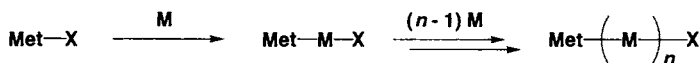


# Lewis acid-assisted anionic polymerizations for synthesis of polymers with controlled molecular weights

TAKUZO AIDA and DAISUKE TAKEUCHI

## 1. Introduction

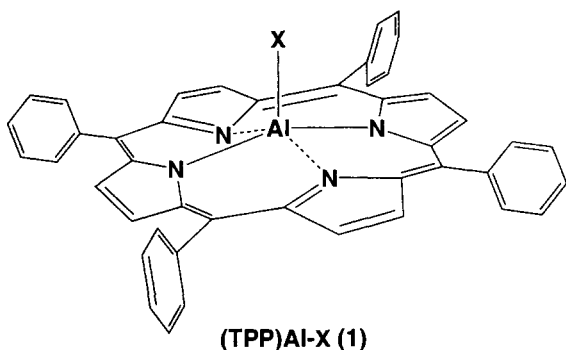
Unlike some naturally occurring macromolecules such as enzymes, synthetic polymers, except those obtained by stepwise approach, are of broad molecular weight distributions (MWD). In other words, they are mixtures of macromolecules with different molecular weights. Since 'molecular weight' is an essential factor affecting fundamental properties of polymer materials, it is important to develop a method for the synthesis of a polymer with a desired molecular weight with a narrow MWD. MWD is caused by the heterogeneity of the growth of polymer chains. Scheme 14.1 shows a schematic diagram of



Scheme 14.1

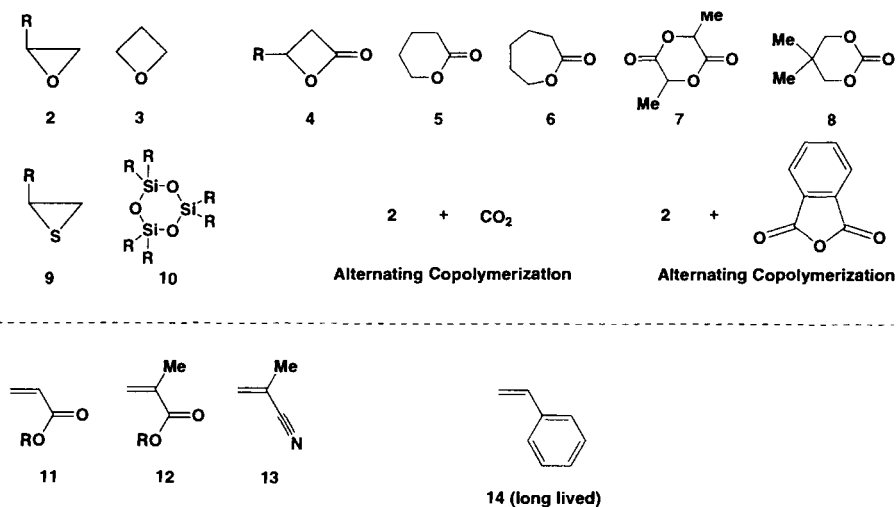
addition polymerization of an unsaturated monomer (M) with Met-X as initiator, where the chain growth of a polymer molecule starts by the reaction of Met-X with M to generate an active species (Met-M-X) (initiation step), followed by repeated additions of M to Met-M-X (propagation step), to furnish a higher molecular weight polymer (met-(M)<sub>n</sub>-X). In this case, if (1) the initiation is much faster than the propagation, and (2) the propagation proceeds uniformly with respect to all growing polymer molecules (Met-(M)<sub>n</sub>-X), a polymer with a uniform molecular weight should be formed. However, polymerization is generally accompanied by side reactions such as termination and chain transfer reactions, which lead to irreversible deactivation of the growing species. Since these side reactions interfere with the uniform growth of polymer chains, broadening of polymer MWD results.

In 1956, the first example of the formation of a narrow MWD polymer was discovered by Szwarc.<sup>1</sup> In his basic study on electron transfer reactions from organometallic compounds to unsaturated compounds, he noticed that mixing of styrene with sodium naphthalide resulted in the formation of a polymer, which is of very narrow MWD, as indicated by the ratio of weight- to number-average molecular weights ( $M_w/M_n$ ) close to unity.<sup>2</sup> Upon addition of a fresh feed of styrene to this system after the complete consumption of the first feed, second-stage polymerization ensues, resulting in further growth of all growing polymer molecules. Polymerization with this character is named 'living polymerization', since the growth pattern of polymer can be viewed as analogous to the growth of a biological organism.



In order to achieve 'living polymerization', it is essential to develop well-behaved initiators, since the initiator affects the relative rate of initiation to propagation, and the potential for side reactions during chain growth. Aida and Inoue *et al.*<sup>3</sup> have discovered that some metalloporphyrin complexes such as aluminium porphyrins ((TPP)Al-X, **1**; TPP = 5, 10, 15, 20-tetraphenylporphinato) serve as excellent initiators for living anionic polymerization, where the most characteristic feature is their exceptionally wide applicability for a variety of monomers (Scheme 14.2).<sup>4</sup> With **1** as initiator, the polymerization proceeds by the insertion of a monomer (M) into the Al-X bond in **1** to give a (TPP)Al-M-X (initiation step), which reacts with further monomer molecules (M) to grow to a higher polymer molecule ((TPP)Al-(M)<sub>n</sub>-X). By virtue of the 'living' character of the polymerization, block copolymers ((TPP)Al-(M')<sub>m</sub>-(M)<sub>n</sub>-X) with narrow MWDs can be synthesized by addition of different monomers (M') to (TPP)Al-(M)<sub>n</sub>-X.<sup>5-10</sup>

The polymerization with **1** is strongly affected by the structure of the porphyrin ligand of **1**, since the nucleophilic growing species always carries a (porphinato)aluminium, derived from **1**, as the counter species.<sup>11-14</sup> In the course of this study, we have discovered that bulky Lewis acids such as **2** dramatically accelerate the polymerization without spoiling the living character, and the polymerization is called 'Lewis acid-assisted high-speed living

