

# Synthesis and characterization of optically active star-shaped poly(*N*-phenylmaleimide)s with a calixarene core

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**Abstract:** Two *N*-phenylmaleimide derivatives bearing a chiral oxazoline group, *N*-[*o*-(4-phenyl-4,5-dihydro-1,3-oxazol-2-yl)phenyl]maleimide [(*R*)-PhOPMI] and *N*-[*o*-(4-isopropyl-4,5-dihydro-1,3-oxazol-2-yl)phenyl]maleimide [(*S*)-Pr<sup>i</sup>OPMI], were polymerized using *in situ* generated calixarene-based phenates as initiators to yield optically active polymers. The formation of star-shaped architectures was strongly dependent on both polymerization conditions and calixarene moieties. In the case of polymerization conducted in toluene at 80–100 °C, the arm-chain numbers achieved their respective maxima for the polymers with these multifunctional initiators. In contrast, the polymers obtained in polymerizations at lower temperature possessed fewer arm chains. The structure and chiroptical properties were investigated on the basis of <sup>13</sup>C NMR, multiangular laser light scattering, gel permeation chromatography, and circular dichroism for the macromolecules with calixarene cores.

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**Keywords:** *N*-substituted maleimides; optically active polymers; calixarene; oxazoline; star architecture

## INTRODUCTION

Calixarenes are a class of phenol-containing macrocycles that can be prepared by condensation of *para*-substituted phenol and formaldehyde, and their ring sizes can be precisely controlled by synthetic conditions.<sup>1</sup> They are popular materials as building blocks or platforms for assembling more elaborate structures with ligating side arms or pendant groups.<sup>2–4</sup> An advantage of calixarenes is that this class of molecules has the appropriate stereochemistry and multiple, equivalent reaction sites for functional modifications at the upper rim or the lower rim of their architecture. More recently, calixarene-based macromolecules have attracted increasing interest, because the use of calixarenes as core units may afford not only the precise control of the number of functional groups but also special functions due to the spatial shape of calixarene.<sup>5–15</sup>

Increasing interest is currently being shown towards investigation of the chiroptical properties of polymeric materials, especially the induction of helical handedness in polymers or oligomers because of the possible applications in optical devices or data storage and also its relevance to chiral amplification.<sup>16,17</sup> Inoue and co-workers<sup>18</sup> described hexaarmed poly(amino acid) derivatives with a phosphazene core, which can act as membrane materials for the optical resolution of tryptophan, phenylalanine, and tyrosine. Their results indicate that the structural change from linear to star-shaped polymers greatly improves the functionality

of molecular recognition. In our previous work,<sup>19,20</sup> we synthesized *N*-phenylmaleimide-based monomers in which the phenyl moiety possessed a bulky chiral oxazoline substituent at its *ortho*-position (OPMIs; Scheme 1). These compounds exhibited a moderate polymerizability under anionically initiating conditions and the optical activity of resulting poly(OPMI)s might be attributed not only to the chirality of oxazolanyl groups in the monomeric units but also to the partial helical structure due to an excess of *threo*-diisotactic configuration in the main chain.<sup>19</sup> In this study reported here, we employed a series of *in situ* formed *p*-*tert*-butylcalix[*n*]arene-core multifunctional initiators (*n* = 4, 6, 8) to induce the polymerization of chiral OPMIs for the preparation of optically active polymers with well-defined star architecture. To the best of our knowledge, no reports are available on the synthesis of calixarene-constructed optically active polymaleimides.

