



**HAL**  
open science

## Post-Modification of Copolymers Obtained by ATRP for an Application in Heterogeneous Asymmetric Salen Catalysis

Erigene Bakangura, Philippe Roger, Rafaela S B Soares, Mohamed Mellah, Nadine Barroca-Aubry, Anne-Chantal Gouget-Laemmel, François Ozanam, Ludovic Costa, Jean-Pierre Baltaze, Emmanuelle Schulz

► **To cite this version:**

Erigene Bakangura, Philippe Roger, Rafaela S B Soares, Mohamed Mellah, Nadine Barroca-Aubry, et al.. Post-Modification of Copolymers Obtained by ATRP for an Application in Heterogeneous Asymmetric Salen Catalysis. *Molecules*, 2022, 27 (14), pp.4654. 10.3390/molecules27144654 . hal-03799839

**HAL Id: hal-03799839**

**<https://hal.science/hal-03799839>**

Submitted on 6 Oct 2022

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1 Type of the Paper (Article, Review, Communication, etc.)

# 2 Post-Modification of Copolymers Obtained by ATRP for an 3 Application in Heterogeneous Asymmetric Salen Catalysis

4 Erigene Bakangura,<sup>1,2</sup> Philippe Roger,<sup>1\*</sup> Rafaela S. B. Soares,<sup>1,2</sup> Mohamed Mellah,<sup>1</sup> Nadine Barroca-Aubry,<sup>1</sup>  
5 Anne-Chantal Gouget-Laemmel,<sup>2</sup> François Ozanam,<sup>2</sup> Ludovic Costa,<sup>1</sup> Jean-Pierre Baltaze<sup>1</sup> and Emmanuelle Schulz<sup>1\*</sup>

6 1 Institut de Chimie Moléculaire et des Matériaux d'Orsay, UMR 8182, Université Paris-Saclay, CNRS, Bâti-  
7 ment 420, 91405 Orsay Cedex, France

8 2 Laboratoire de Physique de la Matière Condensée, CNRS, Ecole Polytechnique, Institut Polytechnique de  
9 Paris, 91120 Palaiseau, France

10 Correspondence : philippe.roger@universite-paris-saclay.fr; emmanuelle.schulz@universite-paris-saclay.fr

11 **Abstract:** Copolymers are valuable supports for obtaining heterogeneous catalysts which allow  
12 their recycling and therefore substantial savings, particularly in the field of asymmetric catalysis.  
13 This contribution reports the use of two comonomers; Azido-3-propylmethacrylate (AZMA) bear-  
14 ing a reactive azide function was associated with 2-methoxyethyl methacrylate (MEMA), used as a  
15 spacer, for the ATRP synthesis of copolymers, then post-functionalized with a propargyl chromium  
16 salen complex. The controlled homopolymerization of MEMA by ATRP is firstly described and  
17 proves to be more controlled in molar mass than that of AZMA for conversions up to 63 %. The  
18 ATRP copolymerization of both monomers made it possible to control the molar masses and the  
19 composition, with nevertheless a slight increase in the dispersity (from 1.05 to 1.3) when the in-  
20 corporation ratio of AZMA increases from 10 to 50 mol%. These copolymers were  
21 post-functionalized with chromium salen units by click chemistry and their activity was evaluated  
22 in the asymmetric ring-opening of cyclohexene oxide with trimethylsilyl azide. At equal catalytic  
23 ratio, a significant increase in enantioselectivity was obtained by using the copolymer containing  
24 the largest part of salen units, probably allowing in this case a more favorable bimetallic activation  
25 of both the engaged nucleophile and electrophile. Moreover, the catalytic polymer was recovered  
26 by simple filtration and re-engaged in subsequent catalytic runs, up to seven times, without loss of  
27 activity or selectivity.

28 **Keywords:** Copolymerization; ATRP; Post-modification; Salen; Heterogeneous asymmetric cataly-  
29 sis

## 31 1. Introduction

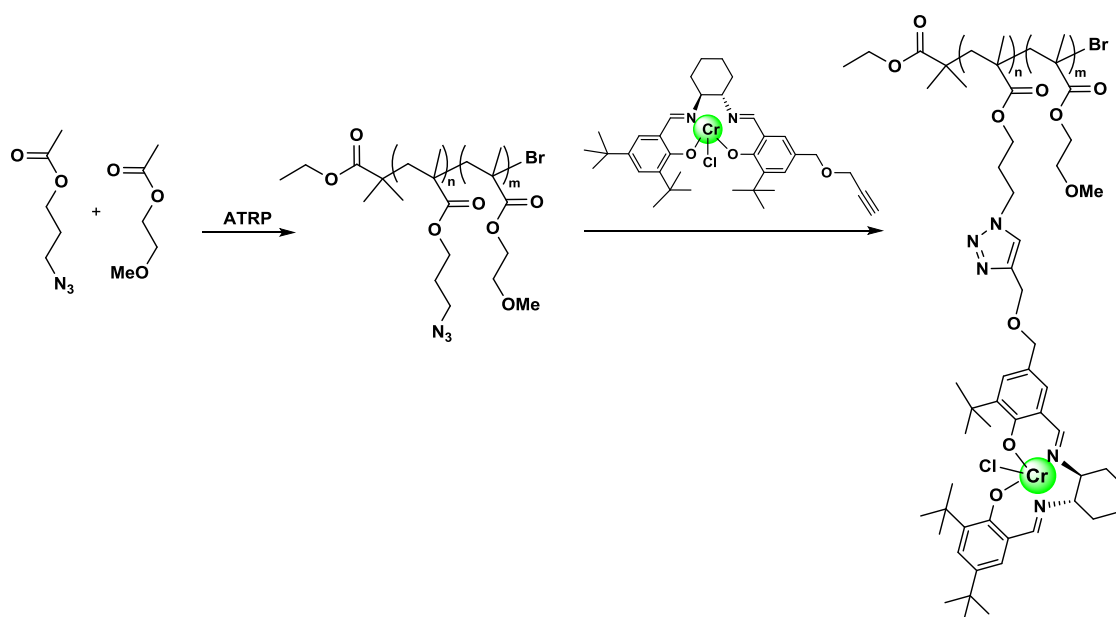
32 Chiral salen-type metal complexes are known for their catalytic activity allowing the  
33 preparation of scalemic building blocks. Associated with many metals (Cr, Cu, Co, Mn,  
34 Fe, ...), they promote the enantioselective catalytic formation of carbon-carbon or car-  
35 bon-heteroatom bonds with excellent efficiency both in terms of activity and selectivity  
36 [1]. The immobilization of such catalysts is currently particularly under study [2] to solve  
37 two problems; the anchoring of such complexes on a support allows on the one hand  
38 their easy separation at the end of the reaction with minimal contamination of the target  
39 products in metallic traces. On the other hand, their recovery being greatly facilitated by  
40 simple filtration, these robust salen complexes can be engaged again in asymmetric cat-  
41 alytic transformations, leading to an important increase of TON (turn over number).  
42 Beyond these two objectives, these immobilization procedures also target the association  
43 of these catalytic species in a controlled manner to favor, for example, reactions for which  
44 the excellence of the activity and of the enantioselectivity of the process is intimately

45 linked to the efficiency of the cooperativity of two metallic salt centers [3]. In these cases,  
46 indeed, a precise location of the active sites is foreseen to favor the activation of both the  
47 engaged electrophiles and nucleophiles by two metallic centers, to yield an intermediate  
48 possessing the optimized shape in the selectivity-determining transition state for the  
49 formation of enantioenriched products [4]. Towards this end, we wanted to exploit the  
50 controlled atom transfer radical polymerization (ATRP) process [5] implying  
51 salen-containing monomers to target uniform chain growth. A styrenyl-modified salen  
52 derivative has thus been prepared and engaged in ATRP to aim at controlling the co-  
53 polymerization of this monomer with styrene, in variable ratios between the two species  
54 [6]. Unfortunately, the control of the synthesis could only be obtained when the level of  
55 incorporation of the salen comonomer remained below 10%. After complexation with  
56 cobalt, these copolymers were able to achieve efficient cooperative activation, leading to  
57 the target product in high yields and enantioselectivities, when used as catalysts in the  
58 dynamic hydrolytic kinetic resolution of epibromohydrin. Despite its uncontrolled molar  
59 mass character, the copolymer containing the highest fraction of the salen unit showed to  
60 be the most effective in terms of enantioselectivity values, in accordance with easier ac-  
61 cess to cooperative catalysis under these conditions. The resulting catalytic materials  
62 were recycled to promote the same reaction, showing stability during their reuse for five  
63 cycles.

64 A different methodology is proposed here to master the control of polymerization  
65 with higher active species content for catalysis; the ATRP process is carried out in the  
66 presence of suitable monomers. This way, simple analytical techniques demonstrate the  
67 polymerization control whatever the proportion of catalytic monomers and the integra-  
68 tion of active enantioselective catalytic species by post-modification.