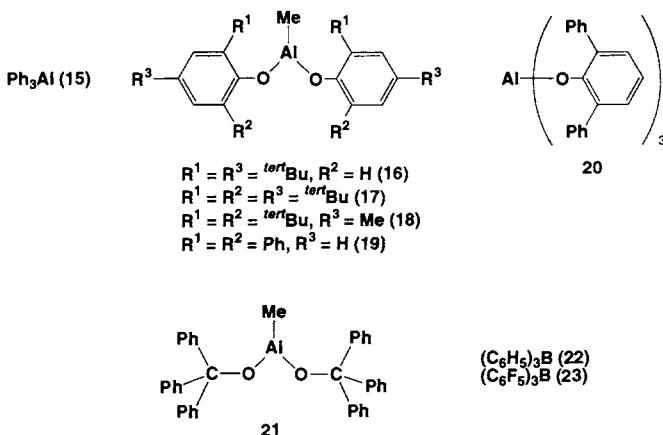
Scheme 14.2. Monomers of living polymerization with metallorhorphyrins<sup>3</sup>.

anionic polymerization'.<sup>15</sup> Such bulky organoaluminium phenolates have been pioneered by Yamamoto *et al.* in organic syntheses.<sup>16–17</sup>

## 2. Principle, scope, and limitations of 'Lewis acid-assisted high-speed living anionic polymerization'

Detailed studies on the above-mentioned accelerated polymerization have shown that nucleophiles (initiators or active polymer terminals) attached to aluminium porphyrins and bulky Lewis acids do not directly interact (react) with each other but can coexist due to a steric repulsion between them.<sup>16,17</sup> Therefore, the Lewis acids can retain their inherently high ability to coordinate with and activate Lewis basic monomers for nucleophilic attack. This is the basic principle of the 'Lewis acid-assisted high-speed living anionic polymerization'.<sup>18</sup>

As shown in Scheme 14.3, representative Lewis acids for the high-speed living anionic polymerization involve methylaluminium diphenoxides having *ortho*-substituents at the phenyl rings.<sup>18,19</sup> In sharp contrast, with simple trialkylaluminium compounds and methylaluminium diphenoxides without *ortho*-substituents at the phenyl rings, the polymerization is terminated before completion due to undesired direct reactions between the nucleophilic growing species and the Lewis acids, resulting in the formation of a polymer with a broad MWD. An exceptional case is the polymerization with 'hindered' aluminium tetraphenylporphyrins as initiators, where simple trialkylaluminium compounds without any steric protection are usable as accelerators. For



**Scheme 14.3.** Lewis acids as monomer activators for high-speed living anionic polymerization with aluminium porphyrins as nucleophilic initiators<sup>18</sup>.

example, the polymerization of methyl methacrylate initiated with methylaluminium tetramesitylporphyrin is accelerated by the addition of tri-isobutylaluminium, and proceeds to attain 100% monomer conversion, affording a polymer with a narrow MWD.<sup>20</sup> Triphenylaluminium is also usable, but the activity is lower than the hindered aluminium phenoxides. Trialkylboron compounds, in sharp contrast with trialkylaluminums, do not terminate nor accelerate the polymerization. On the other hand, triarylborens such as triphenylboron and tris(pentafluorophenyl)boron serve as accelerators for the living polymerization.<sup>21</sup>

In addition to the acceleration of anionic polymerization, combined use of bulky nucleophiles and Lewis acids also allows controlled polymerization of monomers with cationic polymerizability: Although cyclic ethers such as oxiranes are polymerizable both anionically and cationically, oxetanes are only cationically polymerizable due to their strong basicity, and no example had been reported for the controlled synthesis of polyoxetanes because of inherently high potentials of cationic processes for side reactions. In contrast, by using an aluminium porphyrin as nucleophilic initiator in conjunction with a bulky Lewis acid, the polymerization of non-substituted oxetane proceeds in a living anionic fashion to give a polymer with a narrow MWD.<sup>22</sup> A sequential high-speed living anionic polymerization of methyl methacrylate and oxetane with this amphiphilic initiating system results in the formation of a narrow MWD block copolymer. Without this method, such a block copolymer could not be available, since methacrylic esters are polymerizable anionically and radically but not cationically.

In place of aluminium porphyrins, Schiff base and phthalocyanine complexes of aluminium can be used in conjunction with bulky Lewis acids for the controlled polymerization of cyclic ethers.<sup>23</sup> Later, this method has been

extended to much simpler systems composed of quaternary onium salts and bulky Lewis acids, which allow high-speed living anionic polymerization of oxiranes and oxetanes.<sup>24</sup> In this case, bulky ate complexes are formed from onium salts and Lewis acids, which attack activated monomers through coordination with excess Lewis acids. Alcohol/bulky Lewis acid systems are also effective for the polymerization of lactones and cyclic carbonates.<sup>25</sup> More recently, organolithium compounds coupled with bulky Lewis acids have been found to initiate the living stereospecific polymerization of methacrylates at a low temperature to give narrow MWD polymers rich in heterotactic sequence.<sup>26</sup>

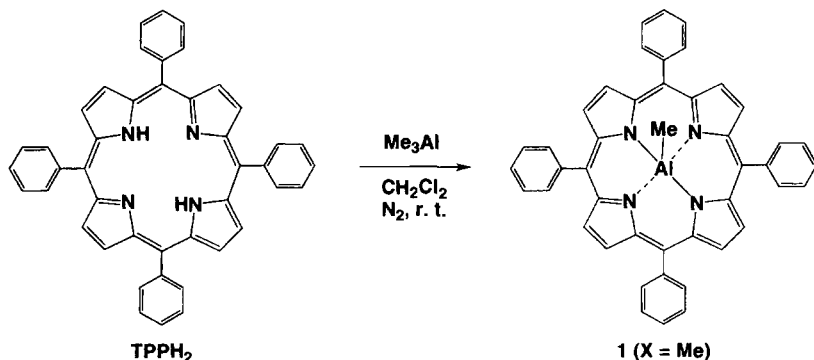
### Protocol 1.