## EXPERIMENTAL

### Materials

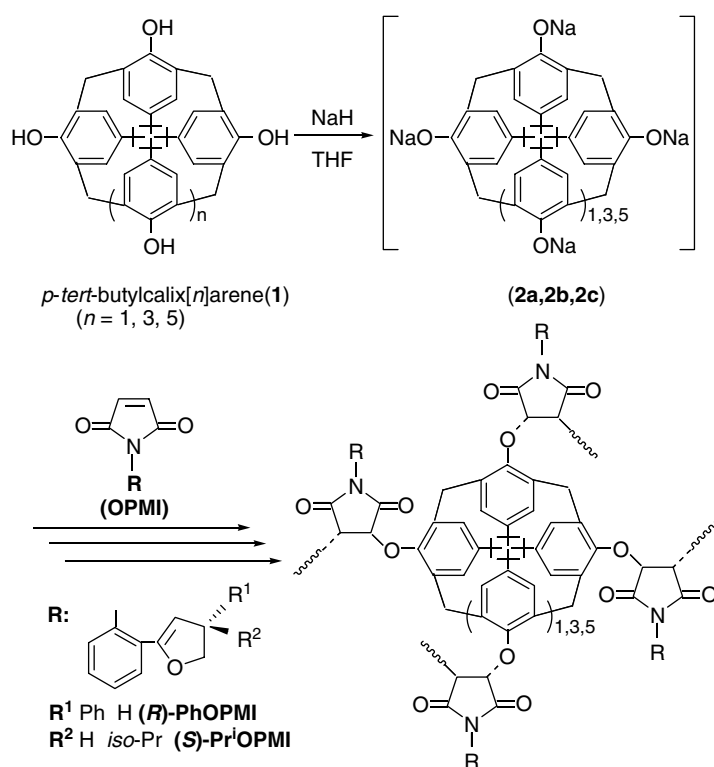
All chemicals were of reagent grade and used without further purification. Isatoic anhydride and 2-amino alcohols were purchased from Aldrich Chemicals. Other chemicals were purchased from Shanghai Reagent Co. Solvents were dried over a benzophenone–sodium complex for 3 days and then distilled prior to use. *p*-*tert*-Butylcalixarenes

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**Scheme 1.** Synthesis of star-shaped polymers with calixarene cores.

were synthesized with the reported procedure.<sup>2</sup> Syntheses of *N*-phenylmaleimide derivatives bearing a chiral oxazoline group (OPMIs) have been described previously.<sup>19,20</sup>

### Polymerization procedure

The polymerization was carried out using the Schlenk techniques under a dry nitrogen atmosphere. A typical example is given below. To a dry Schlenk tube, NaH (0.25 mmol), *p*-*tert*-butylcalix[4]arene (0.06 mmol), and tetrahydrofuran (THF) (2 mL) were added. After refluxing for 30 min, the mixture became a lacteous solution, indicating the formation of multifunctional phenate. Then, a toluene solution of (*R*)-PhOPMI (4–16 mL, 0.72 mol L<sup>-1</sup>) was added to the above initiator solution using a syringe. After 48 h, the reaction mixture was poured into a large amount of methanol. The precipitated product was separated by suction filtration and washed with methanol. Further purification of the polymer sample was performed with reprecipitation from a THF–MeOH system (1:10) in three cycles, and dried at 30 °C under vacuum for 2 days.

### Measurements

NMR spectra were obtained in CDCl<sub>3</sub> with tetramethylsilane (TMS) as an internal standard using a Bruker Avance AMX-500 NMR spectrometer. Gel permeation chromatography (GPC) measurements were performed at 40 °C using a Waters-150C instrument equipped with a differential refractometer detector and a set of Styragel<sup>®</sup> columns (HT-3, HT-4, and

HT-5), using THF as an eluent at 1.0 mL min<sup>-1</sup>. Linear polystyrene standards were used for calibration. The actual molecular weights of polymer samples were calculated from the response of an 18-angle light scattering detector (Wyatt technology) that was connected to a GPC line. The  $dn/dc$  values for the polymers obtained were measured in THF at 40 °C with a laser source operating at 633 nm. The *D*-line specific optical rotation ( $[\alpha]_D^{25}$ ) was measured in THF at 25 °C using a Wzz-2s automatic digital polarimeter (Shanghai Pudong optics apparatus Co.). Circular dichroism (CD) spectra were obtained in THF at 25 °C using a quartz cell of 1 cm with a JASCO J-820 spectropolarimeter (JASCO Co. Ltd). UV-visible spectra were recorded in THF at 25 °C with a JASCO V-570 spectrophotometer using a quartz cell of 1 cm.

### RESULTS AND DISCUSSION

The multifunctional anionic initiators 2 with anticipated active sites were prepared in one step starting from *p*-*tert*-butylcalix[ $n$ ]arene (abbreviated to Calix[ $n$ ],  $n = 4, 6, 8$ ) and NaH. The reaction was readily conducted in THF under reflux using a slight excess of NaH relative to the calixarene functionalities. In the case of Calix[4] used as a precursor, the appearance of characteristic milk white indicated the formation of the corresponding multifunctional initiator. In contrast, the Calix[6]- or Calix[8]-derived phenates were soluble in THF to give a transparent solution. These *in situ* formed calixarene phenates were then utilized as a multifunctional initiator for the polymerization of chiral OPMIs (Scheme 1).

