

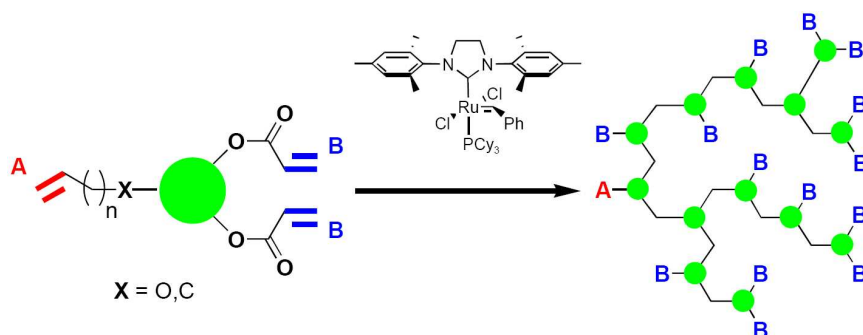
## **CHAPTER 2**

### **Hyperbranched Polymers via Acyclic Diene Metathesis Polymerization**

Portions of this chapter have previously appeared as: Gorodetskaya, I. A.; Choi, T. L.; Grubbs, R. H. *J. Am. Chem. Soc.* **2007**, *129*, 12672-12673.

## Abstract

A facile route to hyperbranched polymers via acyclic diene metathesis is described. According to this new methodology, a variety of molecules functionalized with two or more acrylate groups and one terminal aliphatic alkene can serve as an  $AB_n$  monomer when exposed to an imidazolinyldene-based ruthenium olefin metathesis catalyst, due to the cross metathesis selectivity of this catalyst. For the polymers obtained by this method, both  $^1\text{H}$  NMR spectroscopy and triple detector size exclusion chromatography conclusively indicate a branched architecture.

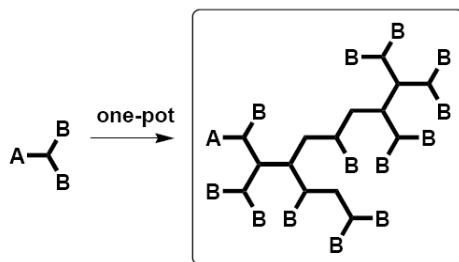


## Introduction

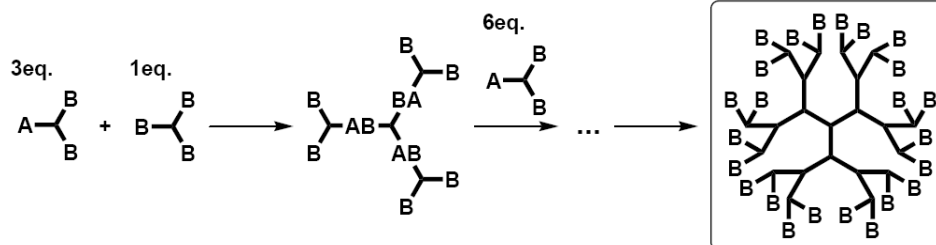
Hyperbranched polymers are highly branched macromolecules typically prepared via a one-pot polymerization of  $AB_{n \geq 2}$  monomers (Scheme 2.1A).<sup>1-6</sup> The A and B functionalities of these monomers readily react with each other (A reacts with B and vice versa) but not with themselves (A does not react with A and B does not react with B). The approach to the preparation of hyperbranched polymers was originally described by Flory as early as 1952, but, at the time, such an architecture was mainly of theoretical interest.<sup>7</sup> However, it has since been discovered that the unique macromolecular architecture of these polymers gives rise to many attractive, practical features such as multiple end groups, improved solubility, and lower solution viscosity (relative to linear analogues of the same molecular weight).<sup>1-6</sup> Moreover, dendrimers<sup>8-10</sup>—structurally perfect, monodisperse hyperbranched macromolecules—have already found applications in medicine,<sup>11,12</sup> catalysis,<sup>13,14</sup> and nanofabrication.<sup>15,16</sup> Unfortunately, dendrimer iterative synthesis and purification can be rather labor-intensive and, thus, expensive (Scheme 2.1B).<sup>8-10</sup> As such, the preparation and study of hyperbranched polymers, which typically exhibit properties similar to those of monodisperse dendrimers,<sup>17,18</sup> have been extensively pursued in recent years.<sup>3-6</sup>

### Scheme 2.1. Synthesis of dendritic polymers.

#### A. Synthesis of Hyperbranched Polymers



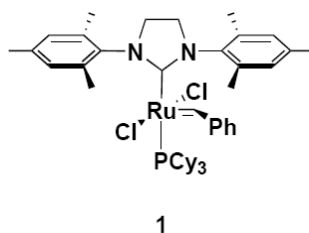
#### B. Synthesis of Dendrimers



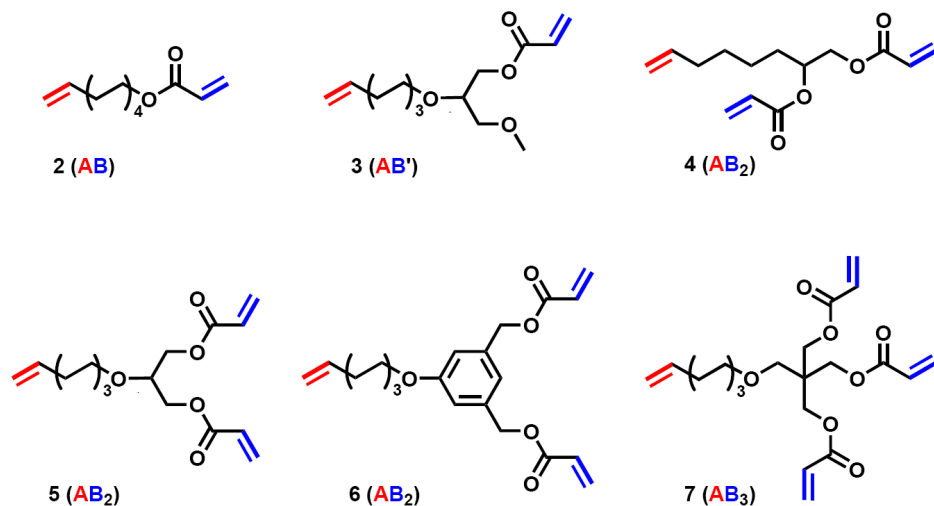
In the 55 years since Flory's theoretical report, as interest in dendrimers and hyperbranched polymers increased, a large number of synthetic approaches to these macromolecules have been reported. Moreover, the range of methods available for hyperbranched synthesis has expanded well beyond classical step-growth condensations and additions of AB<sub>2</sub> monomers<sup>6</sup> to include such notable examples as self-condensing vinyl polymerization (SCVP) of AB\* monomers,<sup>19</sup> various ring-opening polymerizations of latent AB<sub>n</sub> monomers,<sup>20-22</sup> and proton-transfer polymerization.<sup>23</sup> However, many of these methods have significant drawbacks such as harsh reaction conditions and the need for complex monomers. Although olefin metathesis has never previously been used to prepare hyperbranched architectures, it is well-suited for the task because it requires very mild reaction conditions and possesses good functional group tolerance, which allows access to a great variety of polymer backbones from readily available monomers. This chapter describes a simple method for the preparation of hyperbranched polymers via acyclic diene metathesis polymerization (ADMET).<sup>24</sup>

