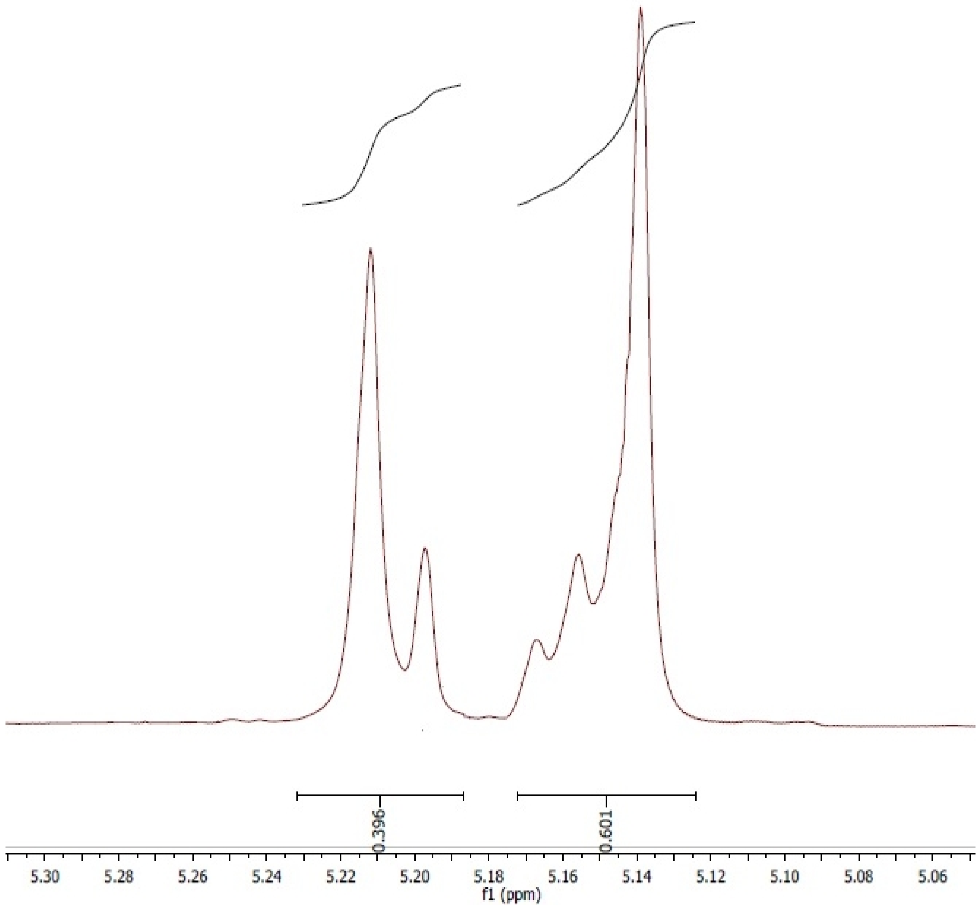


Figure S5. ^{1}H NMR spectrum (500 MHz, 298 K, $CDCl_3$) of the homodecoupled C*H* resonance of poly(*rac*-lactide) prepared employing $[Zn\{N(SiMe_3)_2\}\{(R,R)\text{-bpzmm}\}]$ (**5**) as initiator (Table 2, entry 12). The tacticity of the polymer was assigned using the methine signals with homonuclear decoupling as described by Hillmyer and co-workers.[2]