(*R*)-PhOPMI was first investigated for the anionic polymerization with multifunctional initiators in toluene where the initial molar feed ratio of monomer to the phenate unit was set constant at 10. Thus, the  $[M]_0/[I]_0$  values were 40 for **2a**, 60 for **2b**, and 80 for **2c**. The polymerizations proceeded homogeneously throughout to give the optically active polymers, which were completely soluble in common solvents, such as THF, chloroform, and *N,N*-dimethylformamide. As shown in Table 1, the polymer yields increased with the reaction temperature irrespective of the number of initiator functionality and reached about 40% at 80 °C in 48 h. Further increasing the reaction temperature caused a decrease of the yields. The relatively low polymerizability may be attributable to the fact that the large steric hindrance in monomeric units suppressed the propagation activity during the polymerization. Such a tendency was also observed in the polymerization of other *N*-substituted maleimides.<sup>21–23</sup> On the other hand, as the polymerization temperature increased, there was an decrease in the apparent weight-average molecular weights ( $M_{w,GPC}$ ); furthermore, the molecular weight distribution ( $M_w/M_n$ ) became narrower for each set of samples. However, the corresponding variation of the absolute molecular weight obtained from light scattering measurements ( $M_{w,LS}$ ) was just opposite to that observed for  $M_{w,GPC}$ . That is, the polymers prepared with these calixarene-based initiators at 80 °C exhibited their respective maximum  $M_{w,LS}$  and minimum  $M_{w,GPC}$  values (see runs 3, 7, and 11 in Table 1). In addition, the specific optical rotation of the resulting polymers also showed a dependence on the polymerization temperature, as discussed later in detail.

Comparison of the absolute molecular weights with the apparent values shows that the samples from the polymerization at 80 °C have a considerably

compact structure (Table 1). The molecular weights are significantly underestimated using GPC. To clarify this point, we synthesized linear poly(PhOPMI)s using sodium *p*-*tert*-butylphenate (also *in situ* formed) under the same conditions, and then compared their molecular weights with those of samples obtained from the multifunctional initiating systems. The data indicated that, when compared to linear polymers of the same or similar apparent molecular weights, the calixarene-derived homologs showed a much higher absolute molecular weight. For example, the sample prepared at 80 °C with the octafunctional initiator **2c** had an  $M_{w,LS}$  of 100 000 g mol<sup>-1</sup> (see run 11 in Table 1), while the value was 12 000 g mol<sup>-1</sup> for a linear homolog having the same  $M_{w,GPC}$ ; the former is approximately 8 times higher than the latter. Similar situations were observed in the polymerization with tetrafunctional (**2a**) and hexafunctional (**2b**) initiators. Therefore, it may be concluded that the calixarene-core initiators with four, six, and eight phenate units initiated the polymerization of (*R*)-PhOPMI at 80 °C to give tetra-, hexa-, and octaarmed star polymers, respectively. The lower molecular weights measured by GPC are most probably due to the difference in exclusion volume between star-shaped and linear polymers.<sup>24–26</sup> However, for the polymers resulting from polymerizations carried out at 50 or 0 °C, the arm-chain number was lower than what would have been predicted based on the initiator functionality (see runs 1–2, 5–6, 9–10, respectively, in Table 1). It is noteworthy that **2a** and **2b** initiators yielded corresponding polymers having average arm numbers of 3.4 and 5.3, respectively (runs 3 and 7 in Table 1), which is probably due to their more rigid ring structure than that of calix[8]arene core.