**Accelerated synthesis of a narrow MWD poly(methyl methacrylate). Polymerization of methyl methacrylate (12, = Me) initiated with methylaluminium 5, 10, 15, 20-tetraphenylporphine (1, X = Me) in the presence of methylaluminium bis(2, 6-di-*tert*-butyl-4-methylphenoxy) (18).<sup>28</sup>**

The procedure consists of three steps; (1) preparation of methylaluminium 5, 10, 15, 20-tetraphenylporphine (TPP)AlMe (1, X = Me), (2) preparation of methylaluminium bis(2, 6-di-*tert*-butyl-4-methylphenoxy) (18) and (3) polymerization of methyl methacrylate (MMA; 12 R x5 Me).

**Step 1.** Preparation of methylaluminium 5, 10, 15, 20-tetraphenylporphine ((TPP)AlMe) (1, X = Me) (Scheme 14.4)

**Caution!** Carry out all procedures in a well-ventilated hood, and wear disposable vinyl or latex gloves and chemical-resistant safety goggles.



Scheme 14.4

## Protocol 1. Continued

### Equipment

- Magnetic stirrer
- One-necked, round-bottomed flask (100 mL)
- Three-way stopcock
- Teflon-coated magnetic stirring bar (1 × 0.4 cm)
- All-glass syringes (0.25 and 50 mL) with a needle-lock luer
- Needles
- Source of dry nitrogen (preferably from a nitrogen line)

### Materials

- 5, 10, 15, 20-tetraphenylporphine (TPPH<sub>2</sub>)<sup>a</sup> (FW 614.7), 0.615 g, 1 mmol **light-sensitive**
- Trimethylaluminium<sup>b</sup> (FW 72.1), 0.096 mL, 1 mmol **pyrophoric, air- and moisture-sensitive**
- Dichloromethane (FW 84.9),<sup>c</sup> 40 mL **irritant, toxic**

1. Clean all glassware, syringes, needles, and stirring bar and dry for at least 5 h in a 110°C electric oven before use.
2. Put purified TPPH<sub>2</sub> (0.614 g, 1 mmol) and a Teflon-coated magnetic stirring bar in a one-necked, round-bottomed flask, and equip the neck of the flask with a three-way stopcock using a Demnum grease (Daikin).
3. Support the apparatus using a clamp and a stand with a heavy base, and connect the apparatus to a vacuum/nitrogen line via the three-way stopcock.
4. Dry the above apparatus with a hair dryer under vacuum (10<sup>-2</sup> mm Hg) for 1 h, then back-fill the apparatus with nitrogen. Repeat to a total of three times. Do not use an electric heat gun for drying, since overheating leads to decomposition of TPPH<sub>2</sub>.
5. Charge the apparatus containing TPPH<sub>2</sub> with distilled dichloromethane (40 mL), using a syringe through the three-way stopcock in a nitrogen stream, to give a purple suspension of TPPH<sub>2</sub>.
6. Support a flask, attached to a three-way stopcock, containing distilled trimethylaluminium under nitrogen, using a clamp and a stand with a heavy base, and connect the flask to a nitrogen line via the three-way stopcock.
7. Fill a syringe with trimethylaluminium (0.096 mL, 1 mmol) from the flask through the three-way stopcock in a nitrogen stream, and add the reagent dropwise to the reaction apparatus containing the suspension of TPPH<sub>2</sub> in a nitrogen stream at room temperature. The reaction mixture evolves methane gas and gradually turns homogeneous in 2 h with a colour change from purple to greenish purple, characteristic of methylaluminium 5, 10, 15, 20-tetraphenylporphine ((TPP)AlMe; **1**, X = Me), which displays the appropriate <sup>1</sup>H NMR (in CDCl<sub>3</sub>). (TPP)AlMe is sensitive to oxygen and moisture, and easily decomposes to the corresponding alkoxide on exposure to air.

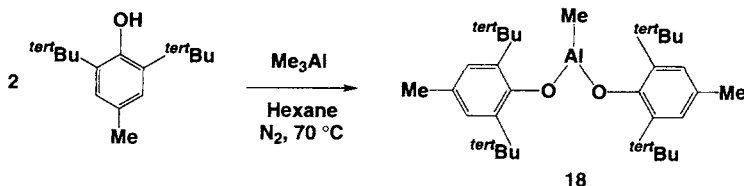
<sup>a</sup> Synthesize TPPH<sub>2</sub> by condensation of benzaldehyde (0.8 mol) and pyrrole (0.8 mol) in refluxing propionic acid (2.5 L) for 0.5 h under air.<sup>27</sup> Isolate the crystalline precipitate and recrystallize it from chloroform/methanol after washing with hot water (~20% yield). Commercial TPPH<sub>2</sub> (Aldrich) can also be used but must be purified in a similar manner as described above.

<sup>b</sup> Distil trimethylaluminium fractionally under reduced pressure in a nitrogen atmosphere.

<sup>c</sup> Wash commercial dichloromethane subsequently with concentrated sulfuric acid/water/aqueous NaHCO<sub>3</sub>/water in order to remove stabilization agents, and distill fractionally after refluxing over calcium hydride under nitrogen.

**Step 2.** Preparation of methylaluminium bis(2, 6-di-*tert*-butyl-4-methylphenolate) (**18**) (Scheme 14.5)

**Caution!** Carry out all procedures in a well-ventilated hood, and wear disposable vinyl or latex gloves and chemical-resistant safety goggles.