## Results and Discussion

Catalyst **1** (Figure 2.1) was selected for the ADMET hyperbranched polymerization. This imidazolinyliene-based catalyst is tolerant of many functional groups, stable to air and moisture, and readily promotes cross metathesis between electron-rich primary olefins. Furthermore, it can catalyze cross metathesis involving low metathesis-reactive olefins, such as electron-deficient alkenes. When treated with **1**, electron-poor olefins do not homodimerize (or do so very slowly), but do participate in a secondary metathesis reaction with homodimers of more reactive olefins.<sup>25</sup> Therefore, a molecule functionalized with one electron-rich olefin, such as a terminal alkene, and two or more electron-poor olefins, such as acrylates, is an AB<sub>n</sub>-type monomer (Figure 2.2) that can be polymerized into a hyperbranched structure using catalyst **1** (Scheme 2.2). In fact, a similar concept has been previously demonstrated in the synthesis of alternating copolymers<sup>26</sup> and various small molecules.<sup>27,28</sup>

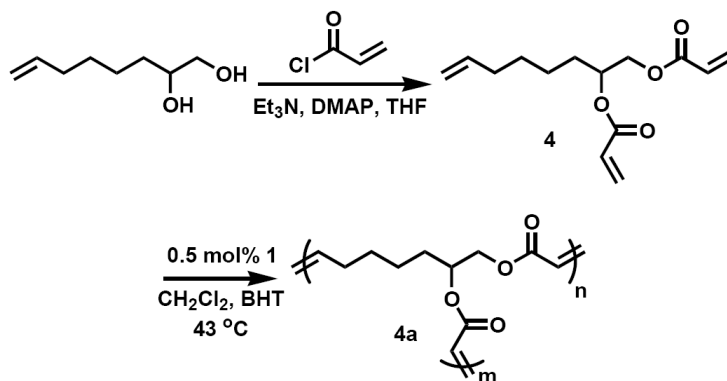


**Figure 2.1.** Acyclic diene metathesis polymerization catalyst.



**Figure 2.2.** Monomers for hyperbranched ADMET polymerization

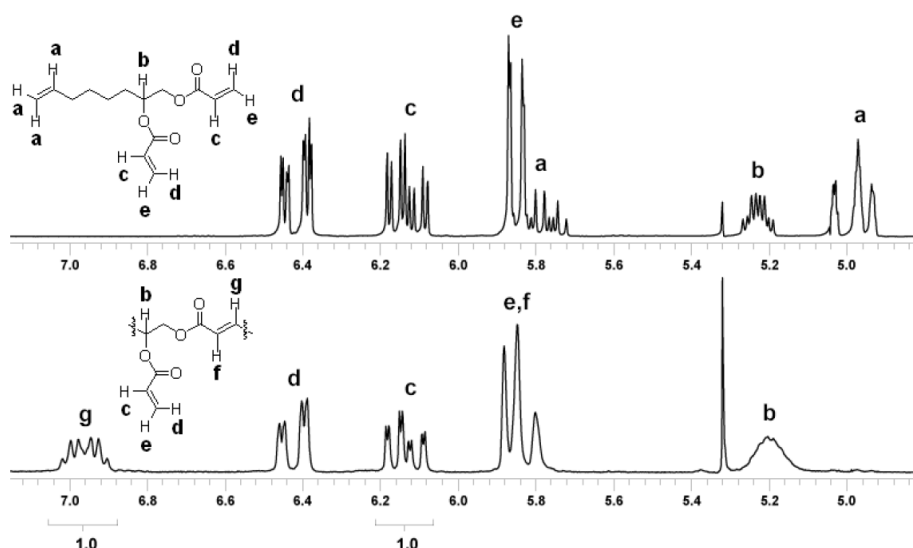
**Scheme 2.2.** Synthesis of AB<sub>2</sub> monomer 4 and its hyperbranched ADMET polymerization.



Monomers **2–7** (Figure 2.2) were utilized for the ADMET hyperbranched polymerization. They were prepared in one to four steps from commercially available, inexpensive starting materials such as glycerol, pentaerythritol, and 5-hydroxyisophthalic acid. **2** and **3** were prepared as linear analogues to AB<sub>2</sub> monomers **4** and **5**, as well as the

AB<sub>3</sub> monomer **7**. To further demonstrate the inherent flexibility of the presented method, monomer **6** was also synthesized to make a hyperbranched polymer with a different backbone.

The polymerization of each monomer is easily monitored by <sup>1</sup>H NMR spectroscopy.<sup>26,29</sup> For example, Figure 2.3 shows the <sup>1</sup>H NMR spectra of **4** and the resulting crude polymer **4a**. Some peak broadening due to formation of macromolecules can be observed in the spectrum of **4a**, especially for the backbone proton **b**. It can also be seen that the terminal olefins (**a**) completely disappear during the polymerization. Moreover, as expected, a new peak (**g**), a doublet of triplets, appears at 6.95 ppm due to formation of internal acrylates (AB olefins). Furthermore, if polymerization proceeds to completion, as is the case here, all of the terminal aliphatic alkenes are consumed and there should be half of the free acrylate groups left in the final polymer. Since there are twice as many B groups as A groups in an AB<sub>2</sub> monomer, an integration ratio of 1 (**g**) to 1 (**c** or **d**) should hold for the product of complete polymerization. Indeed, a 1:1 ratio is observed for **4a** (Figure 2.3), as well as **5a** and **6a**; it is 2:1 for **7a**. Peaks **d**, **c**, and **e** completely disappear, along with the peaks for protons **a**, during the polymerizations of **2** and **3**, and the integration ratio of the corresponding polymer peaks **g** and **f** is 1:1.



**Figure 2.3.** <sup>1</sup>H NMR spectra of monomer **4** (top) and hyperbranched polymer **4a** (bottom).

A multiangle light-scattering (MALS) detector combined with a differential refractometer and an on-line viscometer following size exclusion chromatography (SEC) was used to determine the molecular weights and PDIs of the obtained polymers. Additionally, viscometer data helped to characterize branching of the macromolecules resulting from ADMET of **2–7**. Table 2.1 summarizes the typical crude polymerization results. The observed PDI values are quite high, which is typical for a hyperbranched step-growth type polymerization.<sup>30</sup>

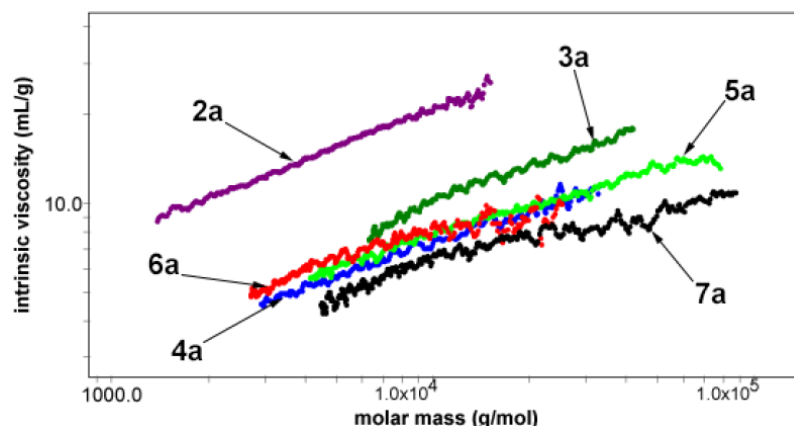
**Table 2.1.** Results of polymerization of **2–7**.<sup>a</sup>

