4

Controlled Polymerization

4.1 Introduction

In the preceding chapters we have examined the two main classes of polymerization, namely step-growth and chain-growth, with the latter exemplified by the free radical mechanism. These are the workhorses of the polymer industry, permitting rapid and facile production of large quantities of useful materials. One common feature that emerged from the discussion of these mechanisms is the statistical nature of the polymerization process, which led directly to rather broad distributions of molecular weight. In particular, even in the simplest case (assuming the principle of equal reactivity, no transfer steps or side reactions, etc.) the product polymers of either a polycondensation or of a free radical polymerization with termination by disproportionation would follow the most probable distribution, which has a polydispersity index (M_w/M_n) approaching 2. In commercial practice the inevitable violation of most of the simplifying assumptions leads to even broader distributions, with polydispersity indices often falling between 2 and 10. In many cases the polymers have further degrees of heterogeneity, such as distributions of composition (e.g., copolymers), branching, tacticity, or microstructure (e.g., cis 1,4-, trans 1,4-, and 1,2-configurations in polybutadiene).

This state of affairs is rather unsatisfying, especially from the chemist's point of view. Chemists are used to the idea that every molecule of, say, ascorbic acid (Vitamin C) is the same as every other one. Now we are confronted with the fact that a tank car full of the material called polybutadiene is unlikely to contain any two molecules with exactly the same chemical structure (recall Example 1.4). As polymers have found such widespread applications, we have obviously learned to live with this situation to some extent. However, if we could exert more control over the distribution of products, perhaps many more applications would be realized. In this chapter we describe several approaches designed to exert more control over the products of a polymerization. The major one is termed "living polymerization", and leads to much narrower molecular weight distributions. Furthermore, in addition to molecular weight control, living polymerization also enables the large-scale production of block copolymers, branched polymers of controlled architecture, and end-functionalized polymers.

A comparison between synthetic and biological macromolecules may be helpful at this stage. If condensation and free-radical polymerization represent the nadir of structural control, proteins and DNA represent the zenith. Proteins are “copolymers” which draw on 20 different amino acid monomers, yet each particular protein is synthesized within a cell with the identical degree of polymerization, composition, sequence, and stereochemistry. Similarly, DNAs with degrees of polymerization far in excess of those realized in commercial polymers can be faithfully replicated, with precise sequences of the four monomer units. One distant goal of polymer chemistry is to imitate nature's ability to exert complete control over polymerization. There are two ways to approach this. One is to begin with nature, and try to adapt its machinery to our purpose. This is exemplified by "training" cells into growing polymers that we want, for example via recombinant DNA technology. The other approach, and the one described in this chapter, is to start with the polymerizations we already have, and try to improve them. Both approaches have merit, and we select the latter because it is currently much more established, and plays a central role in much of polymer research. It is worth noting that nature also makes use of many other macromolecular materials that are not nearly so well-controlled as proteins and DNA; examples include polysaccharides such as cellulose, chitin, and starch. So in nature, as with commercial polymers, useful properties can still result from materials that are very heterogeneous at the molecular level.

The lack of control over molecular weight in polymerization arises directly from the random character of each step in the reaction. In a polycondensation any molecule can react with any other at any time; the number of molecules is steadily decreasing, but the mole fraction of monomer is always larger than the mole fraction of any other species. In a free radical polymerization, chains may be initiated at any time. Growing chains may also add monomer, or undergo a transfer or termination reaction at any time. The first requirement in controlling molecular weight is to fix the total number of polymers. This cannot be done in an unconstrained step-growth process, but it can in a chain growth mechanism, through the concentration of initiators. The number of initiators will be equal to the number of polymers, assuming 100% initiation efficiency and assuming no transfer reactions that lead to new polymers. The second requirement is to distribute the total number of monomers as uniformly as possible among the fixed number of growing chains. If the polymerization then proceeded to completion, we could predict N_n precisely: it would simply be the ratio of the number of monomers to the number of initiators. To allow the reaction to proceed to completion, we would need to prevent termination steps, or at least defer them until we were ready. Now, suppose further that the reaction proceeds statistically, meaning that any monomer is equally likely to add to any growing chain at any time. If N_n was reasonably large, we could expect a rather narrow distribution of the number of monomers in each chain, just by probability. (This argument also assumes no transfer reactions, so that growing polymers are not terminated prematurely). As an illustration, imagine placing an array of empty cups out in a steady rain; an empty cup is an "initiator" and a raindrop is a "monomer". As time goes on, the raindrops are distributed statistically among the cups, but after a lot of drops have fallen, the water level will be pretty much equal among the various cups. If a cup fell over, or a leaf fell and covered its top, that "polymer'" would be "terminated", and its volume of water would not keep up with the others. Similarly, if you placed a cup outside a few minutes after the others, the delayed initiation would mean that it would never catch up to its neighbors. What we have just described is, in fact, the essence of a controlled polymerization: start with a fixed number of initiators, choose chemistry and conditions to eliminate transfer and termination reactions, and let the reaction start at a certain time and then go to completion. In order to control the local structural details, such as microstructure and stereochemistry, then we have to influence the relative rates of various propagation steps. This can be achieved to some extent by manipulating the conditions at the active site at the growing end of the chain.