Scheme 14.5

**Equipment**

- Magnetic stirrer
- One-necked, round-bottomed flask (50 mL)
- Three-way stopcock
- Teflon-coated magnetic stirring bar (1 × 0.4 cm)
- All-glass syringes (1 and 20 mL) with a needle-lock luer
- Needles
- Source of dry nitrogen (preferably from a nitrogen line)

**Materials**

- 2, 6-Di-*tert*-butyl-4-methylphenol<sup>a</sup> (FW 220.4), 2.75 g, 12.5 mmol **irritant**
- Trimethylaluminium<sup>b</sup> (FW 72.1), 0.6 mL, 6.25 mmol **pyrophoric, air- and moisture-sensitive**
- Hexane (FW 86.2)<sup>c</sup> 10 mL **flammable, irritant**

1. Clean all glassware, syringes, needles, and stirring bar and dry for at least 5 h in a  $110^\circ\text{C}$  electric oven before use.
2. Put recrystallized 2, 6-di-*tert*-butyl-4-methylphenol (2.75 g, 12.5 mmol) and a Teflon-coated magnetic stirring bar in a one-necked, round-bottomed flask, and equip the neck of the flask with a three-way stopcock using a Demnum grease.
3. Support the apparatus using a clamp and a stand with a heavy base, and connect the apparatus to a vacuum/nitrogen line via the three-way stopcock.
4. Dry the above apparatus under vacuum ( $10^{-2}$  mm Hg) for 1 h, then back-fill the apparatus with nitrogen. Repeat to a total of three times. Do not heat the apparatus, so as to avoid sublimation of 2, 6-di-*tert*-butyl-4-methylphenol.
5. Charge the apparatus containing 2, 6-di-*tert*-butyl-4-methylphenol with distilled hexane (10 mL), using a syringe through the three-way stopcock in a nitrogen stream, to dissolve the phenol.
6. Support a flask, attached to a three-way stopcock, containing distilled trimethylaluminium under nitrogen, using a clamp and a stand with a heavy base, and connect the flask to a nitrogen line via the three-way stopcock.

**Protocol 1. Continued**

7. Fill a syringe with trimethylaluminum (0.6 mL, 6.25 mmol) from the flask through the three-way stopcock in a nitrogen stream, and add the reagent in the syringe, through the three-way stopcock in a nitrogen stream, dropwise at 0°C to the reaction apparatus containing the hexane solution of 2, 6-di-*tert*-butyl-4-methylphenol.
8. Stir the content of the above apparatus magnetically at room temperature under nitrogen. The reaction mixture evolves methane gas and produces white precipitates in the initial 5–10 min. Stir the suspension for an additional 2 h at room temperature under nitrogen.
9. Warm the suspension at 70°C under nitrogen until the precipitate completely dissolves. Allow the clear solution to stand overnight at room temperature, to give white crystals.
10. Remove a supernatant, liquid phase with a syringe from the above apparatus in a nitrogen stream, and add distilled hexane (5 mL) by syringe to the residue and stir the mixture for a while. Repeat this procedure to a total of three times in order to wash the crystals.
11. Dry the crystals under reduced pressure ( $10^{-2}$  mm Hg) for 1 h at room temperature to produce methylaluminum bis(2, 6-di-*tert*-butyl-4-methylphenolate) (**18**) in 64% yield (1.9 g, 4.0 mmol).

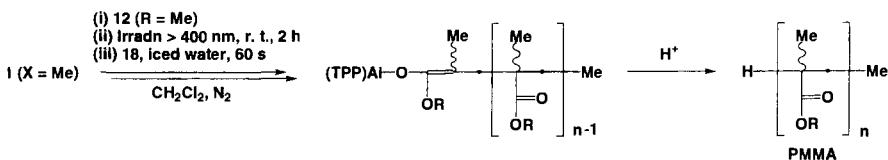
<sup>a</sup> Recrystallize commercial 2, 6-di-*tert*-butyl-4-methylphenol from hexane.

<sup>b</sup> Distil trimethylaluminum fractionally under reduced pressure in a nitrogen atmosphere.

<sup>c</sup> Distil hexane after refluxing over sodium wire under nitrogen.

**Step 3. Polymerization of methyl methacrylate (MMA) (Scheme 14.6)**

**Caution!** Carry out all procedures in a well-ventilated hood, and wear disposable vinyl or latex gloves and chemical-resistant safety goggles.



**Scheme 14.6**

**Equipment**

- Magnetic stirrer
- One-necked, round-bottomed flask (100 mL)
- Three-way stopcock
- Beaker (500 mL)
- Teflon-coated magnetic stirring bars (1 × 0.4 cm, 2 × 0.6 cm)
- Needles
- All-glass syringes (2, 20, and 30 mL) with a needle-lock luer
- Source of dry nitrogen (preferably from a nitrogen line)
- 300-W Xenon arc lamp equipped with thermal- and UV-cutoff filters
- Iced water bath



## 14: Lewis acid-assisted anionic polymerizations

### Materials

- (5, 10, 15, 20-Tetraphenylporphinato)aluminium methyl ((TPP)AlMe; **1**, X = Me) (FW 654.7) 0.655 g, 1 mmol in dichloromethane (40 mL) (prepared in Step 1) **air- and moisture-sensitive, light-sensitive**
- Methylaluminium bis(2, 6-di-*tert*-butyl-4-methylphenoxide) (**18**) (FW 480.4), 1.44 g, 3.0 mmol in dichloromethane (10 mL) (prepared in step 2) **air- and moisture-sensitive**
- Methyl methacrylate (MMA; **12**, R = Me)<sup>a</sup> (FW 100.1), 20 mL, 200 mmol **flammable, corrosive**
- Methanol (FW 32.0), 500 mL **flammable, toxic**
- Benzene (FW 78.1) 200 mL **flammable, toxic**