The polymerization features for (*S*)-Pr<sup>i</sup>OPMI were almost the same as those of (*R*)-PhOPMI (Table 2). The method described above was also employed to

**Table 1.** Anionic polymerization of (*R*)-PhOPMI with calix[*n*]arene-based initiators **2** at different temperatures<sup>a</sup>

Run	Initiator	$[M]_0/[I]_0$	Temp. (°C)	Yield (%)	$M_{w,GPC}^b$	$M_w/M_n^c$	$M_{w,LS}^d$	$[\alpha]_D^{25}$ (degree) <sup>e</sup>
1	2a	40	0	18.5	11 000	1.60	26 000	+27.6
2	2a	40	50	27.7	7 000	1.45	38 000	+13.8
3	2a	40	80	38.6	5 500	1.38	61 000 (3.4)	+8.7
4	2a	40	100	15.2	3 500	1.27	44 000	0
5	2b	60	0	15.5	12 200	2.05	27 000	+25.0
6	2b	60	50	29.2	8 000	1.78	33 000	0
7	2b	60	80	38.0	3 900	1.57	70 000 (5.4)	-10.3
8	2b	60	100	18.6	3 700	1.43	70 000	-10.0
9	2c	80	0	19.2	11 000	1.96	28 000	+26.9
10	2c	80	50	31.5	8 100	1.60	34 000	+10.2
11	2c	80	80	42.1	3 300	1.46	100 000 (8.3)	+5.4
12	2c	80	100	22.3	2 600	1.20	79 000	-1.6

<sup>a</sup>  $[\alpha]_D^{25} = -58^\circ$  for (*R*)-PhOPMI in THF. Polymerization conditions:  $[M]_0 = 0.72$  mol L<sup>-1</sup>, in toluene, 48 h.

<sup>b</sup> Calibrated against polystyrene standard samples, in g mol<sup>-1</sup>.

<sup>c</sup> By GPC, 40 °C.

<sup>d</sup>  $dn/dc = 0.201$  (40 °C). The numbers in parentheses represent the ratio of  $M_{w,LS}$  values between the corresponding sample and its linear homolog with the same or nearly the same apparent molecular weight.

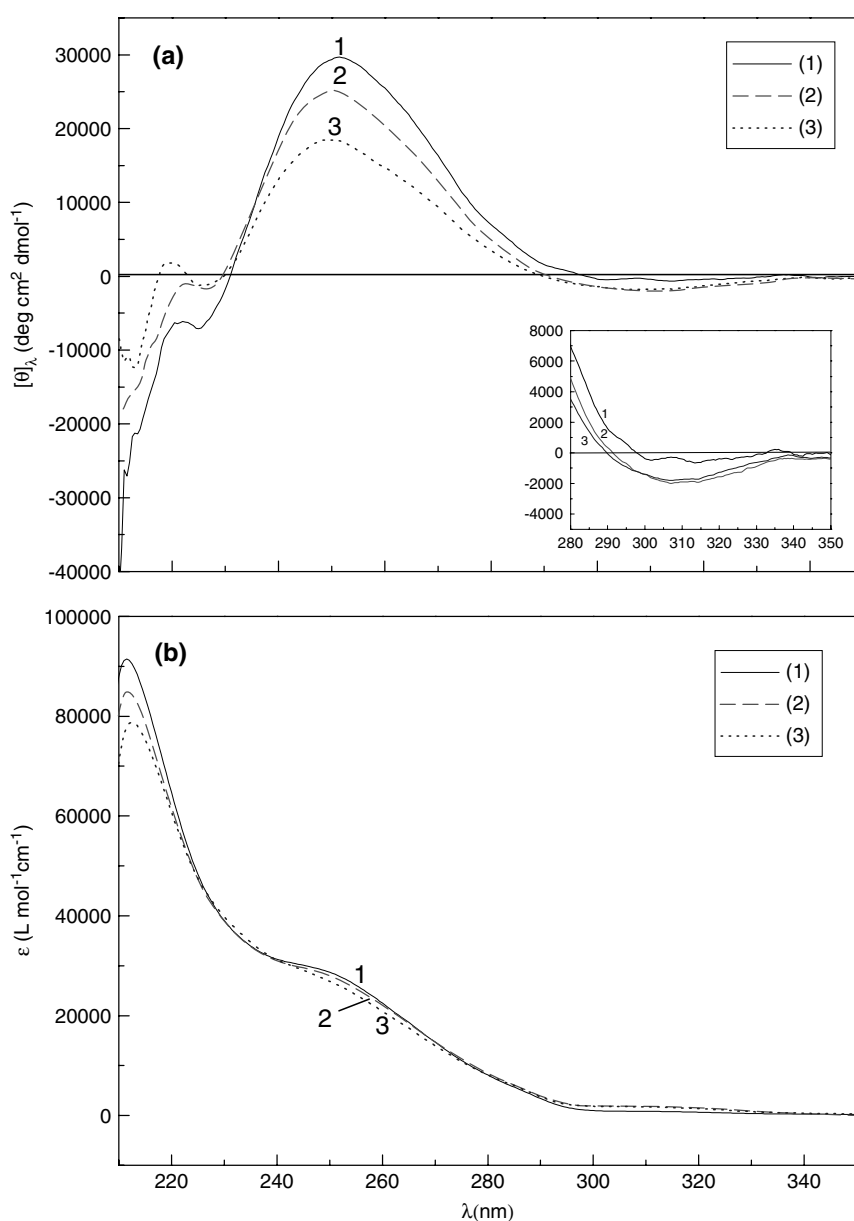
<sup>e</sup>  $c = 0.1$  g dL<sup>-1</sup>, THF,  $l = 10$  cm.