## 69 2. Results and Discussion

70 Our goal is to manage the synthesis of a functionalized polymer in a controlled way  
71 which can then be straightforwardly post-functionalized to deliver an active,  
72 enantioselective and heterogeneous catalyst to promote asymmetric transformations. A  
73 reaction of choice to study the influence of the controlled ATRP on a catalytic transfor-  
74 mation is the ring-opening reaction of *meso*-epoxides with trimethylsilylazide [7], a reac-  
75 tion for which dual bimetallic activation of each reactive partner is known to be of high  
76 importance to reach excellent activity and enantioselectivity. This demanding transfor-  
77 mation leads indeed interestingly to precursors of cyclic 1,2-amino alcohols and has been  
78 efficiently promoted by chiral chromium salen complexes [8] both in homogeneous and  
79 heterogeneous processes [9]. Such a strategy to use polymer methodologies to target the  
80 best composition and location of the catalytic entities has been investigated by the group  
81 of Jones for the preparation of polystyrene brushes containing cobalt salen complexes  
82 grafted either on silica or on superparamagnetic iron oxide nanoparticles, to evaluate the  
83 hydrolytic kinetic resolution of epibromohydrin [10]. Nevertheless, the expected con-  
84 trolled character of ATRP could not be definitely achieved. In this context, the proposed  
85 synthetic scheme (see Scheme 1) includes two steps: the first one is a copolymerization  
86 controlled by ATRP using a functional monomer, azido-3-propylmethacrylate (AZMA),  
87 in the presence of a spacer comonomer, 2-methoxyethyl methacrylate (MEMA). In a se-  
88 cond step, the chiral chromium salen complex carrying a propargyl function will then be  
89 directly incorporated by post-modification by click chemistry using the reactive azide  
90 functions of the AZMA units. Post-functionalization on 4-azidomethyl substituted poly-  
91 styrene by click chemistry with chiral *N*-salicylidene vanadyl(V) *tert*-leucinates has been  
92 previously reported by the group of Chen, with the resulting polymeric catalyst pro-  
93 moting the asymmetric aerobic oxidation of  $\alpha$ -hydroxy acid derivatives with both high  
94 efficiency and recycling ability [11].



**Scheme 1.** Synthetic route towards chiral chromium salen-containing controlled polymers.

### 2.1. ATRP homopolymerization

The copolymerization of AZMA and MEMA by ATRP was preceded by a kinetic study of the ATRP homopolymerization of each of the two aforementioned comonomers. The reaction conditions chosen are those used by Sumerlin *et al.* for the polymerization of AZMA with ethyl 2-bromoisobutyrate (eBiB) as initiator and anhydrous acetone containing 5 vol% diphenyl ether (DPE) as solvent at 50°C with [AZMA]:[eBiB]:[CuBr]:[bpy] = 200:1:1:2 [12].

We have first reproduced a kinetic study of the synthesis of polyAZMA between 1 h and 7 h and the criteria of controlled radical polymerization were indeed verified up to a monomer conversion of 51% (figures S3 and S4 in SI). A linear increase of  $-\ln(1-p)$  (with  $p$ , the monomer conversion in %) as a function of time was obtained with an apparent rate constant of  $0.11 \text{ h}^{-1}$  (figure S4 in SI). The experimental number-average molar mass  $M_n$  increased linearly as a function of the conversion  $p$  (%). But as observed on figure S3 in SI, these experimental  $M_n$  values are systematically higher than the theoretical  $M_n$  data, calculated thanks to the conversion determined by NMR. This can be explained by a possible side chain reaction of the azide function, giving rise to a wider distribution of molar masses. This is corroborated by the dispersity values obtained by SEC between 1.28 and 1.33 (figure S3 in SI), higher than those obtained by typical ATRP as previously reported [12].

A kinetic study of the ATRP synthesis of polyMEMA was then realized under the same conditions as those used for polyAZMA. To the best of our knowledge the kinetics of the controlled homopolymerization of MEMA has never been reported up to now despite the frequent use of this monomer in copolymerization reactions [13]. The kinetic results indicate that the polymerization satisfies all the criteria of a controlled polymerization in molar mass for polymerization times ranging from 1 h to 7 h up to a monomer conversion of 63%. The semi-logarithmic kinetic representation indicates an increase in  $\ln [M]_0/[M] = -\ln(1-p)$  as a function of time with an apparent rate constant of  $0.13 \text{ h}^{-1}$  (figure S4 in SI). Absolute number-average molar masses  $M_n$  obtained by SEC-MALS are close to the theoretical  $M_n$  calculated thanks to the conversion determined by NMR (see figure 1). As expected, the number-average molar mass  $M_n$  obtained by SEC linearly increases as a function of the conversion  $p$  (%). Finally, the SEC profiles (Figure 2.) show monomodal and narrow molar mass distributions with dispersities  $\mathcal{D}$  ( $M_w/M_n$ ) varying

95

96

97

98

99

100

101

102

103

104

105

106

107

108

109

110

111

112

113

114

115

116

117

118

119

120

121

122

123

124

125

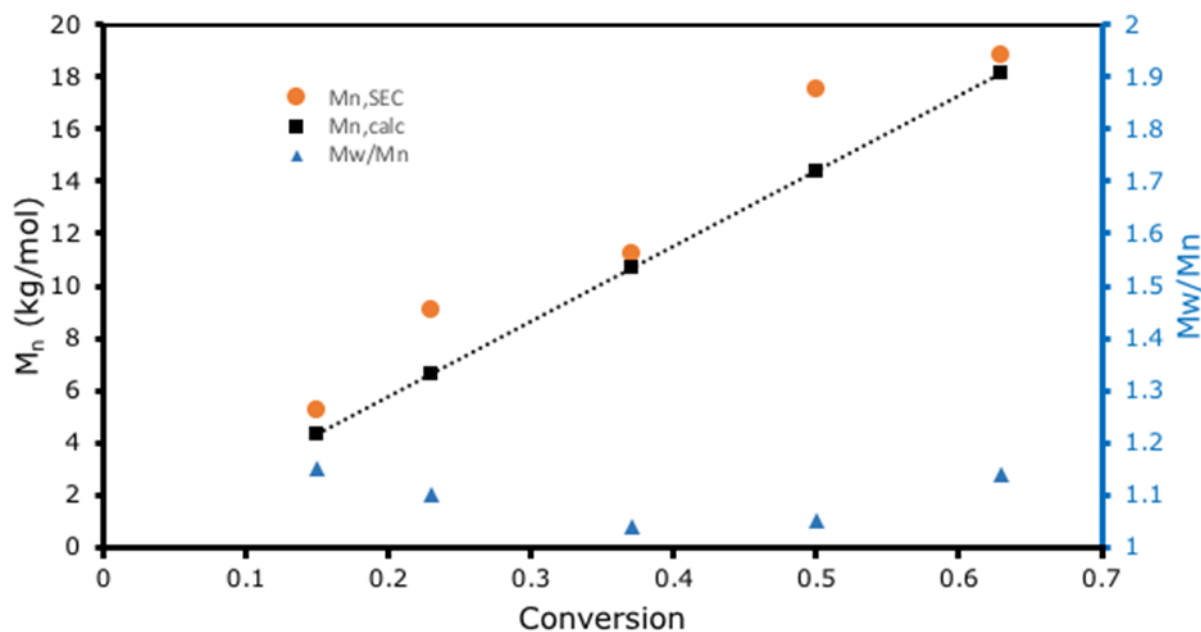
126

127

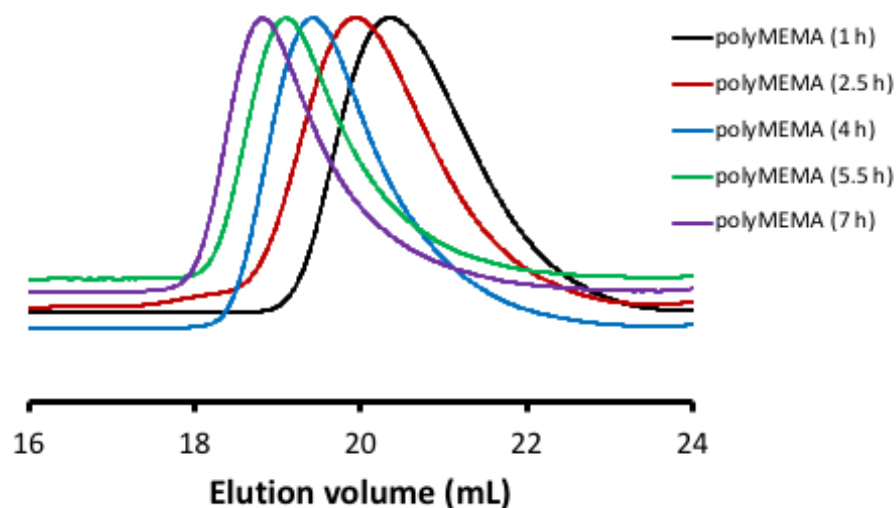
128

129  
130

between 1.04 and 1.14, characteristic of a controlled polymerization in molar mass for a conversion up to 63 %.

131  
132  
133

**Figure 1.** Experimental (Mn SEC) and theoretical (Mn calc) number-average molecular mass, and dispersity versus conversion for polyMEMA.