1. Support the apparatus containing a dichloromethane solution (40 ml) of **1** (X = Me) (0.655 g, 1 mmol; Step 1, using a clamp and a stand with a heavy base, and connect the apparatus to a nitrogen line via the three-way stopcock.
2. Support a flask, attached to a three-way stopcock, containing distilled MMA (**12** R = Me) under nitrogen, using a clamp and a stand with a heavy base, and connect the flask to a nitrogen line via the three-way stopcock.
3. Fill a syringe with **12** (R = Me) (20 mL, 200 mmol) from the flask through the three-way stopcock in a nitrogen stream, and add the reagent in the syringe, through the three-way stopcock in a nitrogen stream, dropwise to the reaction apparatus containing the dichloromethane solution of **1** (X = Me).
4. Stir the contents of the reaction apparatus magnetically at room temperature, and expose for 2 h to a 300-W xenon arc light through thermal- and UV-cutoff filters from a distance of 10 cm. During this period, the solution turns from greenish purple to dark reddish purple, characteristic of an enolatoaluminium porphyrin.
5. Stop the irradiation, and put the reaction apparatus in an iced water bath.
6. Support a flask, attached to a three-way stopcock, containing a dichloromethane solution (0.3 M) of **18** (Step 2) under nitrogen, using a clamp and a stand with a heavy base, and connect the flask to a nitrogen line via the three-way stopcock.
7. Fill a syringe with the dichloromethane solution (10 mL) of **18** (1.4 g, 3 mmol) from the flask through the three-way stopcock in a nitrogen stream, and add the solution in the syringe dropwise to the reaction apparatus containing the above photoirradiated reaction mixture of **1** (X = Me) and **12** (R = Me) while stirring magnetically under nitrogen. The polymerization proceeds with a considerable evolution of heat, and reaches 100% monomer conversion within a few seconds.
8. After 30 s, add methanol (1 mL, 24.7 mmol) to the reaction apparatus containing the polymerization mixture, and pour the contents into a large volume of methanol (500 mL) with vigorous stirring magnetically, to give a precipitate.

**Protocol 1. Continued**

9. Collect the precipitate, dissolve it in benzene (200 mL), and freeze-dry to give a poly(methyl methacrylate) ( $M_n = 21500$ ,  $M_w/M_n = 1.10$ ) in 90% yield (18 g) based on the charged monomer.

<sup>a</sup> Distil **12** (R = Me) after stirring with calcium hydride or more vigorously with trimethylaluminum under nitrogen.

By changing the mole ratio of **12** (R = Me) to **1** (X = Me), the molecular weight of the polymer can be controlled over a wide range up to  $10^6$ , retaining the narrow MWD ( $M_w/M_n = 1.05\text{--}1.2$ ).<sup>28</sup> The present procedure is also applicable to the living anionic polymerization of other methacrylates (**12**; R = ethyl, isopropyl, n-butyl, isobutyl, benzyl, and dodecyl,<sup>29</sup> and methacrylonitrile (**13**).<sup>30</sup>

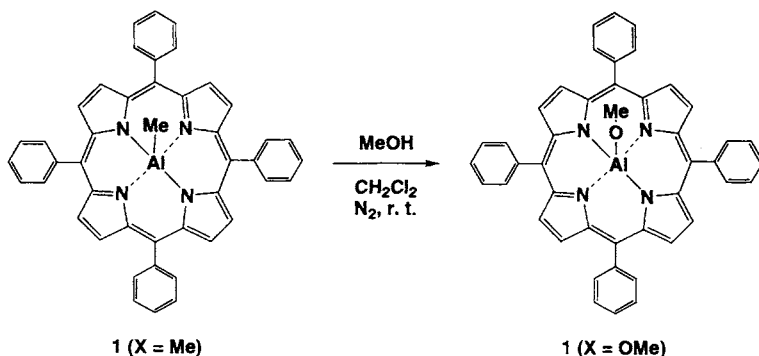
**Protocol 2.**

**Accelerated synthesis of a narrow MWD poly( $\delta$ -valerolactone).**  
**Polymerization of  $\delta$ -valerolactone (5) initiated with (5, 10, 15, 20-tetraphenylporphinato)aluminium methoxide ((TPP)AlOMe; **1**, X = OMe) in the presence of methylaluminium bis(2, 6-diphenylphenoxide) (**19**)<sup>31</sup>**

The procedure consists of three steps; (1) preparation of (5, 10, 15, 20-tetraphenylporphinato)aluminium methoxide ((TPP)AlOMe; **1**, X = OMe), (2) preparation of methylaluminium bis(2, 6-diphenylphenoxide) (**19**) and (3) polymerization of  $\delta$ -valerolactone (**5**).

**Step 1.** Preparation of (5, 10, 15, 20-tetraphenylporphinato)aluminium methoxide ((TPP)AlOMe; **1**, X = OMe) (Scheme 14.7)

**Caution!** Carry out all procedures in a well-ventilated hood, and wear disposable vinyl or latex gloves and chemical-resistant safety goggles.



Scheme 14.7

### Equipment

- Magnetic stirrer
- One-necked, round-bottomed flask (50 mL)
- Three-way stopcock
- Teflon-coated magnetic stirring bar (1 × 0.4 cm)
- All-glass syringes (10 and 30 mL) with a needle-lock luer
- Needles
- Source of dry nitrogen (Preferably from a nitrogen line)

### Materials

- Methylaluminum 5, 10, 15, 20-tetraphenylporphine ((TPP)AlMe; **1**, X = Me)<sup>a</sup> (FW 654.7), 0.065 g, 0.1 mmol in dichloromethane (4 mL) (for preparation, see Protocol 1, Step 1)

air- and moisture-sensitive, light-sensitive  
flammable, toxic

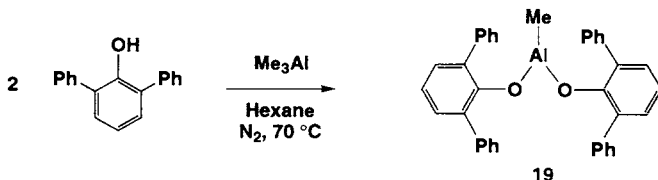
- Methanol (FW 32.0),<sup>a</sup> 1 mL, 24.6 mmol

1. Support the reaction apparatus, containing a dichloromethane solution (4 mL) of **1** (X = Me) (0.065 g, 0.1 mmol), under nitrogen (see Protocol 1, Step 1), using a clamp and a stand with a heavy base, and connect the apparatus to a vacuum/nitrogen line via the three-way stopcock.
2. Support a flask, attached to a three-way stopcock, containing distilled methanol under nitrogen, using a clamp and a stand with a heavy base, and connect the flask to a nitrogen line via the three-way stopcock.
3. Fill a syringe with methanol (1 mL, 24.6 mmol) from the flask through the three-way stopcock in a nitrogen stream, and add the reagent in the syringe, through the three-way stopcock in a nitrogen stream, to the reaction apparatus containing the dichloromethane solution of **1** (X = Me) at room temperature.
4. Stir the contents of the reaction apparatus magnetically for 15 h at room temperature under nitrogen. The solution gradually turns from greenish purple to bright reddish purple, characteristic of a (porphinato)aluminum alkoxide.
5. Connect the reaction apparatus to a vacuum line, and remove volatile fractions from the contents under reduced pressure ( $10^{-2}$  mm Hg), and back-fill the apparatus with nitrogen, leaving (TPP)AlOMe (**1**, X = OMe) as a reddish purple powder, which displays the appropriate <sup>1</sup>H NMR (in CDCl<sub>3</sub>).