Polymer	$M_w$ (kDa)	$M_n$ (kDa)	PDI	$\alpha \times 10^{-1}$
2a	4.31	2.07	2.1	$4.45 \pm 0.01$
3a	21.43	4.44	4.8	$4.12 \pm 0.02$
4a	3.61	0.55	6.5	$3.82 \pm 0.02$
5a	14.77	3.08	4.8	$3.24 \pm 0.02$
6a	10.24	3.17	3.2	$3.34 \pm 0.03$
7a	30.90	5.00	6.2	$2.69 \pm 0.02$

<sup>a</sup> Polymerization conditions: 0.5 mol % of **1** was used and the polymerizations were conducted in near-refluxing methylene chloride (43 °C) with venting.  $M_w$ ,  $M_n$ , and PDI were calculated from triple-angle laser light scattering and refractive index measurements.  $\alpha$  was measured with an on-line differential viscometer.

Figure 2.4 compares the plots of intrinsic viscosity (IV) vs. molecular weight (Mark–Houwink–Sakurada plots) for polymers **2a–7a**. As expected, the IV of branched polymers **4a–7a** is much lower than that of the linear polymer **2a** for any given molecular weight. Interestingly, the supposedly linear polymer **3a** has a drastically reduced intrinsic viscosity compared to that of **2a**, although not quite as low as the viscosities of branched polymers. This property of **3a** can be attributed to the presence of a methoxy-methyl pendant group in each monomer unit. This group is inert during the polymerization, but its length is comparable to the monomer’s overall size. Such an architecture results in a “comb”-type polymer with a lower than expected IV (relative to that of a linear analogue).<sup>31</sup> Across the molecular weight range studied, the viscosity of polymer **7a**, based on an AB<sub>3</sub> monomer **7**, is even lower than that of AB<sub>2</sub> polymers **4a–6a**. This observation indicates even more branching in the AB<sub>3</sub>-based polymer. On the other hand, the intrinsic

viscosity does not change dramatically with slight variations in the backbone; it can be seen from Figure 2.4 that the Mark–Houwink plots for **4a–6a** completely overlap.



**Figure 2.4.** Mark-Houwink-Sakurada plots for polymers **2a–7a**.

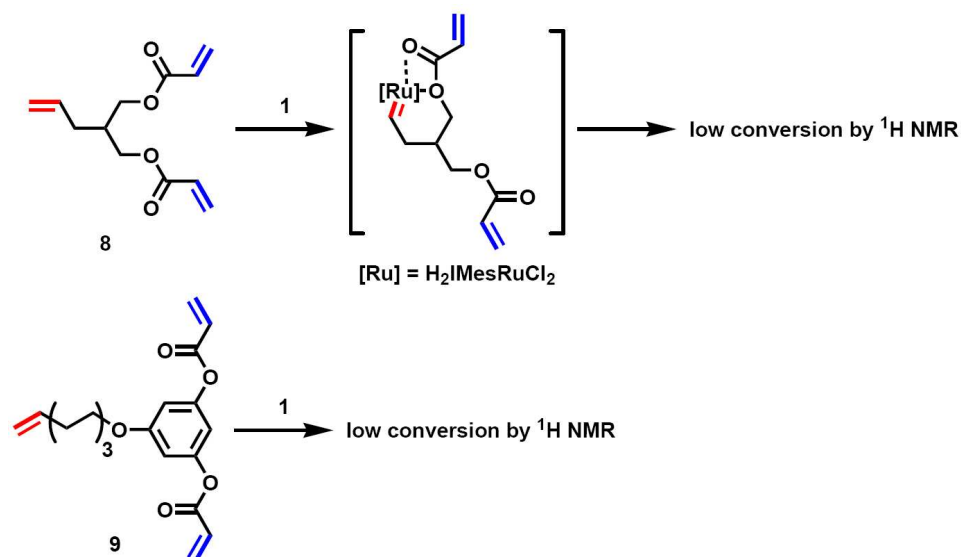
To extend the analysis, the Mark–Houwink shape parameter  $\alpha$  ( $[\eta] = KM^\alpha$ ) for polymers **2a–7a** were compared (Table 2.1). An  $\alpha$  parameter of 0.5–1.0 is typical for randomly coiled linear polymers.<sup>32</sup> Polymers with a rigid-rod shape have an  $\alpha$  of 2.0, and spherically shaped macromolecules are expected to have an  $\alpha < 0.5$ .<sup>32</sup> The linear polymer **2a** was found to have the highest  $\alpha$  value of 0.45 (Table 2.1), closely followed by an  $\alpha$  of 0.41 for **3a**. This observation confirms that **3a** is a linear polymer despite its low viscosity. It also validates that polymers **4a–7a** are not simply linear, alternating A,B comb-shaped polymers. Branched AB<sub>2</sub>-based polymers **4a**, **5a**, and **6a** all have  $\alpha$  parameters indicative of a spherical shape in solution. Moreover, polymer **7a** yielded the lowest  $\alpha$  value, which is in agreement with the AB<sub>3</sub>-based polymer having the lowest intrinsic viscosity and, thus, the most branching. Overall, the  $\alpha$  values found strongly suggest a spherical shape in solution and, therefore, a hyperbranched architecture for polymers **4a–7a**.

Interestingly, some of the structurally altered ADMET AB<sub>2</sub> monomers were found to test the general utility of this method. Both substrates **8** and **9** (Scheme 2.3) produced poor polymerization results when exposed to **1**. In the case of **8**, the decreased reactivity must stem from the shortened length of the aliphatic chain between the tertiary carbon and the terminal alkene, since it is the only feature distinguishing this monomer from **4** or **5**, both of which underwent ADMET successfully. It can be speculated that the chain length



of **8** allows for the formation of a stable, 6-membered chelates between the ruthenium and the polar acrylate moiety upon cross metathesis (Scheme 2.3). This deactivates the catalyst and prevents or slows down the polymerization process.<sup>33</sup> On the other hand, the low conversion observed with **9** must be a result of the poor metathesis reactivity of the aryl acrylate groups. The acrylates directly attached to the aryl ring are too electron-poor to undergo olefin metathesis efficiently even with the highly active NHC-catalyst. This explanation is supported by the fact that removing the acrylate groups from the aromatic ring by just one carbon, as is the case with **6**, completely restores their metathesis reactivity. The observed metathesis behavior of **6** and **8**, as compared to **5** and **6** correspondingly, shows that although there are certain limitations to ADMET polymerization with **1**, they can be easily overcome by careful monomer design.