**Table 2.** Anionic polymerization of (S)-Pr<sup>i</sup>OPMI with calix[*n*]arene-based initiators **2** at different temperatures<sup>a</sup>

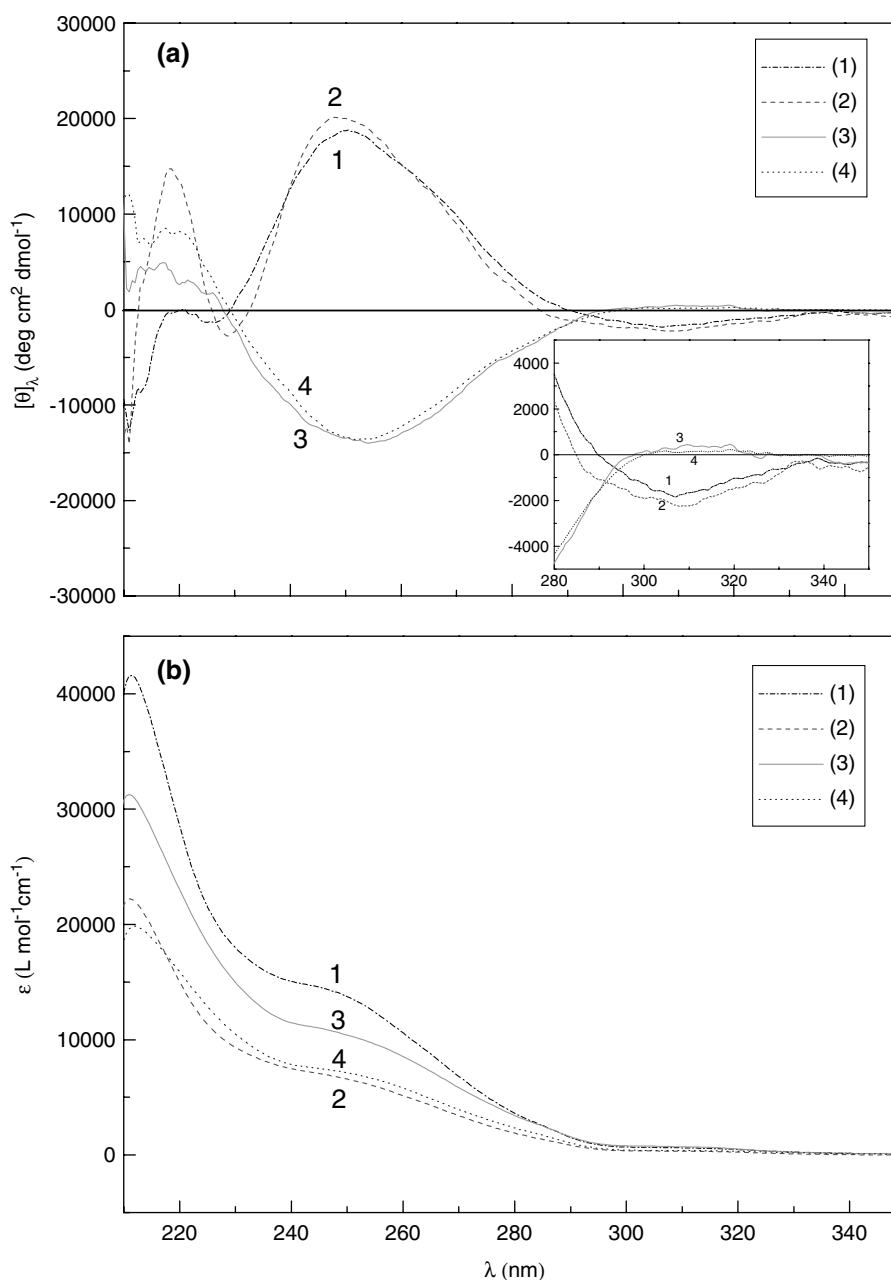
Run	Initiator	[M] <sub>0</sub> /[I] <sub>0</sub>	Temp. (°C)	Yield (%)	<i>M</i> <sub>w,GPC</sub> <sup>b</sup>	<i>M</i> <sub>w</sub> / <i>M</i> <sub>n</sub> <sup>c</sup>	<i>M</i> <sub>w,LS</sub> <sup>d</sup>	[α] <sub>D</sub> <sup>25</sup> (degree) <sup>e</sup>
1	2a	40	0	22.3	7 700	1.47	21 000	−51.1
2	2a	40	50	18.6	4 000	1.41	47 000	−30.0
3	2a	40	80	20.6	2 700	1.31	55 000	−27.2
4	2a	40	100	11.6	2 100	1.19	57 000 (3.1)	−27.4
5	2b	60	0	20.4	7 900	1.96	18 000	−72.5
6	2b	60	50	23.1	5 900	1.79	35 000	−50.0
7	2b	60	80	18.0	4 800	1.54	50 000	−48.7
8	2b	60	100	15.0	4 700	1.47	50 000 (4.0)	−35.2
9	2c	80	0	28.0	8 400	2.28	23 000	−67.9
10	2c	80	50	25.2	5 700	1.63	31 000	−45.8
11	2c	80	80	23.0	4 300	1.51	45 000	−22.0
12	2c	80	100	16.7	2 900	1.38	86 000 (8.4)	0