134  
135

**Figure 2.** SEC profiles of polyMEMA.

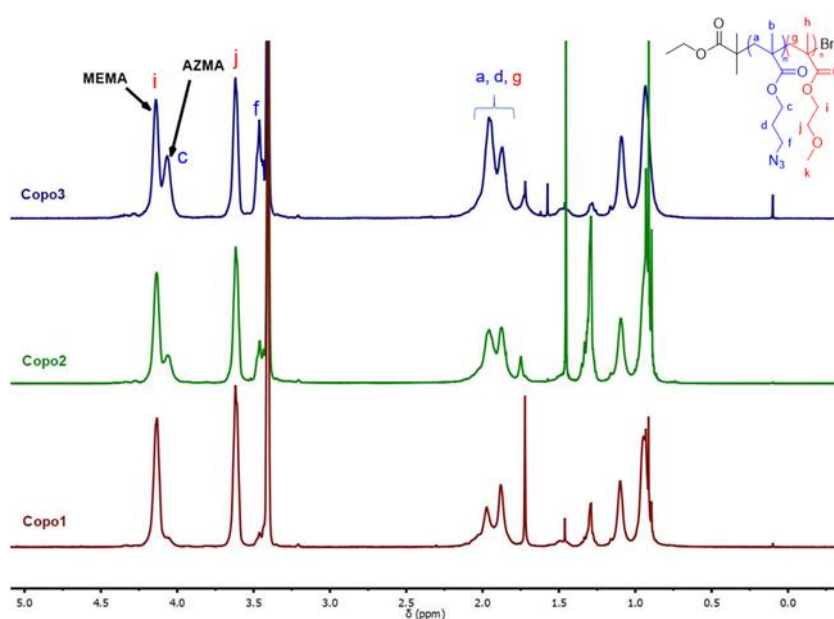
136  
137  
138  
139  
140  
141

Figure S4 in SI represents the semilogarithmic kinetic plots for the ATRP homopolymerizations of MEMA and AZMA with  $[\text{monomer}]:[\text{eBiB}]:[\text{CuBr}]:[\text{bpy}] = 200:1:1:2$ , in anhydrous acetone (with 5 vol% DPE) at 50 °C. This figure demonstrates that the apparent rate constants are very close ( $K_{\text{app}} = 0.13 \text{ h}^{-1}$  and  $0.11 \text{ h}^{-1}$ ). This indicates that both comonomers should be incorporated at the same rate during the copolymerization reaction, considering that the reactivity ratios of AZMA and MEMA are similar. This

142 must actually be the case given the fact that these two monomers have an identical  
143 chemical structure at the level of the polymerizable methacrylate function.

## 144 2.2. ATRP copolymerization

145 Considering these data, three copolymerizations were performed during 6 h under  
146 the same experimental conditions as before, with initial comonomer loadings  
147 MEMA/AZMA (mol %) of 90/10, 70/30 and 50/50 targeting approximately the same final  
148 comonomer incorporation in the copolymers. The obtained polymers are designated as  
149 Copo1, Copo2 and Copo3 in the remainder of the text, respectively.



152  
153 **Figure 3.** NMR spectra of copolymers.

154 NMR spectra (Figure 3) clearly demonstrate the difference in composition of the  
155 three copolymers. The complete assignment of the signals corresponding to the protons  
156 of each comonomer is to be found in figure S5 in the SI. Thus, the calculation of the ratio  
157 of the intensities of the two signals corresponding to the chemical shifts of the protons  
158 belonging respectively to AZMA ( $\delta_{\text{Hc}} = 4.02$  ppm) and to MEMA ( $\delta_{\text{Hi}} = 4.10$  ppm) leads to  
159 a percentage of AZMA incorporation of 6, 24 and 53%, close to the percentage of the  
160 comonomer feed composition which was 10, 30 and 50%, respectively. The signals lo-  
161 cated around 2 ppm correspond to the two methylene groups of each monomer in the  
162 backbone (Ha and Hg for AZMA and MEMA, respectively), together with the methylene  
163 (Hd) in the substituent of the AZMA monomer. The calculation made from the evolution  
164 of their intensities leads to similar results.

165 As can be observed in table 1, the composition of the copolymers obtained by NMR  
166 is also in agreement with the initial comonomer feed with values of 7, 22 and 40 %, re-  
167 spectively. There is an increase of 8, 11 and 20% in the incorporation of MEMA compared  
168 to its initial feed. This greater incorporation of MEMA relative to AZMA in the copoly-  
169 mer increases with conversion.

171 **Table 1.** Copolymerization of MEMA and AZMA in anhydrous acetone at 50 °C with 5 vol% DPE  
172 with  $[M]:[e\text{BiB}]:[\text{CuBr}]:[\text{bpy}] = 200:1:1:2$  for a polymerization time of 6 h.

Comonomer feed	Conversions <sup>a</sup>	$Mn_{\text{calc}}$ <sup>b</sup>	$Mn_{\text{SEC}}$ <sup>c</sup>	$\bar{D}$ <sup>c</sup>	Composition <sup>d</sup> M
----------------	--------------------------	---------------------------------	--------------------------------	------------------------	----------------------------

	MEMA/AZMA (%/%)	P <sub>MEMA</sub> /P <sub>AZMA</sub> (%/%)	(g/mol)	(g/mol)		EMA/AZMA (%/%)
<b>Copo1</b>	90/10	73/71	21300	22500	1.05	93/7
<b>Copo2</b>	70/30	64/61	19200	25700	1.20	78/22
<b>Copo3</b>	50/50	66/63	21200	30800	1.28	60/40

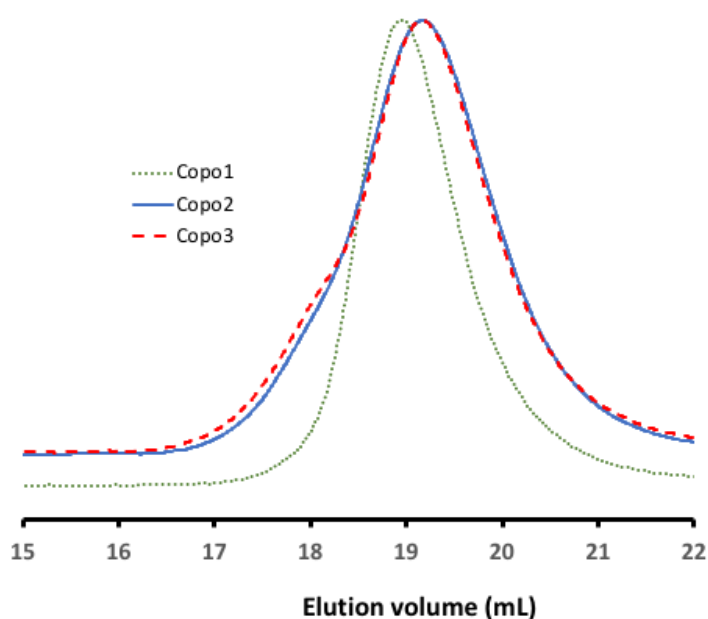
<sup>a</sup> Obtained from <sup>1</sup>H-NMR (see in SI, figure S1 (P<sub>AZMA</sub>) and figure S2 (P<sub>MEMA</sub>)).

<sup>b</sup> Calculated from NMR conversions :  $Mn_{calc} = M_{EtBriBu} + p_{MEMA} * M_0_{MEMA} * DP_{target(MEMA)} + p_{AZMA} * M_0_{AZMA} * DP_{target(AZMA)}$ .

<sup>c</sup> Obtained from SEC analysis.

<sup>d</sup> Obtained from NMR analysis of the copolymers (see SI, figure S5).

This observation is validated by the kinetic results obtained for the two homopolymers (see figure S4 in the SI). The increase in dispersity **D** from 1.05 to 1.28 is correlated with the composition of AZMA. The copolymerization reaction is indeed less controlled in molar mass when the initial percentage of AZMA is higher, which is consistent with homopolymerization results. The broader molar mass distributions of Copo2 and Copo3 are compared to the narrower molar mass distributions of Copo1 as observed by SEC profiles on figure 4. SEC profiles of all copolymers were unimodal, assessing the efficiency of the copolymerization versus homopolymerization. The discrepancy between the calculated number-average molar masses and the number-average molar masses obtained by SEC for Copo2 and Copo3 in table 1 can also be explained by the higher dispersity values obtained for higher AZMA content.



**Figure 4.** Evolution of SEC profiles of copolymers.

### 2.3. DOSY NMR experiments

DOSY experiments were also performed to provide further evidence for the efficiency of the copolymerization. In this type of experiment, a single translational diffusion coefficient is obtained if the copolymerization is quantitative. Otherwise, several diffusion coefficients would be found. For example, if two homopolymers are synthesized then two diffusion coefficients should be observed by DOSY NMR.