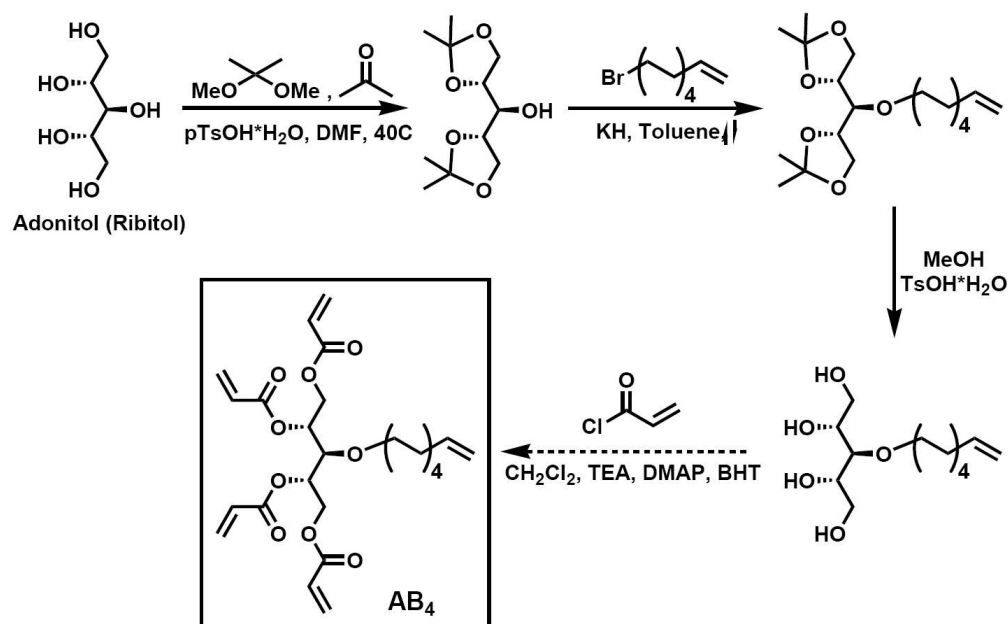
**Scheme 2.3.** AB<sub>2</sub> monomers which were found to be challenging for ADMET.



In general, despite the minor limitations noted above, the structural diversity and availability of monomer cores that can be used in the hyperbranched ADMET polymerization present unprecedented opportunities for fine-tuning the properties of dendritic polymers. For example, the evidence presented in this chapter indicates that polymers prepared from AB<sub>3</sub> monomers have an even lower viscosity and a more compact structure in solution than the ones prepared from the analogous AB<sub>2</sub> monomers. Consequently, it would be interesting to extend the comparison to AB<sub>n</sub>-based polymers,

where  $n > 3$ . For example, an  $AB_4$  monomer should be readily available via a straightforward 4-step route described in Scheme 2.4. Such explorations should provide even greater insight into the properties of hyperbranched polymers.

**Scheme 2.4.** Synthesis of  $AB_4$  monomer for hyperbranched ADMET polymerization.



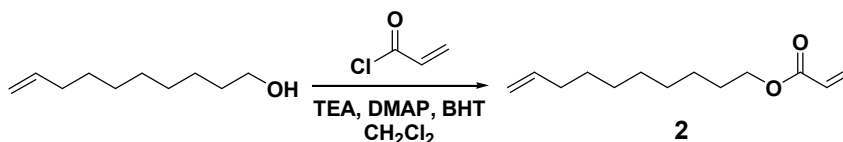
## Conclusion

This chapter demonstrates that olefin metathesis can be used to prepare hyperbranched polymers with a variety of backbones in a very simple and truly modular fashion. Moreover, the method presented here is amenable to the synthesis of functionalized hyperbranched polymers that can be employed in biological and material applications. Therefore, as an extension of this work, Chapter 3 investigates functionalization of the peripheral groups (acrylates) of the hyperbranched polymers presented here.

## Experimental Procedures

**Materials and Instrumentation.** All reagents (except catalyst **1** and phloroglucinol) were purchased from Aldrich at the highest available purity grade and used without further purification. Catalyst **1** was obtained from Materia, Inc. and phloroglucinol was bought from Fluka. NMR spectra were obtained using a Varian Mercury-300 spectrometer; samples were dissolved in (methylene chloride)-d<sub>2</sub>, unless noted otherwise. Size exclusion chromatography (SEC) analysis was performed using a Wyatt triple detector system equipped with a refractive index (Optilab rex) detector, a viscometer (ViscoStar) detector, and a triple angle light scattering (miniDAWN TREOS, with laser wavelength of 658 nm) detector all operating at 25°C. Viscotek ViscoGEL I-Series (one mixed bed medium MW and one mixed bed high MW) columns were used for SEC with THF as the eluent and a Shimadzu LC-10AD pump operating at 1 mL/minute.

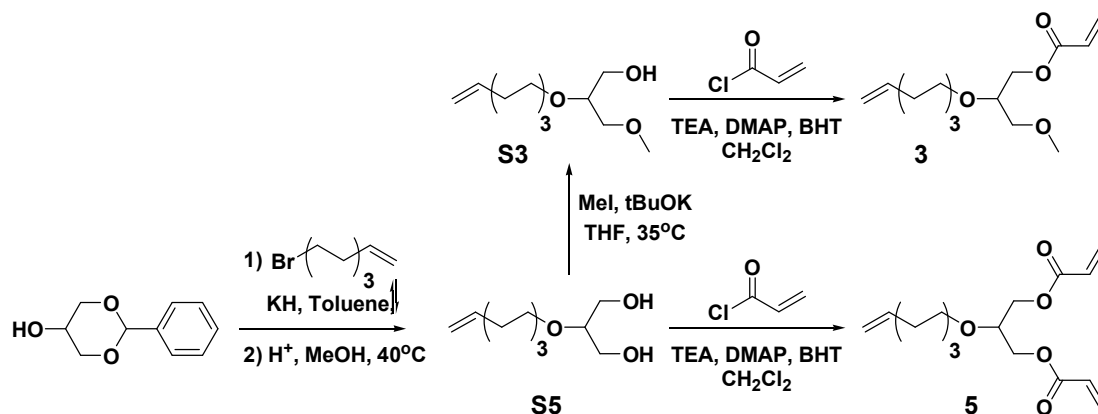
**Scheme 2.5.** Synthesis of monomer **2**.



**Representative procedure for the addition of acryloyl chloride to alcohol groups (2).** Acryloyl chloride (0.8 mL, 9.6 mmol) was slowly added via syringe to a stirring solution of 9-decene-1-ol (1 g, 6.4 mmol), triethylamine (TEA) (2.2 mL, 16 mmol), and a small amount of 2,6-di-*tert*-butyl-4-methoxyphenol (BHT) in dry THF (2 mL) at 0 °C (Scheme 2.5). After the solution was allowed to warm to room temperature, a catalytic amount of 4-(dimethylamino)pyridine (DMAP) (3.9 mg, 0.06 mmol) was added, and the flask was stirred for an additional 2 h. The reaction mixture was then filtered, and the solvent was removed under reduced pressure. The crude product was purified by silica gel (TSI) chromatography, eluting with 95:5 hexane:ethyl acetate to afford 0.99 g (73% yield) of a viscous colorless oil **2**. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>, ppm): δ 6.36 (dd, J = 17.5 Hz, J = 1.6 Hz, 1H), 6.11 (dd, J = 17.5 Hz, J = 10.2 Hz, 1H), 5.89–5.75 (m, 1H), 5.80 (dd, J = 10.2 Hz, J = 1.6 Hz, 1H), 5.03–4.89 (m, 2H), 4.12 (t, J = 6.9 Hz, 2H), 2.04 (m, 2H), 1.65 (m, 2H), 1.31 (m, 10H). <sup>13</sup>C NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>, ppm): δ 166.62, 139.81, 130.58,

129.27, 114.42, 65.15, 34.35, 29.91, 29.77, 29.61, 29.49, 29.17, 26.47. HRMS(EI+)  $m/z$ : 210.1617  $[M]^{+}$ .