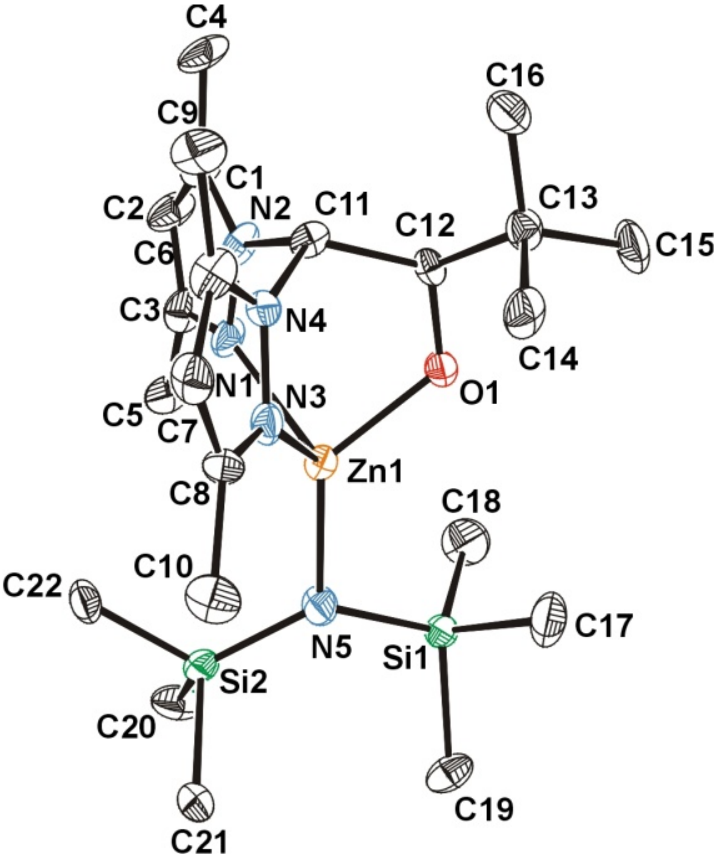


Figure S6. ORTEP view of the *S* enantiomer of [Zn{N(SiMe$_3$)$_2$}(bpzbe)] (**1**). Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

Table S3. Crystal data and structure refinement for **1**, **3** and **8·2.5C$_7$H$_8$**.

	1	**3**	**8·2.5C$_7$H$_8$**
Molecular formula	$C_{22}H_{43}N_5OSi_2Zn$	$C_{25}H_{41}N_5OSi_2Zn$	$C_{53.5}H_{84}ClN_9O_2Si_2Zn_2$
Formula weight	515.16	549.18	1107.66
Temperature (K)	230(2)	293(2)	230(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$C2/c$	$P\bar{1}$
a(Å)	12.364(1)	31.746(9)	11.503(5)
b(Å)	15.670(2)	10.760(4)	13.630(6)
c(Å)	15.710(2)	21.751(8)	21.074(10)
α(°)			86.10(1)
β(°)	112.720(7)	124.508(11)	78.53(1)
γ(°)			70.53(1)
Volume(Å^3)	2807.5(6)	6123(4)	3053(2)
Z	4	8	2
Density (calculated) (g/cm^3)	1.219	1.192	1.205
Absorption coefficient (mm^{-1})	0.982	0.905	0.912
F(000)	1104	2336	1178
Crystal size (mm^3)	0.23 × 0.19 × 0.13	0.23 × 0.19 × 0.15	0.31 × 0.22 × 0.19
Index ranges	$-14 \leq h \leq 14$ $-18 \leq k \leq 18$ $-10 \leq l \leq 18$	$-36 \leq h \leq 45$ $-10 \leq k \leq 15$ $-30 \leq l \leq 29$	$-13 \leq h \leq 12$ $-16 \leq k \leq 13$ $-25 \leq l \leq 25$
Reflections collected	19507	16774	29343
Independent reflections	4926	9022	9680

	[R(int) = 0.0903]	[R(int) = 0.0834]	[R(int) = 0.0877]
Data / restraints / parameters	4926 / 0 / 401	9022 / 0 / 318	9680 / 206 / 601
Goodness-of-fit on F^2	1.128	0.861	0.918
Final R indices [$I>2\sigma(I)$]	R1 = 0.1116 wR2 = 0.2680	R1 = 0.0634 wR2 = 0.1345	R1 = 0.0806 wR2 = 0.2161
Largest diff. peak / hole, e.Å^{-3}	1.184 and –0.653	0.295 and –0.361	1.100 and –0.925

Note and references

(1) (a) J. Baran, A. Duda, A. Kowalski, R. Szymanski and S. Penczek, *Macromol. Rapid Commun.*, 1997, **18**, 325; (b) I. Barakat, P. Dubois, R. Jérôme and P. Teyssié, *J. Polym. Sci. Pol. Chem.* 1993, **31**, 505.

(2) M. T. Zell, B. E. Padden, A. J. Paterick, K. A. M. Thakur, R. T. Kean, M. A. Hillmyer, E. J. Munson, *Macromolecules* 2002, **35**, 7700.