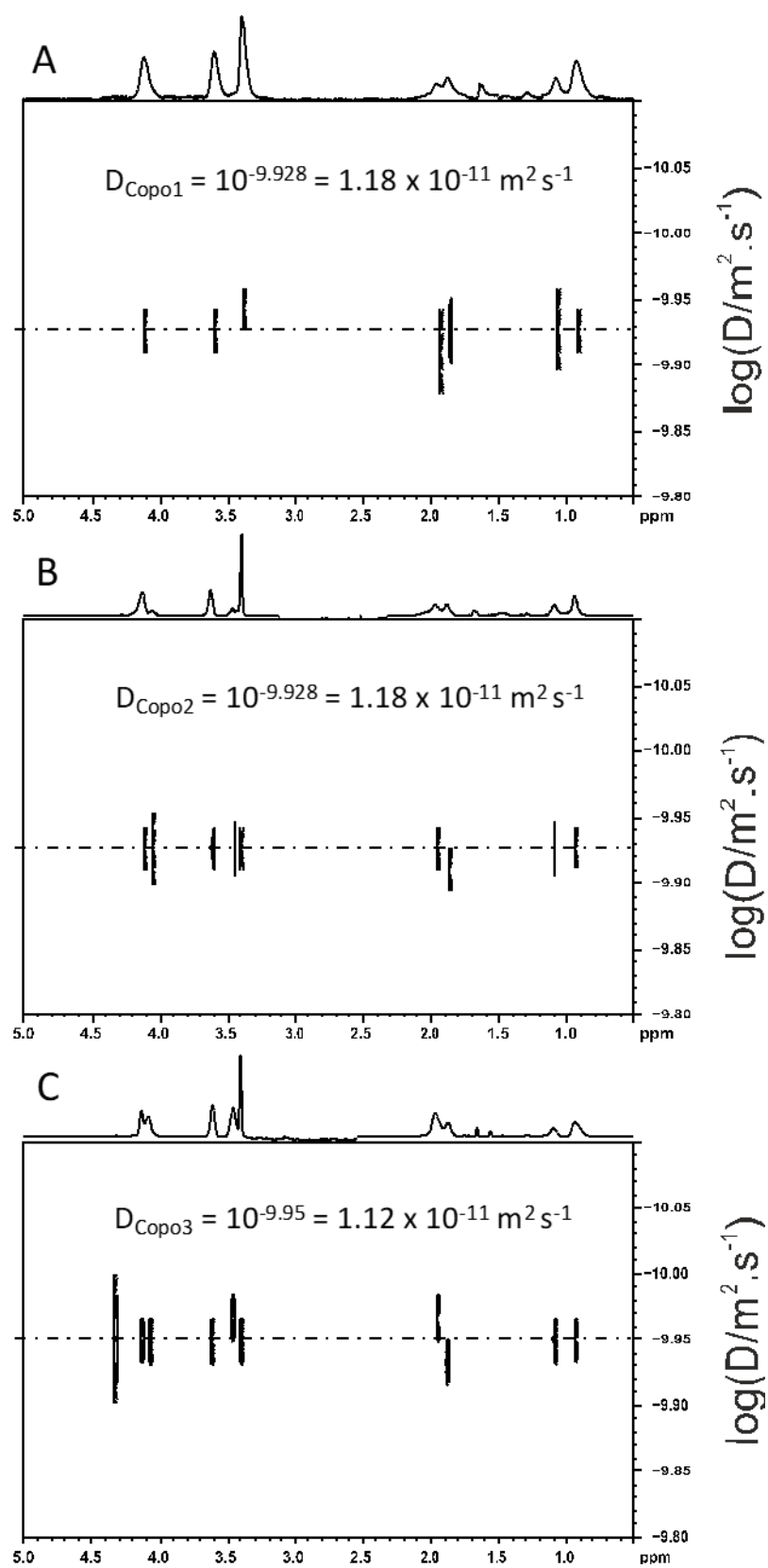


Figure 5. DOSY NMR of copolymers: A. Copo1, B. Copo2 and C. Copo3.

Figure 5 shows for each copolymer that all the NMR signals are correlated to a single value of the translational diffusion coefficient  $D$ . The values of  $D$  are identical for Copo1 and Copo2:  $D = 1.18 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$ . For Copo3, the value of  $D$  decreased down to  $D =$

199

200

201

202

203



1.12x10<sup>-10</sup> m<sup>2</sup>.s<sup>-1</sup>. These values are not significantly different (considering a precision of 10 % on the value of D). This result is not surprising given that the diffusion coefficient depends on the molar mass of the polymer:  $D \sim M^{-\nu}$  (with  $\nu$  a scaling law coefficient) and that in our case all three copolymers are expected to have a very similar molar mass (See Mn calc, table 1).

#### 2.4. IR Characterization

Chemical composition of the synthesized copolymers was also assessed by FTIR spectroscopy in the range of 4000 to 600 cm<sup>-1</sup> (figure 6). Mainly, the bands at 2950 and 2900 cm<sup>-1</sup> were associated with the stretching vibration modes of the CH<sub>2</sub> from aliphatic moieties. A strong azide stretching mode is observed at 2090 cm<sup>-1</sup>, and the C=O stretching mode is observed at 1725 cm<sup>-1</sup> and C-O at 1130 cm<sup>-1</sup>. The intensity of the azide band is clearly increasing with the AZMA content in the copolymers. To determine the AZMA content, the ratio of the transmittance of the azide band to the transmittance of the C=O band at 1725 cm<sup>-1</sup> can be considered because this last band is present in all methacrylate units (neglecting the C=O contribution of the initiator). Therefore, the ratio of the peaks intensities  $I(N_3)/I(CO)$  leads to a percentage of AZMA of 13:32:55 almost similar to the AZMA feed 10:30:50.

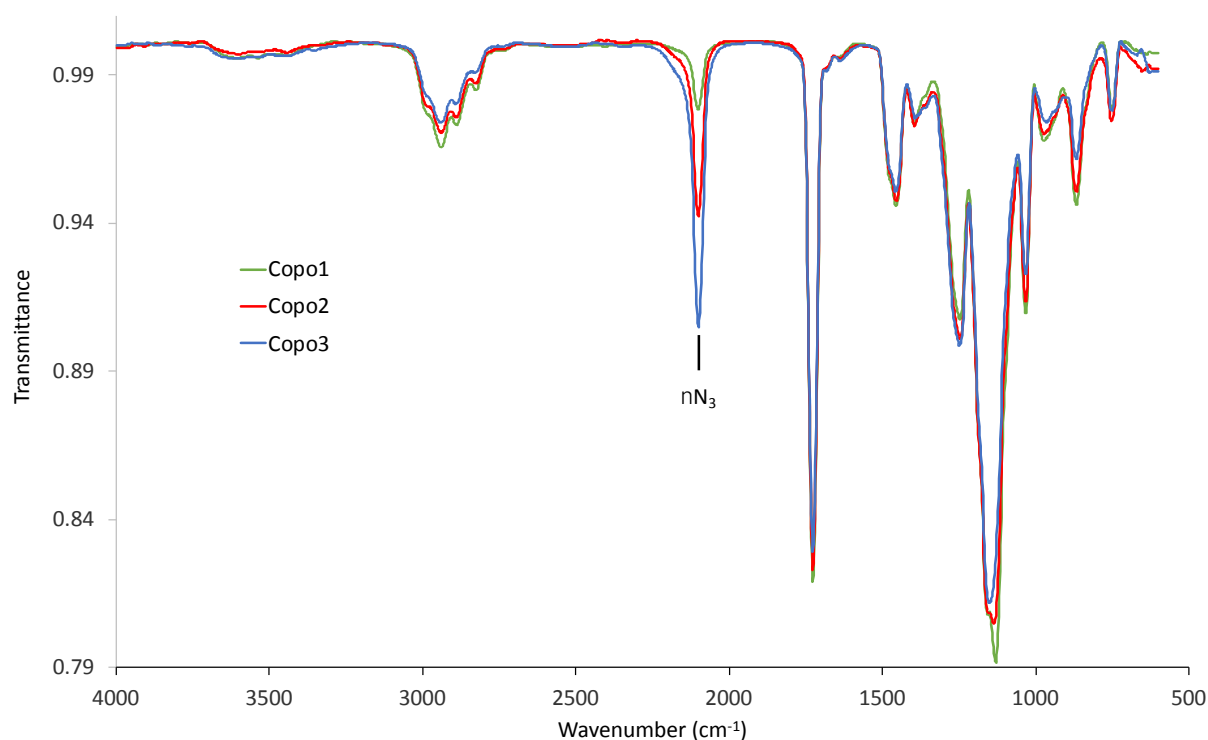


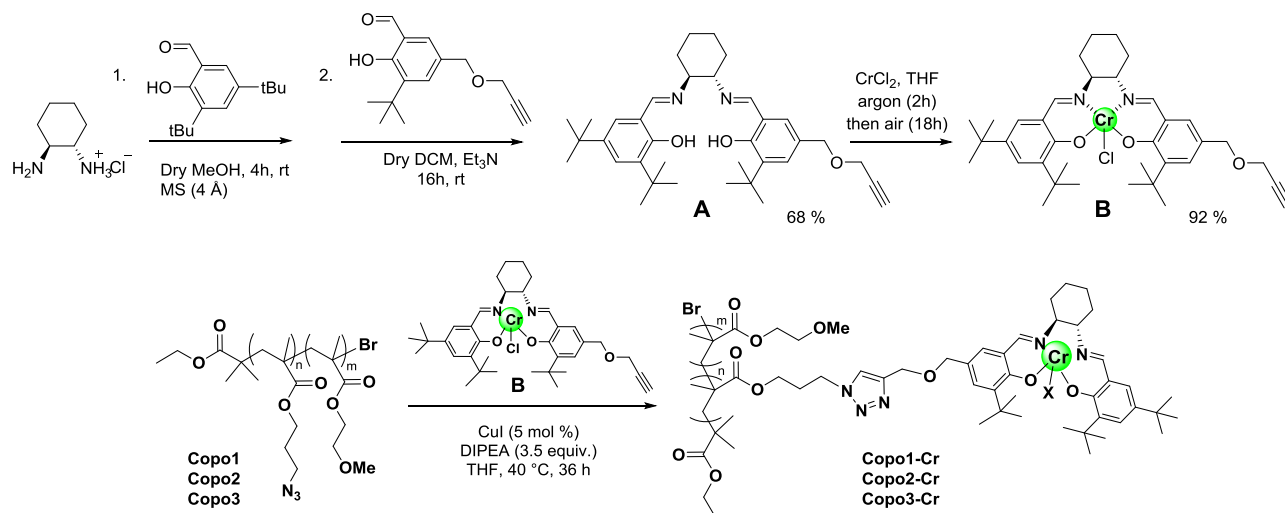
Figure 6. ATR-IR spectra of copolymers.

#### 2.5. Preparation of the chromium salen copolymer catalysts

With these three azide-functionalized copolymers in hands, a “clickable” enantioselective chromium catalyst was thus synthesized, following a two-step procedure. The procedure described by Weck *et al.* was reproduced to afford the enantiopure unsymmetrical salen ligand **A** [14]. This implies the prior preparation of the (1*S*,2*S*)-cyclohexane-1,2-diamine monoammonium salt [14] and of the 3-*tert*-butyl-2-hydroxy-5-((prop-2-ynoxy)methyl)benzaldehyde [11]. The novel targeted

232  
233  
234  
235

salen derivative was then isolated in 68 % yield (see Scheme 2). Insertion of chromium in the coordinating sites was finally performed from CrCl<sub>2</sub> in THF under argon atmosphere and then oxidation in air [15].