**Scheme 2.6.** Synthesis of monomers **3** and **5**.



(**3**). Monomer **3** was derived from the same starting material as **5** (see synthesis of **5** below). The intermediate **S5** (Scheme 2.6) was treated with 0.5 equivalents of MeI and tBuOK each in THF at 35°C for 10 h. The unreacted base was then neutralized with tBuOH, and the reaction mixture was concentrated and purified by silica gel chromatography (4:1 hexane:EtOAc). A clear viscous oil **S3** was produced in 54% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ , ppm):  $\delta$  5.82 (m, 1H), 5.03–4.90 (m, 2H), 3.67–4.41 (m, 7H), 3.33 (s, 3H), 2.28 (broad s, 1H), 2.04 (m, 2H), 1.55 (m, 2H), 1.34 (m, 6H).  $^{13}\text{C}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ , ppm):  $\delta$  139.73, 114.47, 79.03, 73.10, 70.69, 63.09, 59.56, 34.28, 30.60, 29.50, 29.44, 26.48. HRMS(FAB+)  $m/z$ : 217.1813  $[M+H]^+$ .

Colorless oil **3** (Scheme 2.6) was made from **S3** according to the representative procedure outlined above for **2** in 79% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ , ppm):  $\delta$  6.38 (dd,  $J = 17.1$  Hz,  $J = 1.8$  Hz, 1H), 6.14 (dd,  $J = 17.4$  Hz,  $J = 10.5$  Hz, 1H), 5.89–5.75 (m, 1H), 5.84 (dd,  $J = 10.2$  Hz,  $J = 1.8$  Hz, 1H), 5.02–4.89 (m, 2H), 4.25 (dd,  $J = 11.4$  Hz,  $J = 4.3$  Hz, 1H), 4.13 (dd,  $J = 11.4$  Hz,  $J = 5.7$  Hz, 1H), 3.63 (doublet of quintets,  $J = 5.4$  Hz,  $J = 4.5$  Hz, 1H), 3.53 (t,  $J = 6.6$  Hz, 2H), 3.44 (d,  $J = 4.8$  Hz, 2H), 3.34 (s, 3H), 2.04 (m, 2H), 1.53 (m, 2H), 1.42–1.27 (m, 6H).  $^{13}\text{C}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ , ppm):  $\delta$  166.35, 139.75, 131.12, 128.89, 114.44, 76.95, 72.65, 70.97, 64.53, 59.57, 34.28, 30.53, 29.48, 29.46, 26.43. HRMS(EI+)  $m/z$ : 271.1907  $[M+H]^+$ .

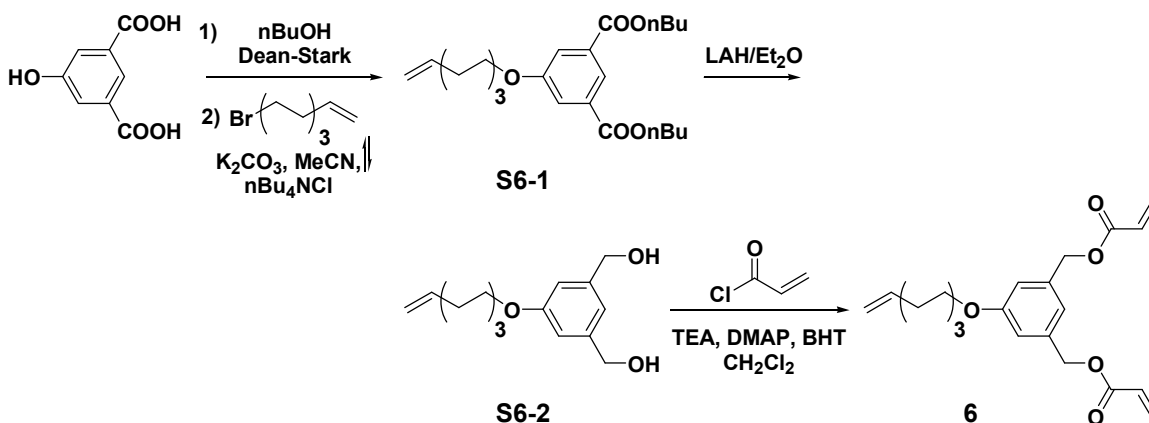
(4). Colorless oil **4** was prepared using the same procedure as described for **2** from 7-octene-1,2-diol (Scheme 2.2) in 67% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ , ppm): 6.37 (ddd,  $J = 17.1$  Hz,  $J = 4.2$  Hz,  $J = 1.2$  Hz, 2H), 6.11 (ddd,  $J = 17.1$  Hz,  $J = 10.5$  Hz,  $J = 2.7$  Hz, 2H), 5.85–5.73 (m, 1H), 5.83 (dd,  $J = 10.5$  Hz,  $J = 1.8$  Hz, 2H), 5.17 (m, 1H), 5.05–4.91 (m, 2H), 4.30 (dd,  $J = 12.0$  Hz,  $J = 3.6$  Hz, 1H), (dd,  $J = 12.0$  Hz,  $J = 6.5$  Hz, 1H), 2.05 (m, 2H), 1.65 (m, 2H), 1.43–1.36 (m, 6H).  $^{13}\text{C}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ , ppm):  $\delta$  166.21, 166.06, 139.28, 131.44, 131.20, 129.00, 128.61, 114.79, 72.13, 65.60, 34.03, 31.10, 29.16, 25.08. HRMS(EI+)  $m/z$ : 253.1441  $[\text{M}]^{+\bullet}$ .

(5). *cis*-1,3-*O*-Benzylideneglycerol (2 g, 11.1 mmol) was combined with potassium hydride (35% suspension in oil, 2.5 g, 22.2 mmol) in 8 mL of toluene (Scheme 2.6) in a 50 mL round bottom flask equipped with a stir bar. The solution was stirred at room temperature until gas evolution ceased, at which point 7-bromo-octene (2 mL, 12.2 mmol) was slowly added to the reaction flask. The reaction was subsequently heated to reflux for 10 h. The reaction mixture was then cooled to room temperature, and the unreacted potassium hydride was neutralized with a small amount of *i*PrOH before the solution was filtered and concentrated. The crude product was redissolved in 5 mL of methanol, a catalytic amount of pTsOH monohydrate was added, and the mixture was stirred at 40°C for 2 h (Scheme 2.6). Subsequently, the solution was basified with 1M aqueous NaOH. The resulting mixture was filtered and the filtrate was concentrated *en vacuo*. The product was purified by silica gel chromatography, eluting with 95:5  $\text{CH}_2\text{Cl}_2$ :MeOH, to give 1.20 g (53% overall yield) of viscous colorless oil **S5**.  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ , ppm):  $\delta$  5.81 (m, 1H), 5.02–4.89 (m, 2H), 3.64 (m, 4H), 3.52 (t,  $J = 6.6$  Hz, 2H), 3.41 (m, 1H), 3.37 (t,  $J = 5.1$  Hz, 2H; OH), 2.04 (m, 2H), 1.57 (m, 2H), 1.34 (m, 6H).  $^{13}\text{C}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ , ppm):  $\delta$  139.62, 114.55, 80.53, 70.65, 62.12, 34.27, 30.54, 29.52, 29.43, 26.45. HRMS(EI+)  $m/z$ : 202.1569  $[\text{M}]^{+\bullet}$ .