<sup>a</sup> Distil methanol after refluxing over magnesium ribbon under nitrogen.

**Step 2.** Preparation of methylaluminum bis(2, 6-diphenylphenoxide) (**19**) (Scheme 14.8)

**Caution!** Carry out all procedures in a well-ventilated hood, and wear disposable vinyl or latex gloves and chemical-resistant safety goggles.



Scheme 14.8

**Protocol 2. Continued****Equipment**

- Magnetic stirrer
- One-necked, round-bottomed flask (5 mL)
- Three-way stopcock
- Teflon-coated magnetic stirring bar (1 × 0.4 cm)
- All-glass syringes (0.5 and 20 mL) with a needle-lock luer
- Needles
- Source of dry nitrogen (preferably from a nitrogen line)

**Materials**

- Trimethylaluminum<sup>a</sup> (FW 72.09), 0.29 mL, 3 mmol **pyrophoric, air- and moisture-sensitive**
- 2, 6-Diphenylphenol<sup>b</sup> (FW 246.3), 1.5 g, 6 mmol **irritant**
- Dichloromethane (FW 84.0,<sup>c</sup> 10 mL **irritant, toxic**)

1. Clean all glassware, syringes, needles, and stirring bar and dry for at least 5 h in a 110°C electric oven before use.
2. Put recrystallized 2, 6-diphenylphenol (1.5 g, 6 mmol) and a Teflon-coated magnetic stirring bar in a one-necked, round-bottomed flask, and equip the neck of the flask with a three-way stopcock using a Demnum grease (Daikin).
3. Support the apparatus using a clamp and a stand with a heavy base, and connect the apparatus to a vacuum/nitrogen line via the three-way stopcock.
4. Dry the above apparatus under vacuum ( $10^{-2}$  mm Hg) for 1 h, then back-fill the apparatus with nitrogen. Repeat to a total of three times. Do not heat the apparatus, so as to avoid sublimation of 2, 6-diphenylphenol.
5. Using a syringe, add dichloromethane (10 mL) to the apparatus containing 2, 6-diphenylphenol through the three-way stopcock in a nitrogen stream, to dissolve the phenol.
6. Support a flask, attached to a three-way stopcock, containing distilled trimethylaluminium under nitrogen, using a clamp and a stand with a heavy base, and connect the flask to a nitrogen line via the three-way stopcock.
7. Fill a syringe with trimethylaluminium (0.29 mL, 3 mmol) from the flask through the three-way stopcock in a nitrogen stream, and add the reagent in the syringe, through the three-way stopcock in a nitrogen stream, dropwise to the reaction apparatus containing the dichloromethane solution of 2, 6-diphenylphenol at 0°C.
8. Stir the contents of the apparatus at room temperature under nitrogen. The reaction mixture evolves methane gas during the initial 5–10 min. Stir the solution for an additional 2 h at room temperature under nitrogen. Use the resulting pale-yellow solution containing **19** for the subsequent polymerization (Step 3).

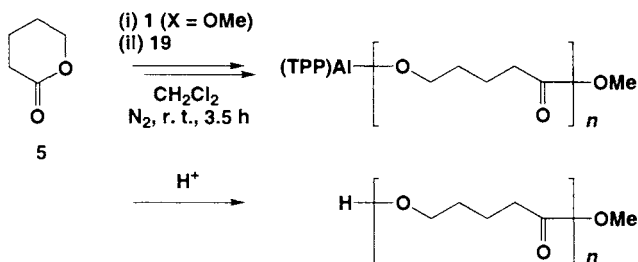
<sup>a</sup> Distil trimethylaluminium fractionally under reduced pressure in a nitrogen atmosphere.

<sup>b</sup> Recrystallize commercial 2, 6-diphenylphenol from hexane.

<sup>c</sup> Wash commercial dichloromethane successively with concentrated sulfuric acid/water/aqueous NaHCO<sub>3</sub>/water in order to remove stabilization agents, and fractionally distil after refluxing over calcium hydride under nitrogen.

**Step 3.** Polymerization of  $\delta$ -valerolactone (**5**) (Scheme 14.9)

**Caution!** Carry out all procedures in a well-ventilated hood, and wear disposable vinyl or latex gloves and chemical-resistant safety goggles.



Scheme 14.9

**Equipment**

- Magnetic stirrer
- One-necked, round-bottomed flask (100 mL)
- Three-way stopcock
- Teflon-coated magnetic stirring bars (1 × 0.4 cm, 2 × 0.6 cm)
- All-glass syringes (2, 5, and 20 mL) with a needle-lock luer
- Needles
- Source of dry nitrogen (preferably from a nitrogen line)

**Materials**

- (5, 10, 15, 20-Tetraphenylporphinato)aluminium methoxide ((TPP)AlOMe; **1**, X = OMe)<sup>a</sup> (FW 670.7), 0.067 g, 0.1 mmol (prepared in Step 1)
- Methylaluminium bis(2, 6-diphenylphenoxide) (**19**) (FW 532.6) 0.16 g, 0.3 mmol in dichloromethane (10 mL) (prepared in Step 2)
- $\delta$ -Valerolactone (**5**)<sup>a</sup> (FW 100.1), 1.86 mL, 20 mmol
- Dichloroethane<sup>b</sup> (FW 98.96), 4 mL, 50 mmol
- methanol (FW 32.0), 500 mL
- Benzene (FW 78.1), 200 mL

moisture-sensitive, light-sensitive

air- and moisture-sensitive  
irritant  
flammable, toxic  
flammable, toxic  
flammable, toxic