236  
237

**Scheme 2.** Chromium salen complex synthesis and click reactions with Copo1-3.

238  
239  
240  
241  
242  
243  
244  
245  
246  
247  
248  
249  
250  
251

Subsequent azide-alkyne Huisgen cycloadditions promoted by Cu(I) salts were conducted to react the propargyl-tagged chromium salen complex with the azide groups of all three copolymers [9f, 11], delivering in high yield the corresponding supported salen catalysts, as brown powders. Completion of this reaction was verified by FTIR spectroscopy, since the typical strong azide band at 2090 cm<sup>-1</sup> fully disappeared, at least for Copo1 and Copo2, after 36 hours of stirring at 40 °C (see figure 7 as illustration for Copo1, and figures S6 and S7 in SI). A residual band at 2090 cm<sup>-1</sup> is nevertheless still present for Copo3 indicating an incomplete Cr-salen addition. However, in each case, a peak at 1538 cm<sup>-1</sup> appears clearly, characteristic of a triazole-cycle deformation mode [16]. A new peak at 1622 cm<sup>-1</sup> is, moreover, visible, which can be attributed to the  $\nu$ C=N stretching vibration of the salen complex [7a]. The three supported catalysts were then recovered and thoroughly washed with an aqueous ethylenediamine tetracetic acid solution to remove residual copper salts, dried and further used as catalysts to promote the ring opening of cyclohexene oxide with trimethylsilylazide.

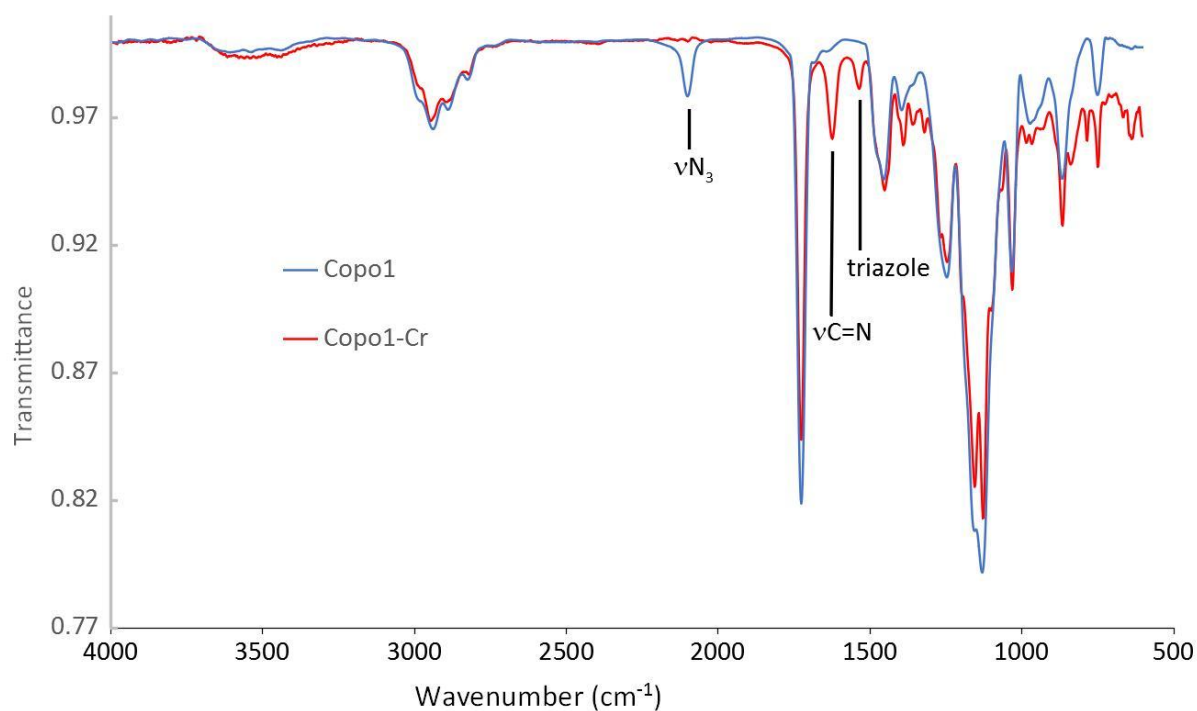
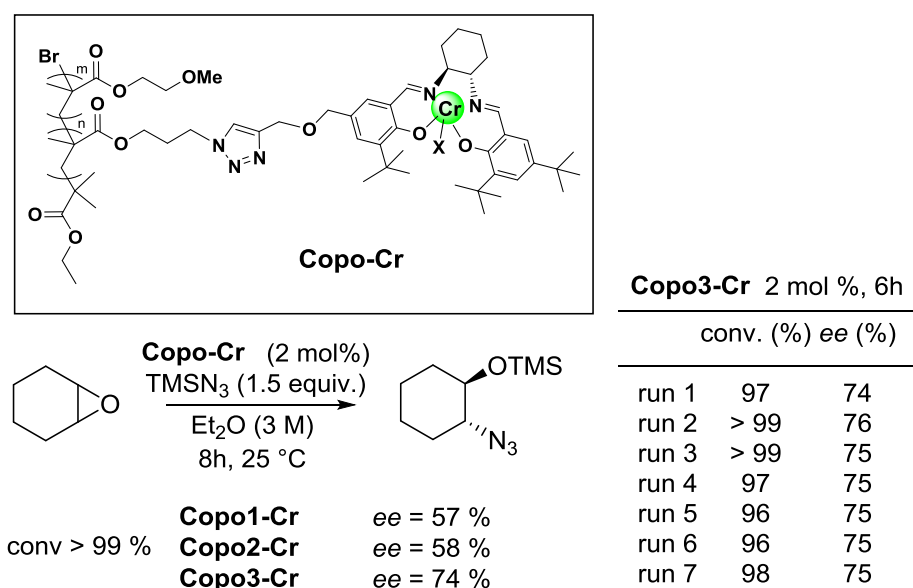


Figure 7. ATR-IR spectra of **Copo1** (in blue) and **Copo1-Cr** (in red).

### 2.6. Asymmetric heterogeneous catalysis

This catalytic reaction was performed in the presence of the supported catalysts containing 2 mol% of active sites relative to the engaged substrate, in diethylether, solvent in which the polymeric complexes are almost insoluble. When performed in our hands with the classical Jacobsen chromium catalyst, the ring-opened product was obtained with 88 % *ee*, but full conversion was not achieved after 24 h of reaction. This was further confirmed during the preparation of a racemic sample of ((2-azidocyclohexyl)oxy)trimethylsilane with a racemic Jacobsen chromium catalyst which only led to a conversion of 27% after 8 h of reaction. On the contrary, all attempts involving the use of the three Copo-Cr polymer complexes reached full conversion in only 8 h of reaction, under the same dilution conditions, indicating an efficient accelerating effect which is not usual in heterogeneous catalysis (Scheme 3) [17].



**Scheme 3.** Asymmetric ring opening of cyclohexene oxide in the presence of Copo-Cr catalysts.

This high activity was accompanied with variations in terms of enantioselectivity values, according to the composition of the catalyst. Indeed, the copolymers for which the catalyst is diluted by the presence of the MEMA units (Copo1-Cr and Copo2-Cr), delivered the ring-opened product in 57–58 % *ee*. Conversely, Copo3-Cr, which is supposed to contain an equivalent amount of MEMA units and catalytically active sites afforded the product with 74 % *ee*. We assume that this higher enantioselectivity is due to the enhanced possibility of performing a bimetallic activation, with two Cr-active sites placed in proximity to activate both the epoxide and the nucleophile.

The recyclability of this catalyst giving the best activity and selectivity values was then explored. As all the Copo-Cr species were insoluble in the reaction solvent, they were easily filtered from the reaction mixture, to be engaged in a next run with renewed addition of both substrates. This procedure was in particular tested in the presence of Copo3-Cr, for which the supernatant solution was recovered after a first run, carried out at room temperature for 6 h of reaction time, sufficient to obtain complete conversion. The catalyst was washed with diethylether at 0 °C, dried and reused in subsequent additional six runs (see table in Scheme 3). The second use of this recovered supported catalyst was also very efficient, as were subsequent ones, allowing 7 uses of the same batch of catalyst. Delightfully, both the activity of the catalyst and the enantioselectivity values of the recovered product have remained stable, at the exact level of the first cycle, *i.e.* a total conversion and an enantiomeric excess stable at 75 %.

### 3. Materials and Methods

#### 3.1. General Information

3-*tert*-butyl-2-hydroxybenzaldehyde, trioxane, (1*S*,2*S*)-1,2-cyclohexanediamine, HCl 1M in diethyl ether, tetrabutylammonium iodide (TBAI), sodium hydride (NaH) were purchased from Aldrich and used as received. 3-(*Tert*-butyl)-5-(chloromethyl)-2-hydroxybenzaldehyde[6] and (1*S*,2*S*)-1,2-cyclohexanediamine mono (hydrogen chloride)[13] were synthesized as described in previous published work. Dichloromethane, methanol, ethanol, diethyl ether were dried before use. Copper bromide was purified by treating it with glacial acetic acid and washed several times with ethanol absolute and diethyl ether. Diphenyl ether was dried on molecular sieves. The AZMA synthesis was performed according to a described procedure [12].