Clear colorless oil **5** was made from **S5** according to the representative procedure outlined above for **2** (Scheme 2.6) in 72% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ , ppm):  $\delta$  6.39 (dd,  $J = 17.1$  Hz,  $J = 1.2$  Hz, 2H), 6.14 (dd,  $J = 17.3$  Hz,  $J = 10.5$  Hz, 2H), 5.88–5.75 (m, 1H), 5.85 (dd,  $J = 10.5$  Hz,  $J = 1.2$  Hz, 2H), 5.02–4.89 (m, 2H), 4.23 (m, 4H), 3.77 (quintet,  $J = 5.3$  Hz, 1H), 3.56 (t,  $J = 6.6$  Hz, 2H), 2.03 (m, 2H), 1.54 (m, 2H), 1.32 (m,

6H).  $^{13}\text{C}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ , ppm):  $\delta$  166.22, 139.74, 131.46, 128.65, 114.43, 75.70, 71.14, 63.88, 34.26, 30.41, 29.44, 26.37. HRMS(FAB+)  $m/z$ : 311.1855  $[\text{M}+\text{H}]^+$ .

**Scheme 2.7.** Synthesis of monomer **6**.



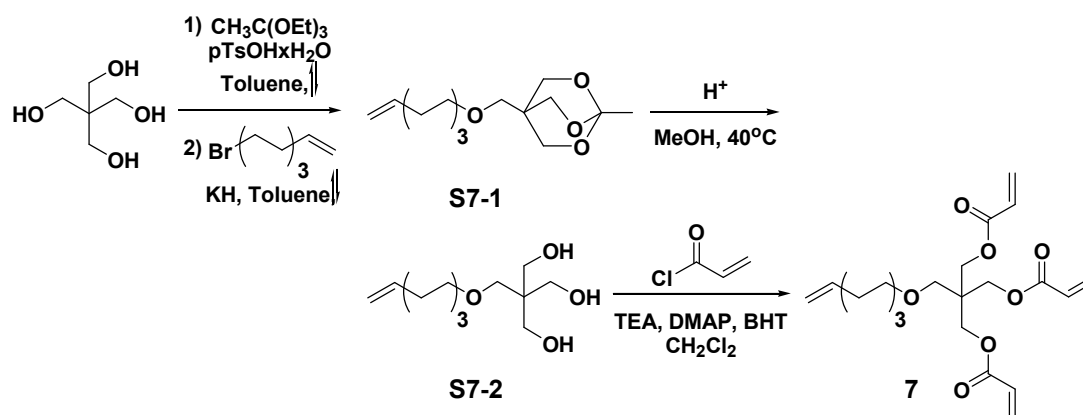
(**6**). 5-Hydroxyisophthalic acid (5.46 g, 30 mmol) was combined with n-butyl alcohol (10 mL), benzene (10 mL), and pTsOH monohydrate (57 mg, 0.3 mmol) in a 50 mL round bottom flask which was equipped with a Dean-Stark trap and a reflux condenser (Scheme 2.7). The reaction was refluxed until the white suspension in the reaction flask completely dissolved and water collection in the Dean-Stark trap had ceased (12 h). The reaction solution was then concentrated under reduced pressure and dried under high vacuum for an additional 6 h. The very thick, yellow residue obtained (1.5 g, 5 mmol) was redissolved in MeCN (7 mL) before being combined with 7-bromo-octene (1 mL, 5.35 mmol), potassium carbonate (1.17 g, 8.46 mmol) and a catalytic amount of tetra-n-butylammonium chloride; this reaction was refluxed for 10 h. The mixture was then cooled to room temperature, filtered, concentrated, and purified by silica gel chromatography. Elution with 95:5 hexane:EtOAc afforded **S6-1** (Scheme 2.7) in quantitative yield. NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ , ppm):  $\delta$  8.21 (t,  $J$  = 1.5 Hz, 1H), 7.72 (d,  $J$  = 1.5 J, 2H), 5.83 (m, 1H), 5.04–4.91 (m, 2H), 4.32 (t,  $J$  = 6.8 Hz, 4H), 4.05 (t,  $J$  = 6.6 Hz, 2H), 2.07 (m, 2H), 1.77 (m, 6H), 1.55–1.37 (m, 10H), 0.99 (t,  $J$  = 7.4 Hz, 6H).  $^{13}\text{C}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ , ppm):  $\delta$  166.16, 159.80, 139.66, 132.75, 122.90, 119.96, 114.55, 69.17, 65.74, 34.26, 31.27, 29.61, 29.40, 29.37, 26.35, 19.84, 14.11. HRMS(FAB+)  $m/z$ : 405.2645  $[\text{M}+\text{H}]^+$ .

**S6-1** (2.06 g, 5.1 mmol) was added to a stirring 1M solution of LAH in ethyl ether (11 mL) at 0 °C; the mixture was allowed to slowly warm up to room temperature, before

being heated to reflux. After 6 hours, the reaction was cooled to room temperature, and sodium sulfate decahydrate was slowly added to the reaction mixture with vigorous stirring until gas evolution had ceased. The suspension was then stirred for 0.5 h, filtered through Celite (the filter cake was washed with Et<sub>2</sub>O and boiling hot THF), and concentrated under reduced pressure. **S6-2** was further purified by recrystallization from EtOH/hexane to afford 1.27 g (94% yield) of a white solid. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>, ppm): δ 6.89 (s, 1H), 6.80 (s, 2H), 5.83 (m, 1H), 5.03–4.90 (m, 2H), 4.61 (s, 4H), 3.96 (t, J = 6.6 Hz, 2H), 2.05 (m, 2H), 1.77 (m, 2H), 1.64 (broad s, 2H; OH), 1.40 (m, 6H). <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>, ppm): δ 160.12, 143.55, 139.18, 117.64, 114.49, 112.35, 68.55, 65.42, 34.25, 29.75, 29.40, 26.40. HRMS(FAB+) *m/z*: 264.1723 [M]<sup>+</sup>.