1. Support the apparatus containing **1** (X = OMe) (0.067 g, 0.1 mmol; Step 1) under nitrogen, using a clamp and a stand with a heavy base, and connect the apparatus to a nitrogen line via the three-way stopcock.
2. Using a syringe add distilled dichloroethane (4 mL) through the three-way stopcock in a nitrogen stream, to give a clear, bright reddish purple solution.
3. Support a flask, attached to a three-way stopcock, containing distilled **5** under nitrogen, using a clamp and a stand with a heavy base, and connect the flask to a nitrogen line via the three-way stopcock.
4. Fill a syringe with **5** (1.86 mL, 20 mmol) from the flask through the three-way stopcock in a nitrogen stream, and add the reagent in the syringe, through the three-way stopcock in a nitrogen stream, dropwise to the reaction apparatus containing the dichloroethane solution of **1** (X = OMe) upon stirring magnetically at room temperature.

**Protocol 2. Continued**

- Support a flask, attached to a three-way stopcock, containing a dichloromethane solution (0.3 M) of **19** under nitrogen (prepared in Step 2), using a clamp and a stand with a heavy base, and connect the apparatus to a nitrogen line via the three-way stopcock.
- Fill a syringe with the dichloromethane solution (1 mL) of **19** (0.16 g, 0.3 mmol) from the flask through the three-way stopcock in a nitrogen stream, and add the solution in the syringe, through the three-way stopcock in a nitrogen stream, to the reaction apparatus containing the mixture of **1** ( $X = \text{OMe}$ ) and **5** in dichloroethane upon stirring magnetically at room temperature.
- Stir the mixture in the reaction apparatus magnetically for 3.5 h at room temperature under nitrogen. The polymerization reaches 74% monomer conversion to give a viscous, partially solidified solution.
- Pour the polymerization mixture in a large volume of methanol (500 mL) with vigorous stirring, to give a precipitate.
- Collect the precipitate, dissolve it in benzene (200 mL), and freeze-dry, to give a poly( $\delta$ -valerolactone) ( $M_n = 24000$ ,  $M_w/M_n = 1.13$ ) in 67% yield (1.3 g) based on the charged monomer.

<sup>a</sup> Distil **5** after stirring with calcium hydride under nitrogen.

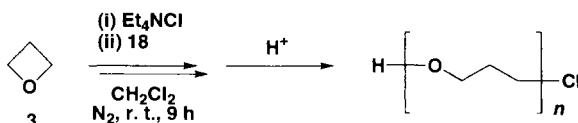
<sup>b</sup> Wash commercial dichloroethane successively with concentrated sulfuric acid/water/aqueous  $\text{NaHCO}_3$ /water in order to remove stabilization agents, and fractionally distil after refluxing over calcium hydride under nitrogen.

By changing the mole ratio of **5** to **1** ( $X = \text{OMe}$ ), the molecular weight of the polymer can be controlled over a wide range up to  $10^5$ , retaining the narrow MWD ( $M_w/M_n < 1.2$ ). Use of **18** as accelerator results in broadening of MWD at a high conversion ( $>70\%$ ), due to undesired transesterification of the produced polymer caused by **18**.<sup>31</sup>

**Protocol 3.**

**Accelerated synthesis of a narrow MWD polyoxetane. Polymerization of oxetane (**3**) initiated with tetraethylammonium chloride ( $\text{Et}_4\text{NCl}$ ) in the presence of methylaluminum bis(2, 6-di-*tert*-butyl-4-methylphenolate) (**18**).<sup>24</sup> (Scheme 14.10)**

**Caution!** Carry out all procedures in well-ventilated hood, and wear disposable vinyl or latex gloves and chemical-resistant safety goggles.



Scheme 14.9

## 14: Lewis acid-assisted anionic polymerizations

### Equipment

- Magnetic stirrer
- One-necked, round-bottomed flask (50 mL)
- Three-way stopcock
- Teflon-coated magnetic stirring bar (1 × 0.4 cm)
- Needles
- All-glass syringes (1, 2, and 3 mL) with a needle-lock luer
- Source of dry nitrogen (preferably from a nitrogen line)
- Glass column for chromatography (50 × 4 cm)

### Materials

- Tetraethylammonium chloride ( $\text{Et}_4\text{NCl}$ )<sup>a</sup> (FW 165.7), 0.0166 g, 0.1 mmol **hygroscopic, irritant**
- Methylaluminum bis(2, 6-di-*tert*-butyl-4-methylphenolate) (**18**)<sup>b</sup> (FW 480.7), (0.14 g, 0.3 mmol) in dichloromethane solution (0.3 M, 1 mL) (for preparation, see Protocol 1, Step 2) **air- and moisture-sensitive**
- Dichloromethane,<sup>b</sup> 2 mL **irritant, toxic**
- Oxetane (**3**) (FW 58.1),<sup>c</sup> 0.65 mL, 10 mmol **flammable**
- Silica gel (C300) 150 g

1. Clean all glassware, syringes, needles, and stirring bar and dry for at least 5 h in a 110°C electric oven before use.
2. Put recrystallized tetraethylammonium chloride ( $\text{Et}_4\text{NCl}$ ) (0.0166 g) and a Teflon-coated magnetic stirring bar in a one-necked, round-bottomed flask, and equip the neck of the flask with a three-way stopcock using a Demnum grease (Daikin).
3. Support the above apparatus using a clamp and a stand with a heavy base, and dry the content under vacuum ( $10^{-2}$  mm Hg) for 1 h, then back-fill the apparatus with nitrogen. Repeat to a total of three times. Do not heat the apparatus, so as to avoid decomposition of  $\text{Et}_4\text{NCl}$ .
4. Using a syringe add dichloromethane (2 mL) through the three-way stopcock in a nitrogen stream, to dissolve  $\text{Et}_4\text{NCl}$ .
5. Support a flask, attached to a three-way stopcock, containing a dichloromethane solution of **18** (0.3 M) under nitrogen (Protocol 1, Step 2), using a clamp and a stand with a heavy base, and connect the flask to a nitrogen line via the three-way stopcock.
6. Fill a syringe with the dichloromethane solution (1 mL) of **18** (0.14 g, 0.3 mmol) from the flask through the three-way stopcock in a nitrogen stream, and add the solution in the syringe, through the three-way stopcock in a nitrogen stream, dropwise to the reaction apparatus containing the dichloromethane solution of  $\text{Et}_4\text{NCl}$  while stirring magnetically at room temperature.
7. Likewise, add **3** (0.65 mL, 10 mmol) to the above reaction apparatus, and stir the contents for 9 h at room temperature. The polymerization reaches 100% monomer conversion, to give a viscous solution.
8. Evaporate the polymerization mixture to dryness with a rotary evaporator. Separate the residue by silica gel column chromatography with ethyl acetate–hexane (4:1) as eluant. Evaporate the fraction containing polymeric