<sup>1</sup>H and <sup>13</sup>C NMR was recorded on Bruker AV360 spectrometer, operating at 360 MHz for <sup>1</sup>H NMR, and 90 MHz for <sup>13</sup>C NMR. Chemical shifts are reported downfield from CDCl<sub>3</sub> (δ: 7.26 ppm, for <sup>1</sup>H NMR and δ: 77.0 ppm for <sup>13</sup>C NMR) used as an internal reference. Data are represented as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz), integration. ESI-HRMS was detected on Bruker MicroTOF-Q daltonics spectrometer by electrospray ionization (ESI). GC analyses were performed on a Shimadzu GC 2010-plus using chiraldex β-PM column (50m\*0.25mm\*0.12μm) and hydrogen as carrier gas (isothermal 110 °C). Conversion was calculated using dodecane as internal standard. Attenuated Total Reflectance (ATR) FTIR was carried out on fine powder of the studied copolymers. Basically, the copolymer powder was deposited on the diamond crystal of an ATR module of Pike technologies and the infrared spectrum was recorded using a Bruker IFS 66 spectrometer. 200 scans of resolution 4 cm<sup>-1</sup> were recorded between 600 cm<sup>-1</sup> to 4000 cm<sup>-1</sup>. Spectra visualization and treatment were done using OPUS software; spectra integration was done using the built-in integration function of Origin® v8.0724. Size Exclusion Chromatography (SEC) analysis of polymers was carried out at 35°C using THF as eluent. Typically, the polymer solution was prepared at 4 mg.mL<sup>-1</sup> and then filtered through 0.45 μm PTFE filter to remove insoluble residues. The separation system includes one guard column (Malvern TGuard) and two separation columns: 1) Viscotek LC3000L (300 x 8.0 mm) and 2) ViscoGEL™ GM<sub>HH</sub> r-H (300 x 7.8 mm). The intensities were recorded using a refractive index (RI) detector (Walter 410) and a multi-angle light scattering (MALS) detector (Viscotek SEC-MALS 20). Absolute number and weight-average molar masses were calculated using OmniSec™ 5.12.467 software distributed by Malvern Panalytical. The refractive index increment (dn/dc) of 0.078 mL.g<sup>-1</sup> determined by Stejskal *et al.* for polyMEMA in THF at 546 nm was also used for polyAZMA based on roughly similar chemical structures [18].

### 3.2. Method for the synthesis of the alkyne-modified salen ligand and the corresponding chromium complex

#### Synthesis of 3-*tert*-butyl-2-hydroxy-5-((prop-2-ynyl)oxy)methyl)benzaldehyde

In a three-necked bottom flask, sodium hydride (60% dispersion in mineral oil, 1.5 eq, 7.96 mmol, 0.316 g) was suspended in 15 mL of dry THF under argon atmosphere. The solution was cooled down at 0°C in an ice bath. Propargyl alcohol (1.5 eq, 7.96 mmol, 463 μL) in 15 mL of dry THF was added dropwise, and the mixture was stirred at ambient temperature for 4 hours. The reaction mixture was cooled at 0°C and then 3-(*tert*-butyl)-5-(chloromethyl)-2-hydroxybenzaldehyde (1 eq, 5.30 mmol, 1.2 g) in 15 mL of dry THF was added dropwise and TBAI (0.03 eq, 0.16 mmol, 0.058 g) was added under argon atmosphere. The reaction mixture was allowed to stir while refluxing for 16 hours and was then cooled down at 0°C. Deionized water (2 mL) was slowly added. Solvents were removed under reduced pressure. The obtained residues were partitioned in dichloromethane (30 mL) and deionized water (30 mL). The aqueous layer was extracted two times by DCM (30 mL). The organic phase was combined, washed with brine solution (2 x 60 mL) and dried over MgSO<sub>4</sub>. After filtration and removal of solvents under reduced pressure, the crude product was purified by column chromatography (hexane/AcOEt; 19/1). The product was obtained as a brown viscous liquid (320 mg, 24 % yield). <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>): δ 11.80 (s, 1H), 9.87 (s, 1H), 7.51 (d, 1H, *J* = 2.0 Hz), 7.41 (d, 1H, *J* = 2.0 Hz), 4.56 (s, 2H), 4.20 (s, 2H), 2.49 (s, 1H), 1.42 (s, 9H). These data are identical to those previously described [11].

#### Synthesis of the salen ligand bearing a propargyl moiety

(1*S*,2*S*)-1,2-cyclohexanediamine mono(hydrogen chloride) (1 eq, 1 mmol, 150.6 mg), 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (1 eq, 1 mmol, 234.3 mg) and molecular sieve (4 Å, 0.83 g) were charged into a Schlenk tube. The tube was then evacuated three times and

filled with argon. Under argon atmosphere, 9 mL of anhydrous methanol were added, and the mixture was stirred at room temperature for 4 hours. A solution of 3-*tert*-butyl-2-hydroxy-5-((prop-2-ynoxy) methyl)benzaldehyde (1.1 eq, 1.1 mmol, 273 mg) in 9 mL of dried dichloromethane and 0.42 mL of anhydrous triethylamine (3 eq, 3 mmol) was added to the above mixture and was stirred at room temperature for 18 hours. The reaction mixture was filtered through a short pad of celite and flushed with anhydrous dichloromethane. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel (hexane/AcOEt/Et<sub>3</sub>N: 95/5/1) to afford the title product as a yellow powder (382 mg, 68% yield). <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>): δ 14.02 (s, 1H), 13.69 (s, 1H), 8.31 (s, 1H), 8.30 (s, 1H), 7.33 (d, *J* = 2.5 Hz, 1H), 7.25 (d, *J* = 2.1 Hz, 1H), 7.03 (d, *J* = 2.1 Hz, 1H), 6.99 (d, *J* = 2.5 Hz, 1H), 4.47 (s, 2H), 4.11 (d, *J* = 2.4 Hz, 2H), 3.34 (m, 2H), 2.45 (t, *J* = 2.4 Hz, 1H), 2.00–1.87 (m, 4H), 1.81–1.71 (m, 2H), 1.55–1.46 (m, 2H), 1.44 (s, 9H), 1.43 (s, 9H), 1.25 (s, 9H). <sup>13</sup>C NMR (90 MHz, CDCl<sub>3</sub>): δ 166.01, 165.38, 160.44, 158.05, 140.03, 137.44, 136.46, 130.14, 129.93, 126.95, 126.10, 126.07, 118.40, 117.86, 79.89, 74.63, 72.56, 72.48, 71.56, 56.76, 35.08, 34.89, 34.14, 33.28, 31.54, 29.55, 29.43, 24.44. FTIR (cm<sup>-1</sup>): 3299; 2952; 2865; 2093; 1627; 1448; 1360; 1263; 1206; 1168; 1087; 1036; 979; 936; 870; 776; 708; 652. HRMS (M+H<sup>+</sup>): calc for C<sub>36</sub>H<sub>51</sub>N<sub>2</sub>O<sub>3</sub>; 559.3894 found for C<sub>36</sub>H<sub>51</sub>N<sub>2</sub>O<sub>3</sub>: 559.3864.

### Synthesis of the chromium salen complex bearing a propargyl moiety

A solution of the salen ligand (1eq, 0.358 mmol, 200 mg) in dry, degassed THF (5 mL) was assessed to a solution of anhydrous CrCl<sub>2</sub> (1.15 eq, 0.538 mmol, 66 mg) in dry, degassed THF (8 mL). The resulting brown solution was stirred under argon for 2 hours and then in air for additional 18 hours. The solution was then diluted with dichloromethane and washed with saturated NH<sub>4</sub>Cl and brine. The organic phase was dried over anhydrous MgSO<sub>4</sub>, and filtered. The solvent was removed under reduced pressure to afford the salen complex as a brown powder (213 mg, 92 % yield). FTIR (cm<sup>-1</sup>): 3306, 2950, 2868, 2093, 1622, 1538, 1440, 1392, 1350, 1319, 1250, 1203, 1166, 1078, 1031, 971, 924, 871, 828, 787, 742, 665. HRMS (M-Cl): calc for C<sub>36</sub>H<sub>48</sub>CrN<sub>2</sub>O<sub>3</sub>; 608.3070; found for C<sub>36</sub>H<sub>48</sub>CrN<sub>2</sub>O<sub>3</sub>: 608.3029.

### 3.3. General procedure for the homopolymerization: Poly(MEMA) synthesis

A mixture of dry acetone (3 mL) and diphenyl ether (DPE) (0.2 mL) was deoxygenated in a Schlenk tube by 5 freeze-pump-thaw cycles. CuBr (0.005 eq, 0.15 mmol, 21.4 mg) and 2,2'-bipyridine (bpy) (0.01 eq, 0.30 mmol, 46.8 mg) were added under argon atmosphere. Vacuum was applied followed by 3 freeze-pump-thaw cycles. Concomitantly, 2-methoxyethyl methacrylate (MEMA) was passed through an Al<sub>2</sub>O<sub>3</sub> column to remove inhibitors, then, degassed by argon gas bubbling followed by 3 freeze-pump-thaw cycles. To the mixture containing acetone/DPE/CuBr/bpy, MEMA (1 eq, 30.00 mmol, 4.3 g) was added using inert syringe techniques. Two cycles of vacuum and argon flow were applied and the mixture was placed to a preheated oil bath at 50 °C. While stirring, ethyl 2-bromoisobutyrate (eBiB) (0.005 eq, 0.125 mmol, 18 μL) was added. The mixture was allowed to stir for 6 hours and periodically samples were taken in between for kinetics study. After completion of the reaction, the mixture was dissolved in DCM and filtered through a short column of Al<sub>2</sub>O<sub>3</sub>. The solvent was then removed under reduced pressure and the polymer was precipitated in cold methanol under stirring. For the NMR studies, the sample taken from the reaction was immediately solubilized in CDCl<sub>3</sub> and then filtered in a small pipette plugged with cotton and filled with Al<sub>2</sub>O<sub>3</sub> to remove the CuBr. (Figure S2 in SI shows the NMR of PolyMEMA synthesis at partial conversion at T5). The following proton NMR description only describes the signals for the polymer: <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>) δ 4.09 (s, 2H), 3.58 (s, 2H), 3.36 (s, 3H), 1.84 (s, 2H), 1.09 and 0.91 (2 bs, 3H). For poly(AZMA) synthesis, see SI.