<sup>a</sup> [α]<sub>D</sub><sup>25</sup> = −60.6° for (S)-Pr<sup>i</sup>OPMI in THF. Polymerization conditions are same as those for Table 1.

<sup>b–e</sup> As Table 1.



**Figure 1.** (a) CD and (b) UV-visible spectra of poly(PhOPMI) samples: (1) run 5 in Table 1, [α]<sub>D</sub><sup>25</sup> = +25.0° (solid line), (2) run 6 in Table 1, [α]<sub>D</sub><sup>25</sup> = 0° (dashed line), and (3) run 7 in Table 1, [α]<sub>D</sub><sup>25</sup> = −10.3° (dotted line).

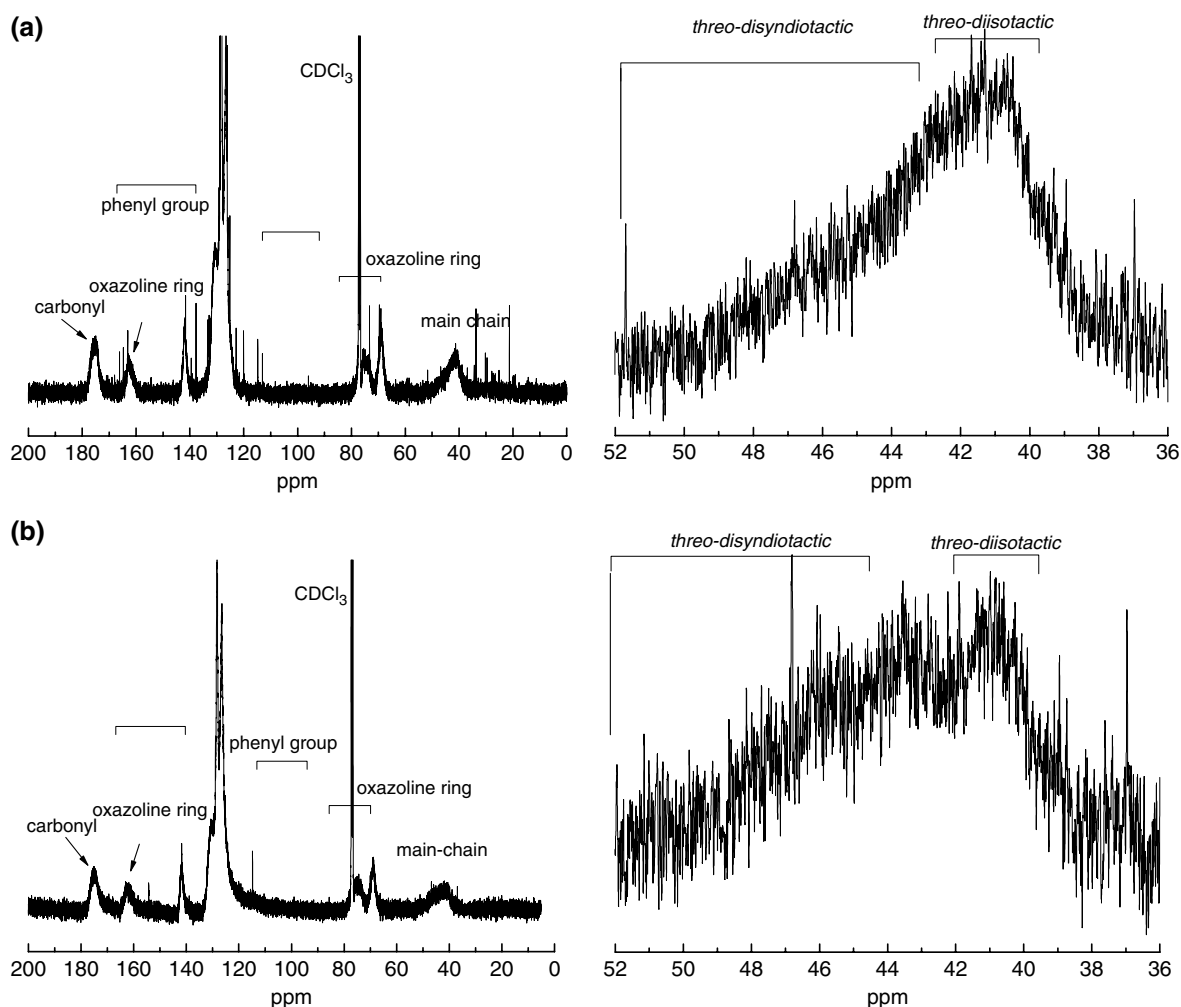


**Figure 2.** (a) CD and (b) UV-visible spectra of octaarmed poly(OPMI)s and their linear homologs: (1) run 11 in Table 1,  $[\alpha]_{\text{D}}^{25} = +5.4^\circ$  (dotted line), (2) linear homologous poly(PhOPMI),  $[\alpha]_{\text{D}}^{25} = +15.2^\circ$  (dashed line), (3) run 12 in Table 2,  $[\alpha]_{\text{D}}^{25} = 0^\circ$  (dash-dot line), and (4) linear homologous poly( $\text{Pr}^i$ OPMI),  $[\alpha]_{\text{D}}^{25} = -26.7^\circ$  (solid line).

ascertain the number of arm-chains of the polymer obtained. As can be seen from the data, the monomer was less reactive compared with its phenyl counterpart, in that a somewhat higher temperature was required to get the star-shaped structures. The optimized temperature was around  $100^\circ\text{C}$  to achieve the maximal arm-chain number in the case of **2a** and **2c** initiators. As for the hexafunctional initiator (**2b**), however, it appeared to prefer forming tetra- rather than hexaarmed polymer under such conditions. An illustrative example is the poly( $\text{Pr}^i$ OPMI) obtained at  $100^\circ\text{C}$  (run 8 in Table 2), where the arm-chain number was estimated as four, because its absolute molecular weight was  $50\,000\text{ g mol}^{-1}$  while the linear homolog of the same apparent molecular weight

( $4700\text{ g mol}^{-1}$ ) had the value of  $12\,500\text{ g mol}^{-1}$ . The reason for this may be not only the lower reactivity of this monomer but also the ‘winged’ conformation of the parent calix[6]arene core to some extent.<sup>1</sup>

As mentioned above, the reaction temperature had a strong effect on the structure of the polymers as well as on their optical activity. It is reasonable to consider the fact that an increase of temperature can facilitate the conformation interconversion of calixarene cores, thus endowing every active site with an equal chance to propagate and hence resulting in star-shaped architectures. A closer inspection of both systems revealed that the octaarmed polymers seemed to be obtained easily compared with tetra- or hexaarmed homologs, which may be attributed