**Protocol 3. Continued**

products with a rotary evaporator, to leave a polyoxetane as a colourless viscous liquid ( $M_n = 5200$ ,  $M_w/M_n = 1.12$ ) in 80% yield (0.46 g) based on the monomer charged.

<sup>a</sup> Recrystallize commercial  $\text{Et}_4\text{NCl}$  from acetone–hexane.

<sup>b</sup> Wash commercial dichloromethane successively with concentrate sulfuric acid/water/aqueous  $\text{NaHCO}_3$ /water in order to remove stabilization agents, and distil fractionally after refluxing over calcium hydride under nitrogen.

<sup>c</sup> Distil commercial **3** over sodium wire under reduced pressure in a nitrogen stream at room temperature.

By changing the mole ratio of **3** to  $\text{Et}^4\text{NCl}$ , the molecular weight of the polymer can be controlled up to 20 000, retaining the narrow MWD ( $M_w/M_n = 1.09$ – $1.15$ ).<sup>24</sup> No polymerization takes place when the mole ratio **18**: $\text{Et}_4\text{NCl}$  is less than unity.

**References**

1. Szwarc, M. *Nature* **1956**, *178*, 1168–1170.
2. Szwarc, M.; Levy, M.; Milkovich, R. *J. Am. Chem. Soc.* **1956**, *78*, 2656–2657.
3. Aida, T.; Inoue, S. *Acc. Chem. Res.* **1996**, *29*, 39–48.
4. Aida, T. *Prog. Polym. Sci.* **1994**, *19*, 469–528.
5. Aida, T.; Inoue, S. *Macromolecules* **1981**, *14*, 1162–1166.
6. Yasuda, T.; Aida, T.; Inoue, S. *Macromolecules* **1984**, *17*, 2217–2222.
7. Aida, T.; Sanuki, T.; Inoue, S. *Macromolecules* **1985**, *18*, 1049–1055.
8. Aida, T.; Ishikawa, M.; Inoue, S. *Macromolecules* **1986**, *19*, 8–11.
9. Kuroki, M.; Nashimoto, S.; Aida, Y.; Inoue, S. *Macromolecules* **1988**, *21*, 3114–3115.
10. Hosokawa, Y.; Kuroki, M.; Aida, T.; Inoue, S. *Macromolecules* **1991**, *24*, 824–829.
11. Aida, T.; Inoue, S. *J. Am. Chem. Soc.*, **1985**, *107*, 1358–1364.
12. Kuroki, M.; Aida, T.; Inoue, S. *J. Am. Chem. Soc.*, **1987**, *109*, 4737–4738.
13. Sugimoto, H.; Aida, T.; Inoue, S. *Macromolecules* **1990**, *23*, 2869–2875.
14. Watanabe, Y.; Aida, T.; Inoue, S. *Macromolecules* **1991**, *24*, 3970–3972.
15. Kuroki, M.; Watanabe, T.; Aida, T.; Inoue, S. *J. Am. Chem. Soc.* **1990**, *112*, 5639–5640.
16. Yamamoto, H.; Maruoka, K.; Furuta, K.; Naruse, Y. *Pure Appl. Chem.* **1988**, *61*, 419–422.
17. Yamamoto, H.; Maruoka, K. *J. Syn. Org. Soc. Jpn* **1993**, *51*, 1074–1086.
18. Inoue, S.; Aids, T. *CHEMTECH*, **1994**, *24*, 28–35.
19. Aida, T.; Metalloporphyrin catalysis. In *Catalysis in precision polymerization* (ed S. Kobayashi). Wiley, New York, pp 310–322.
20. Sugimoto, H.; Aida, T.; Inoue, S. *Macromolecules* **1994**, *27*, 3672–3674.
21. Sugimoto, H.; Aida, T.; Inoue, S. *Macromolecules* **1993**, *26*, 4751–4755.
22. Takeuchi, D.; Watanabe, Y.; Aida, T.; Inoue, S. *Macromolecules* **1995**, *28*, 651–652.
23. Sugimoto, H.; Kawamura, C.; Kuroki, M.; Aida, T.; Inoue, S. *Macromolecules* **1994**, *27*, 2013–2018.



24. Takeuchi, D.; Aida, T. *Macromolecules* **1996**, 29, 8096–8100.
25. Akatsuka, M.; Aida, T.; Inoue, S. *Macromolecules* **1995**, 28, 1320–1322.
26. Kitayama, T.; Zhang, Y.; Hatada, K. *Polym. J.* **1994**, 26, 868–872.
27. Adler, A. D. *J. Org. Chem.* **1967**, 32, 476–477.
28. Sugimoto, H.; Kuroki, M.; Watanabe, T.; Kawamura, C.; Aida, T.; Inoue, S. *Macromolecules* **1993**, 26, 3403–3410.
29. Sugimoto, H.; Saika, M.; Hosokawa, Y.; Aida, T.; Inoue, S. *Macromolecules* **1996**, 29, 3359–3369.
30. Adachi, T.; Sugimoto, H.; Aida, T.; Inoue, S. *Macromolecules* **1992**, 25, 2280–2281.
31. Isoda, M.; Sugimoto, H.; Aida, T.; Inoue, S. *Macromolecules* **1997**, 30, 57–62.