Colorless viscous oil **6** was made from **S6-2** according to the standard procedure outlined above for **2**. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>, ppm): δ 6.95 (s, 1H), 6.87 (s, 2H), 6.43 (dd, J = 17.6 Hz, J = 1.4 Hz, 2H), 6.18 (dd, J = 17.6 Hz, J = 10.5 Hz, 2H), 5.90–5.77 (m, 1H), 5.87 (dd, J = 10.5 Hz, J = 1.4 Hz, 2H), 5.15 (s, 4H), 5.05–4.91 (m, 2H), 3.97 (t, J = 6.6 Hz, 2H), 2.11–2.04 (m, 2H), 1.83–1.73 (m, 2H), 1.52–1.35 (m, 6H). <sup>13</sup>C NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>, ppm): δ 166.28, 160.10, 139.68, 138.44, 131.47, 128.79, 120.04, 114.54, 114.32, 68.66, 66.41, 34.27, 29.71, 29.41, 26.40. HRMS(EI+) *m/z*: 372.1924 [M]<sup>+</sup>.

#### Scheme 2.8. Synthesis of monomer 7.



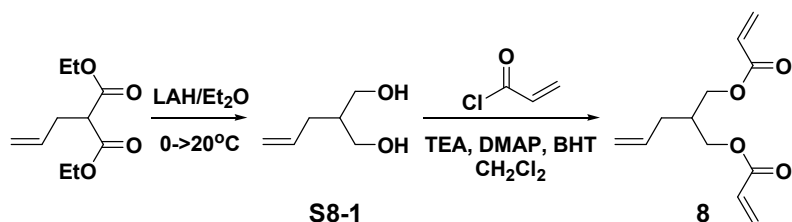
(**7**). Pentaerythritol (2 g, 14.7 mmol.) and pTsOH monohydrate (28 mg, 0.15 mmol) were combined in 25 mL of dry toluene and heated to reflux (Scheme 2.8). Triethyl orthoacetate (2.7 mL, 14.7 mmol) was added to the flask, and the resulting suspension was refluxed until the solution went clear and no solid residue was visible (24–48 hours). A few

drops of TEA were added to the reaction, and the solution was filtered while still hot. The solution was concentrated under reduced pressure, and white, soft crystals were obtained (1.9 g, 80% yield). This orthoacetate protected product (11.7 mmol) was redissolved in hot dry toluene, and potassium hydride (35% suspension in oil, 2 g, 17.6 mmol) was added to the reaction flask followed by 8-bromo-octene (2.2 mL, 12.9 mmol). The reaction mixture was then heated to reflux. After 10 hours, the reaction was cooled to room temperature and unreacted potassium hydride was quenched with a small amount of iPrOH. The solution was filtered and concentrated. (**S7-1** could be purified at this stage by silica gel chromatography, eluting with 95:5 hexane:EtOAc.  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ , ppm):  $\delta$  5.82 (m, 1H), 5.03-4.90 (m, 2H), 3.95 (s, 6H), 3.32 (t,  $J = 6.5$  Hz, 2H), 3.13 (s, 2H), 2.04 (m, 2H), 1.50 (m, 2H), 1.40-1.27 (m, 9H).  $^{13}\text{C}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ , ppm):  $\delta$  139.73, 114.49, 108.91, 72.35, 70.07, 69.58, 35.44, 34.27, 29.88, 29.42, 26.43, 23.91).

The crude **S7-1** was redissolved in 5 mL of methanol, a few drops of hydrochloric acid were added, and the mixture was stirred at 40°C for 2 h (Scheme 2.8). The basified with 1M aqueous NaOH solution was filtered, concentrated, and purified by silica gel chromatography. The product was eluted with 95:5  $\text{CH}_2\text{Cl}_2$ :MeOH and **S7-2** was obtained in 31% overall yield (in three steps from pentaerythritol).  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ , ppm):  $\delta$  5.89-5.75 (m, 1H), 5.03-4.90 (m, 2H), 3.65 (d,  $J = 5.7$  Hz, 6H), 3.42 (s, 2H), 3.41 (t,  $J = 6.3$  Hz, 2H), 2.76 (t,  $J = 5.7$  Hz, 3H; OH), 2.08-2.00 (m, 2H), 1.58-1.51 (m, 2H), 1.41-1.29 (m, 6H).  $^{13}\text{C}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ , ppm):  $\delta$  139.72, 114.47, 73.88, 72.54, 65.07, 45.30, 34.24, 29.98, 29.41, 29.38, 26.48. HRMS(EI+)  $m/z$ : 247.1898  $[\text{M}+\text{H}]^+$ .

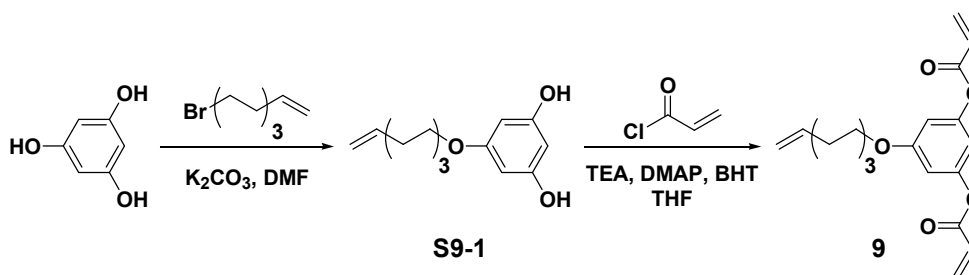
Clear viscous oil **7** was made from **7S-2** according to the typical procedure outlined for **2** above in 57% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ , ppm):  $\delta$  6.37 (dd,  $J = 17.6$  Hz,  $J = 1.7$  Hz, 3H), 6.11 (dd,  $J = 17.6$  Hz,  $J = 10.5$  Hz, 3H), 5.88-5.74 (m, 1H), 5.84 (dd,  $J = 10.5$  Hz,  $J = 1.7$  Hz, 3H), 5.02-4.89 (m, 2H), 4.24 (s, 6H), 3.46 (s, 2H), 3.38 (t,  $J = 6.6$  Hz, 2H), 2.06-1.99 (m, 2H), 1.57-1.47 (m, 2H), 1.40-1.26 (m, 6H).  $^{13}\text{C}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ , ppm):  $\delta$  166.08, 139.73, 131.39, 128.60, 114.45, 72.19, 69.47, 63.64, 43.42, 34.27, 29.91, 29.41, 29.40, 26.44. HRMS(EI+)  $m/z$ : 408.2149  $[\text{M}]^{+\bullet}$ .



**Scheme 2.9.** Synthesis of monomer **8**.

(**8**). Diethyl allylmalonate (2.0 g, 10 mmol) was added to a stirring 1M solution of LAH in ethyl ether (21 mL) at 0°C; the mixture was allowed to slowly warm up to room temperature and stirred for 12 h (Scheme 2.9). After this time, the reaction was cooled to room temperature, and sodium sulfate decahydrate was slowly added to the reaction mixture with vigorous stirring until gas evolution had ceased. The suspension was then stirred for 0.5 h, filtered through Celite (the filter cake was washed with Et<sub>2</sub>O and boiling hot THF), and concentrated under reduced pressure. **S8-1** was further purified by silica gel chromatography, eluting with 4:1 hexane:ethyl acetate to afford 0.65 g (56% yield) of a colorless oil. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>, ppm): δ 5.82 (m, 1H), 5.03 (m, 2H), 3.69 (m, 4H), 2.21 (broad m, 2H; OH), 2.04 (m, 2H), 1.81 (m, 1H). <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>, ppm): δ 137.12, 116.65, 66.06, 42.53, 33.04.