### 3.4. General procedure for the copolymerization

A mixture of dry acetone (3 mL) and DPE (0.5 mL) were degassed in a Schlenk tube by 5 freeze-pump-thaw cycles. Concomitantly, MEMA was passed through an Al<sub>2</sub>O<sub>3</sub> column to remove inhibitors. Then, a mixture of MEMA (see quantity indicated below) and 3-azidopropyl methacrylate (AZMA) (see quantity indicated below) was degassed in a Schlenk tube by 3 freeze-pump-thaw cycles. Over the acetone/DPE mixture, CuBr (see quantity indicated below) and bpy (see quantity indicated below) were added under argon atmosphere. The MEMA and AZMA mixture was subsequently added using inert syringe techniques. Three new freeze-pump-thaw cycles were applied to the mixture, and then it was placed to a preheated oil bath at 50 °C. While stirring, eBiB (see quantity indicated below) was added. The mixture was allowed to stir for 6 hours and periodically samples were taken in between for kinetics study.

**Copo1; MEMA90-co-AZMA10**

2-methoxyethyl methacrylate (0.90 eq, 20.00 mmol, 2.88 g), 3-azidopropyl methacrylate (0.10 eq, 2.20 mmol, 0.37 g), CuBr (0.005 eq, 0.11 mmol, 0.016 g), bpy (0.01 eq, 0.22 mmol, 0.035 g), and eBiB (0.005 eq, 0.11 mmol, 15.9 µL). Isolated yield 87 %

**Copo2; MEMA70-co-AZMA30**

2-methoxyethyl methacrylate (0.7 eq, 19.00 mmol, 2.73 g), 3-azidopropyl methacrylate (0.30 eq, 8.10 mmol, 1.37 g), CuBr (0.005 eq, 0.135 mmol, 0.019 g), bpy (0.01 eq, 0.27 mmol, 0.042 g), and eBiB (0.005 eq, 0.135 mmol, 19.6 µL). Isolated yield 86 %

**Copo3; MEMA50-co-AZMA50**

2-methoxyethyl methacrylate (0.5 eq, 11 mmol, 1.58 g), 3-azidopropyl methacrylate (0.5 eq, 11 mmol, 1.86g), CuBr (0.005 eq, 0.11 mmol, 0.016 g), bpy (0.01 eq, 0.22 mmol, 0.035 g), and eBiB (0.005 eq, 0.11 mmol, 15.9 µL). Isolated yield 83 %

*3.5. General procedure for the post-modification by azide-alkyne Huisgen cycloaddition*

Poly(MEMAn-co-AZMAm) and Salen B were dissolved in 5 mL of degassed dry THF in a Schlenk tube. This mixture was then degassed by 3 freeze-pump-thaw cycles. Over this frozen mixture during the last cycle, CuI was added and let to dissolve under vacuum. *N,N*-diisopropylethylamine (DIPEA) was added under argon atmosphere. The mixture was placed to a preheated oil bath at 40 °C for 36 hours, in constant stirring. Then, 30 mL of dry THF were added to the mixture, and it was filtered through Al<sub>2</sub>O<sub>3</sub> column chromatography. The solvent was removed under reduced pressure and the product was precipitated in excess of hexane. The product was filtered, washed with hexane, and dried under vacuum. The method for calculating the quantity of each of the species to be introduced is detailed in the SI, for obtaining Copo1-Cr, Copo2-Cr and Copo3-Cr.

*3.6. Catalytic procedure (ARO reaction) in heterogeneous conditions*

A tube was charged with the considered Copox-Cr (2 mol%) and maintained under argon. Diethyl ether (300 µL), cyclohexene oxide (0.305 mmol), and dodecane as internal standard (20 µL) were then added. The reaction mixture was stirred for 10 minutes at 25°C before adding the trimethylsilyl azide (60 µL, 0.458 mmol), and then stirred for 6 hours. A sample was prepared to calculate conversion by GC (and ee). The supported catalyst was washed with diethyl ether (15 mL) at 0°C, filtered and dried in the tube for its reuse. (((1*R*,2*R*)-2-azidocyclohexyl)oxy)trimethylsilane; <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>) δ (ppm): 3.46-3.40 (m, 1H), 3.22-3.14 (m, 1H), 1.95-1.84 (m, 2H), 1.70-1.60 (m, 2H), 1.41-1.12 (m, 4H), 0.16 (s, 9H). These analytical data are in accordance with reported ones [19]. The ee was determined by chiral GC (isothermal 110°C), which resolved both enantiomers (tr<sub>maj</sub>= 10.90 min, tr<sub>min</sub>= 11.29 min). The absolute stereochemistry was assigned as (1*R*,2*R*) based on comparison with the literature [7a]. The method for calculating the quantity of Copox-Cr to be introduced is detailed in the SI.

## 4. Conclusions

452  
453 In summary, we have described the controlled copolymerization of AZMA and  
454 MEMA by ATRP and demonstrated the efficiency of this procedure up to an equimolar  
455 mixture of the two monomers. A preliminary rigorous study of the monomers  
456 homopolymerization has indeed indicated that the kinetics of transformation of both  
457 species remained similar for the control of the molar mass and the composition. The ob-  
458 tained copolymers were carefully characterized thanks to  $^1\text{H}$  NMR and SEC analyses.  
459 NMR DOSY experiments further confirmed the efficiency of the procedure since unique  
460 and close values for the diffusion coefficients were obtained, in each case. FTIR analyses  
461 before and after click reaction of the azide functionalities with the alkyne-substituted  
462 chiral chromium salen complex firstly confirmed the AZMA content in each copolymer  
463 and secondly demonstrated the quantitative formation of the triazole ring, at least for the  
464 two copolymers with the lowest AZMA ratio. Under the same experimental conditions,  
465 the copolymer with the highest AZMA content led to an incomplete Cr-salen addition.  
466 Each copolymer was engaged as a heterogeneous catalyst to promote asymmetric  
467 aminolysis of cyclohexene oxide with  $\text{TMSN}_3$  at a low catalyst loading (2 mol%) and  
468 provided the targeted open product in almost quantitative yield at room temperature,  
469 whatever its composition is. These heterogeneous catalysts appear more active than their  
470 homogeneous analogues, even if the enantioselectivity values remain lower. Neverthe-  
471 less, the highest selectivity of the series (74 % *ee*) was reached by using Copo3, in which  
472 the active sites proportion is the largest, conditions for which bimetallic catalysis is most  
473 favorable. As an insoluble species, Copo3 was also easily recovered by filtration and re-  
474 committed to catalysis after solvent washing, drying and further addition of substrates.  
475 This procedure could be repeated 7 times to produce the target compound with particu-  
476 larly stable values in terms of activity and enantioselectivities. The post-modification of  
477 copolymers obtained by ATRP by chiral organometallic complexes therefore makes it  
478 possible to obtain high-value insoluble asymmetric catalysts, with the control of the  
479 composition opening the way to the preparation of tailor-made polymetallic catalysts for  
480 applications in the innovative field of asymmetric heterogeneous multicatalysis.

481 **Supplementary Materials:** synthesis and catalysis details, kinetics results, copolymers characteri-  
482 zation, NMR spectra, GC chromatograms are available on line at...

483 **Author Contributions:** methodology, E.B.; R.S.B.S.; M.M.; N.B.-A.; conceptualization, P.R.;  
484 A.-C.G.-L.; F.O.; E.S.; analysis, J.-P.B.; L.C.; writing—original draft preparation, P.R.; R.S.B.S.; E.S.;  
485 writing—review and editing, all authors; supervision, P.R.; E.S. All authors have read and agreed  
486 to the published version of the manuscript.

487 **Funding:** This research was funded by Charm3At LabEx (ANR-11-LABEX-0039).

488 **Institutional Review Board Statement:** Not applicable.

489 **Informed Consent Statement:** Not applicable.

490 **Data Availability Statement:** Data are contained within the article and Supplementary Materials.

491 **Acknowledgments:** The authors acknowledge Université Paris Saclay, CNRS, Ecole Polytechnique  
492 and Charm3At LabEx for financial support. This article is dedicated to Henri B. Kagan for his out-  
493 standing contribution to asymmetric catalysis and organometallic chemistry.

494 **Conflicts of Interest:** The authors declare no conflict of interest.

## 495 References

- 496 1. a) Cozzi, P. G. Metal–Salen Schiff Base Complexes in Catalysis: Practical Aspects. *Chem. Soc. Rev.* **2004**, *33*, 410–421; b) Shaw, S.; White,  
497 J. D. Asymmetric Catalysis Using Chiral Salen–Metal Complexes: Recent Advances. *Chem. Rev.* **2019**, *119*, 9381–9426.
- 498 2. a) Baleizão, C.; Garcia, H. Chiral Salen Complexes: An Overview to Recoverable and Reusable Homogeneous and Heterogeneous Cata-  
499 lysts. *Chem. Rev.* **2006**, *106*, 3987–4043; b) Zulauf, A.; Mellah, M.; Hong, X.; Schulz, E. Recoverable Chiral Salen Complexes for Asym-  
500 metric Catalysis: Recent Progress. *Dalton Trans.* **2010**, *39*, 6911–6935; c) Abd El Sater, M.; Jaber, N.; Schulz, E. Chiral Salen Complexes for  
501 Asymmetric Heterogeneous Catalysis: Recent Examples for Recycling and Cooperativity. *ChemCatChem* **2019**, *11*, 3662–3687.