**Figure 3.**  $^{13}\text{C}$  NMR spectra of poly(PhOPMI)s: (a) run 5 in Table 1,  $[\alpha]_{\text{D}}^{25} = +25^\circ$ ; (b) run 7 in Table 1,  $[\alpha]_{\text{D}}^{25} = -10.3^\circ$ .

to the more mobility of conformations of the calix[8]arene unit. There was a definite correlation between the specific rotation ( $[\alpha]_{\text{D}}^{25}$ ) of the polymers obtained and polymerization temperature for each set of experiments (Tables 1 and 2). That is, the polymerization carried out at higher temperature gave products with lower specific rotation. Interestingly, the variation from dextrorotation to levorotation was observed in the case of poly(PhOPMI)s with Calix[6]/[8] cores. Some samples even showed optical inactivity (runs 4 and 6 in Table 1 and run 12 in Table 2).

The chiroptical properties in solution of the calixarene-derived polymers were investigated using CD and compared with those of the corresponding linear homologs. Figure 1 depicts the CD spectra for Calix[6]-derived poly(PhOPMI)s prepared at different temperatures. Although these samples showed opposite specific rotation signs, their CD feature was almost the same except for a tiny difference in signal intensity. On the basis of our previous works,<sup>19,20</sup> the large positive Cotton effect at 250 nm and weak negative one at 225 nm are attributable to the electron transition of aryl residue containing an oxazoline substituent and imide carbonyl in the pendant groups, respectively.

The relative intensity of CD signals was proportional to the magnitude of their specific rotations. The multiple peaks in the region 280 to 340 nm suggest that the asymmetrical microenvironment consisting of calixarene core and arm chains had some effects on the chiroptical behavior. However, the exact reason for this still remains unclear at present. In addition, it should be noted that the CD spectra of poly(PhOPMI) or poly(*Pr*<sup>i</sup>OPMI) containing Calix[8] unit, prepared at 80 and 100 °C, respectively, were very similar to those of their linear counterparts, as shown in Fig. 2. The facts indicate that these optically active polymers did not form a higher chiral architecture brought by the ligation among arm chains with the help of the calixarene core.

The chiroptical property described above for these polymers reflects their configurational and/or conformational chirality, which is closely connected to the stereoregularity of the main chain. Thus, NMR spectroscopy was applied to gain further structural information. As an example, Fig. 3 shows  $^{13}\text{C}$  NMR spectra for poly(PhOPMI)s prepared using Calix[6]-based initiator at different polymerization temperatures; Fig. 3(a) and (b) correspond to samples 5 and 7 in Table 1, respectively. There were no differences in

the signals due to phenyl, carbonyl, and oxazoline ring among the polymers. Some difference was observed in the signals due to main chain carbons. The product obtained at 0 °C exhibited a sharper band than the samples prepared at higher temperature, indicating the former had more stereoregular structures than the latter.<sup>27</sup> According to Oishi and co-workers,<sup>28–32</sup> the main chain signals appearing at 41 and 43 ppm are assigned to *threo*-diisotactic and *threo*-disyndiotactic structures, respectively, as shown in Fig. 3. Comparing Fig. 3(a) with Fig. 3(b) suggests that the polymerization conducted at lower temperature gave products having more *threo*-diisotactic structures and vice versa. Along with this, the absolute values of specific rotation varied with *threo*-diisotactic content in the main chains. For some poly(PhOPMI)s, the reversal in sign of optical rotation may be the sum of both the configurational asymmetry of pendant groups and conformational chirality of the backbones containing the calixarene core.

## CONCLUSIONS

For the first time, *in situ* generated calix[*n*]arene-core multifunctional initiators (*n* = 4, 6, 8) have been employed to synthesize optically active polymers through anionic polymerization of chiral *N*-phenylmaleimide derivatives. Higher polymerization temperature (80–100 °C) facilitated the formation of products with star-shaped architecture, but decreased their stereoregularity and hence the optical activity. Comparatively, using the calix[8]arene-based initiator, it was easier to obtain multiarmed polymers due to the conformational mobility. The research on chiral separation using these materials is now in progress.

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