Clear viscous oil **8** was made from **S8-1** according to the typical procedure outlined for **2** above in 59% yield. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>, ppm): δ 6.37 (dd, J = 17.6 Hz, J = 1.7 Hz, 2H), 6.12 (dd, J = 17.6 Hz, J = 10.5 Hz, 2H), 5.82 (dd, J = 10.5 Hz, J = 1.7 Hz, 2H), 5.80 (m, 1H), 5.12-5.06 (m, 2H), 4.16 (m, 4H), 2.21 (m, 3H). <sup>13</sup>C NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>, ppm): δ 166.41, 135.75, 131.12, 128.86, 117.68, 64.47, 37.77, 33.26.

**Scheme 2.10.** Synthesis of monomer **9**.

(**9**). 8-Bromo-1-octene (2.65 mL, 15.9 mmol) was added to a flask charged with phloroglucinol (2 g, 15.9 mmol) and potassium carbonate (3.3 g, 23.9 mmol) in DMF (30 mL) and the reaction mixture was stirred at room temperature for 12 h (Scheme 2.10). The

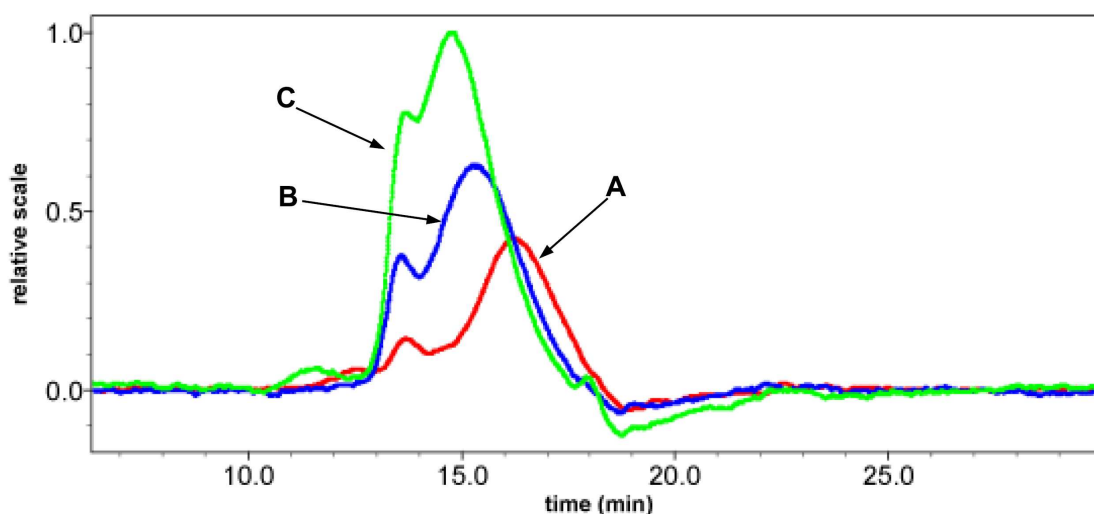
solvent was then removed under reduced pressure, the products redissolved in ether and washed with water three times. The aqueous layers were combined, acidified to pH~2 with 1N HCl, and extracted in ether 3 times. The combined organic layers were washed with saturated solution of sodium chloride and dried over anhydrous MgSO<sub>4</sub>. The solution was then filtered, concentrated, and purified by silica gel chromatography. The product was eluted with 3:1 hexane:ethyl acetate and **S9-1** (Scheme 2.9) was obtained as 0.96 g (26% yield) of a soft, white solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm): δ 6.00 (d, J = 2.1 Hz, 2H), 5.95 (t, J = 2.1 Hz, 1H), 5.82 (m, 1H), 5.04–4.92 (m, 2H), 3.87 (t, J = 6.4 Hz, 2H), 2.06 (m, 2H), 1.74 (m, 2H), 1.38 (m, 6H). <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>, ppm): δ 161.44, 157.50, 139.26, 114.52, 95.77, 95.16, 68.34, 33.91, 29.27, 29.03, 29.00, 26.04.

**9** was prepared from compound **S9-1** (0.86 g, 4.4 mmol), acryloyl chloride (1.08 mL, 13.3 mmol), TEA (3.08 mL, 22.1 mmol), and DMAP (0.054 g, 0.4 mmol) in dry THF (15 mL) according to the procedure for the synthesis of **2** outlined above (THF had to be used as a solvent instead of CH<sub>2</sub>Cl<sub>2</sub> due to the solubility properties of **S9-1**). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm): δ 6.60 (s, 3H), 6.59 (dd, J = 17.3 Hz, J = 1.2 Hz, 2H), 6.25 (dd, J = 17.3 Hz, J = 10.5 Hz, 2H), 5.95 (dd, J = 10.06 Hz, J = 1.2 Hz, 2H), 5.83 (m, 1H), 5.09–4.98 (m, 2H), 3.91 (t, J = 6.44 Hz, 2H), 2.26 (m, 2H), 1.74 (m, 2H), 1.45 (m, 6H). <sup>13</sup>C NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>, ppm): δ 164.60, 160.98, 152.24, 139.68, 133.25, 128.22, 114.56, 108.12, 106.41, 69.16, 34.26, 29.56, 29.41, 29.37, 26.35.

**Representative Polymerization Procedure (4a).** Monomer **4** (0.1 g, 0.4 mmol) and a small amount of radical quencher BHT (0.4 μmol) were dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (1 mL, 0.4 M) under an argon atmosphere. Catalyst **1** (1.7 mg, 2 μmol) was added to the reaction flask, and the solution was stirred at 45°C for 3–8 days (see explanation below) with venting through a bubbler (Scheme 2.2). Subsequently, the solvent was removed *en vacuo* and the product was characterized by <sup>1</sup>H NMR spectroscopy and triple detector–SEC with no further purification. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>, ppm): δ 6.95 (dt, J = 15.6 Hz, J = 5.8 Hz, 1H), 6.40 (ddd, J = 17.4 Hz, J = 4.9 Hz, J = 1.3 Hz, 1H), 6.11 (m, 1H), 5.82 (m, 2H), 5.20 (m, 1H), 4.35–4.17 (m, 2H), 2.2 (broad m, 2H), 1.67–1.38 (broad m, 6H).

Figure 2.5 demonstrates the progress of a typical polymerization as monitored by SEC. It was observed that longer polymerization times result in higher molecular weights.

However, the catalyst lifetime in the reaction solution limits the polymerization time to 3 days. Consequently, it was found that the best results are obtained when the catalyst is added to the reaction vessel in small portions at about 2 to 3 day intervals. In Figure 2.5, trace A corresponds to a progress of the polymerization at 3 days and 0.5% of mole equivalents of the catalyst, trace B corresponds to 2 more days with a fresh batch of 0.5% of mole equivalents of the catalyst, and trace C corresponds to 3 more days with yet another catalyst batch. The gradual peak shift to the left (from A to C) indicates an increase in polymer molecular weight. Moreover, the trace also becomes more narrow and uniform with time, signaling the narrowing of the PDI. Further optimization of polymerization conditions is currently underway.



**Figure 2.5.** Representative MALS-SEC traces for polymerization of **4** with consecutive batch catalyst addition.

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