- 502 3. a) Konsler, R. G.; Karl, K.; Jacobsen, E. N. Cooperative Asymmetric Catalysis with Dimeric Salen Complexes. *J. Am. Chem. Soc.* **1998**,  
503 120, 10780-10781; b) Belsler, T.; Jacobsen, E. N. Cooperative Catalysis in the Hydrolytic Kinetic Resolution of Epoxides by Chiral  
504 [(salen)Co(III)] Complexes Immobilized on Gold Colloids. *Adv. Synth. Catal.* **2008**, 350, 967-971; c) Loy, R. N.; Jacobsen, E. N.  
505 Enantioselective Intramolecular Openings of Oxetanes Catalyzed by (Salen)Co(III) Complexes: Access to Enantioenriched  
506 Tetrahydrofurans. *J. Am. Chem. Soc.* **2009**, 131, 2786-2787; d) Haak, R. M.; Martinez Belmonte, M.; Escudero-Adan, E. C.;  
507 Benet-Buchholz, J.; Kleij, A. W. Olefin Metathesis as a Tool for Multinuclear Co(III)salen Catalyst Construction: Access to Cooperative  
508 Catalysts. *Dalton Trans.* **2010**, 39, 593-602.
- 509 4. Nielsen, L. P. C.; Stevenson, C. P.; Blackmond, D. G.; Jacobsen, E. N. Mechanistic Investigation Leads to a Synthetic Improvement in the  
510 Hydrolytic Kinetic Resolution of Terminal Epoxides. *J. Am. Chem. Soc.* **2004**, 126, 1360-1362.
- 511 5. a) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashiruma, T. Polymerization of Methyl Methacrylate with the Carbon  
512 Tetrachloride/Dichlorotris-(triphenylphosphine)ruthenium(II)/Methylaluminum Bis(2,6-di-tert-butylphenoxide) Initiating System:  
513 Possibility of Living Radical Polymerization. *Macromolecules* **1995**, 28, 1721-1723; b) Wang, J.-S.; Matyjaszewski, K.  
514 Controlled/"Living" Radical Polymerization. Atom Transfer Radical Polymerization in the Presence of Transition-Metal Complexes. *J. Am.*  
515 *Chem. Soc.* **1995**, 117, 5614-5615.
- 516 6. Zidelmal, N.; Aubry-Barroca, N.; Lepoittevin, B.; Mellah, M.; Costa, L.; Ozanam, F.; Gouget-Laemmel, A.-C.; Schulz, E.; Roger, P.  
517 Synthesis, Characterization and Catalytic Properties of Salen-Containing Polymers Obtained by Atom Transfer Radical Polymerization.  
518 *Polymer* **2018**, 135, 261-270.
- 519 7. a) Martínez, L. E.; Leighton, J. L.; Carsten, D. H.; Jacobsen, E. N. Highly Enantioselective Ring Opening of Epoxides Catalyzed by  
520 (salen)Cr(III) Complexes. *J. Am. Chem. Soc.* **1995**, 117, 5897-5898; b) Schaus, S. E.; Larrow, J. F.; Jacobsen, E. N. Practical Synthesis of  
521 Enantiopure Cyclic 1,2-Amino Alcohols via Catalytic Asymmetric Ring Opening of Meso Epoxides. *J. Org. Chem.* **1997**, 62, 4197-4199.
- 522 8. Bandini, M.; Cozzi, P. G.; Umani-Ronchi, A. [Cr(Salen)] as a 'Bridge' between Asymmetric Catalysis, Lewis Acids and Redox Processes.  
523 *Chem. Commun.* **2002**, 919-927.
- 524 9. a) Dioso, B. M. L.; Jacobs, P. A. Heterogenisation of Dimeric Cr(salen) with Supported Ionic Liquids. *J. Catal.* **2006**, 243, 217-219; b)  
525 Zulauf, A.; Mellah, M.; Schulz, E. Original Use of the Same Heterogeneous Chiral Catalyst Batch to Promote Different Asymmetric  
526 Reactions. *Chem. Commun.* **2009**, 6574-6576; c) Bergbreiter, D. E.; Hobbs, C.; Chayanant, C. Polyolefin-Supported Recoverable/Reusable  
527 Cr(III)-Salen Catalysts. *J. Org. Chem.* **2011**, 76, 523-533; d) Xia, Q.; Liu, Y.; Li, Z.; Gong, W.; Cui, Y. A Cr(salen)-Based Metal–Organic  
528 Framework as a Versatile Catalyst for Efficient Asymmetric Transformations. *Chem. Commun.* **2016**, 52, 13167-13170; e) Jiao, J.; Tan, C.;  
529 Li, Z.; Liu, Y.; Han, X.; Cui, Y. Design and Assembly of Chiral Coordination Cages for Asymmetric Sequential Reactions. *J. Am. Chem.*  
530 *Soc.* **2018**, 140, 2251-2259; f) Abd El. Sater, M.; Mellah, M.; Dragoe, D.; Kolodziej, E.; Jaber, N.; Schulz, E. Chiral Chromium  
531 Salen@rGO as Multipurpose and Recyclable Heterogeneous Catalyst. *Chem. Eur. J.* **2021**, 27, 9454-9460.
- 532 10. a) Gill, C. S.; Venkatasubbaiah, K.; Phan, N. T. S.; Weck, M.; Jones, C. W. Enhanced Cooperativity Through Design: Pendant  
533 Co(III)-salen Polymer Brush Catalysts for the Hydrolytic Kinetic Resolution of Epichlorohydrin  
534 (salen=*N,N'*-bis(salicylidene)ethylenediamine dianion). *Chem. Eur. J.* **2008**, 14, 7306-7313; b) Gill, C. S.; Long, W.; Jones, C. W.  
535 Magnetic Nanoparticle Polymer Brush Catalysts: Alternative Hybrid Organic/Inorganic Structures to Obtain High, Local Catalyst  
536 Loadings for Use in Organic Transformations. *Catal. Lett.* **2009**, 131, 425-431.
- 537 11. Salunke, S. B.; Babu, N. S.; Chen, C. -T. Asymmetric Aerobic Oxidation of  $\alpha$ -Hydroxy Acid Derivatives Catalyzed by Reusable,  
538 Polystyrene-Supported Chiral *N*-Salicylidene Oxidovanadium *tert*-Leucinates. *Adv. Synth. Catal.* **2011**, 353, 1234-1240.
- 539 12. Sumerlin, B. S.; Tsarevsky, N. V.; Louche, G.; Lee, R. Y.; Matyjaszewski, K. Highly Efficient "Click" Functionalization of  
540 Poly(3-azidopropyl methacrylate) Prepared by ATRP. *Macromolecules* **2005**, 38, 7540-7545.
- 541 13. a) Liu, H.; Jiang, X.; Bian, R.; Tong, M.; Tang, D.; Zhou, X.; Zhao, Y. Facile Synthesis of  $A_{2m}B_{2n}$ -Type Starlike Copolymers with Two  
542 Types of V-Shaped Arms by Combination of RAFT, ATRP and ROP Processes. *Polymer* **2015**, 64, 249-259; b) Gelbrich, T.; Marten, G.  
543 U.; Schmidt, A. M. Reversible Thermoflocculation of Magnetic Core-shell Particles Induced by Remote Magnetic Heating. *Polymer* **2010**,  
544 51, 2818-2824.
- 545 14. Holbach, M.; Zheng, X.; Burd, C.; Jones, C. W.; Weck, M. A Practical One-Pot Synthesis of Enantiopure Unsymmetrical Salen Ligands. *J.*  
546 *Org. Chem.* **2006**, 71, 2903-2906.
- 547 15. Schaus, S. E.; Branalt, J. Jacobsen, E. N. Asymmetric Hetero-Diels–Alder Reactions Catalyzed by Chiral (Salen)Chromium(III)  
548 Complexes. *J. Org. Chem.* **1998**, 63, 403-405.
- 549 16. Gökce, H.; Sen, F.; Sert, Y.; Abdel-Wahab, B. F.; Kariuki, B.; El-Hiti, G. A. Quantum Computational Investigation of  
550 (*E*)-1-(4-methoxyphenyl)-5-methyl-*N'*-(3-phenoxybenzylidene)-1*H*-1,2,3-triazole-4-carbohydrazide. *Molecules*, **2022**, 27, 2193.
- 551 17. Altava, B.; Burguete, M. I.; Garcia-Verdugo, E.; Luis, S. V. Chiral Catalysts Immobilized on Achiral Polymers: Effect of the Polymer  
552 Support on the Performance of the Catalyst. *Chem. Soc. Rev.* **2018**, 47, 2722-2771.
- 553 18. Stejskal, J. Janca, J. Kratochvil, P. Solution Properties of Poly(2-Methoxyethyl Methacrylate). *Polymer J.* **1976**, 8, 549-555.
- 554 19. Yamashita, H. Metal(II) d-Tartrates Catalyzed Asymmetric Ring Opening of Oxiranes with Various Nucleophiles. *Bull. Chem. Soc. Jpn.*  
555 **1988**, 61, 1213-1220.