The remainder of this chapter is organized as follows. First we demonstrate how the kinetics of an ideal "living" polymerization lead to a narrow, Poisson distribution of chain lengths. Then we consider chain-growth polymerization via an anionic propagating center; this has historically been the most commonly used controlled polymerization mechanism, and it can be conducted in such a way as to approach the ideal case very closely. In Section 4.4 we explore how the anionic mechanism can be extended to the preparation of block copolymers, end-functional polymers and regular branched polymers of various architectures. We then turn our attention to other mechanisms which are capable of controlled polymerization, including cationic (Section 4.5), ring-opening (Section 4.8), and, especially, controlled radical polymerizations (Section 4.6). The concluding sections also address the concept of equilibrium polymerization, and a special class of controlled polymers called dendrimers.

4.2 Poisson distribution for an ideal living polymerization

In this section we lay out the kinetic scheme that describes a living polymerization, and thereby derive the resulting distribution of chain lengths. This scenario is most closely approached in the anionic case, but because it is not limited to anionic polymerizations, we will designate an active polymer of degree of polymerization i by P_i^*, and its concentration by $[P_i^*]$, where * represents the reactive end. A living polymerization is defined as a chain growth process for which there are no termination or transfer reactions. There has been some controversy in the literature about the precise criteria for "livingness" [1], and whether they can ever be met in practice, but we will not concern ourselves with this.

4.2A Kinetic scheme

The concentration of unreacted monomer at time t will be denoted [M]. The initial concentrations of monomer and initiator are $[M]_o$ and $[I]_o$, respectively. The reaction steps can be represented as follows:

Initiation: $$\mathrm{I} + \mathrm{M} \xrightarrow{k_i} \mathrm{P}_1{}^* \tag{4.2.1}$$

Propagation:
$$\begin{aligned} \mathrm{P}_1{}^* + \mathrm{M} &\xrightarrow{k_p} \mathrm{P}_2{}^* \\ \mathrm{P}_i{}^* + \mathrm{M} &\xrightarrow{k_p} \mathrm{P}_{i+1}{}^* \end{aligned} \tag{4.2.2}$$

Note that in using a single propagation rate constant, k_p, we are once again invoking the principle of equal reactivity.

We will now assume that initiation is effectively instantaneous relative to propagation ($k_i >> k_p$), so that at time $t = 0$, $[P_1{}^*] = [I]_o$, and we will not worry about eq 4.2.1 any further. Note that this criterion is not necessary to have a living polymerization, but it is necessary to achieve a narrow distribution of molecular weights. The concentration of unreacted monomer, [M], will decrease in time as propagation takes over. The overall rate of polymerization, R_p, is the sum of the rates of consumption of monomer by all growing chains $P_i{}^*$. However, we know that, in the absence of termination or transfer reactions, the total concentration of $P_i{}^*$ is always $[I]_o$: we have fixed the number of polymers. Therefore we can write

$$R_p = -\frac{d[M]}{dt} = k_p[M]\sum_i [P_i{}^*] = k_p[M][I]_o \tag{4.2.3}$$

This is a linear, first-order differential equation for [M], which has the solution

$$[M] = [M]_o \exp\{-k_p[I]_o t\} \tag{4.2.4}$$

Therefore the concentration of monomer decreases exponentially to zero as time progresses.

At this stage it is very helpful to introduce a *kinetic chain length*, $\bar{\nu}$, analogous to the one we defined in eq 3.5.10, as the ratio of the number of monomers incorporated into polymers to the number of polymers. The former is given by $[M]_o - [M]$, and the latter by $[I]_o$, so we write

$$\bar{\nu} = \frac{[M]_o - [M]}{[I]_o} \tag{4.2.5}$$

When the reaction has gone to completion, [M] will be 0, and the kinetic chain length will be the number average degree of polymerization of the resulting polymer. It will also be helpful in the following development to differentiate eq 4.2.5 with respect to time, and then incorporate eq 4.2.3:

$$\frac{d\bar{\nu}}{dt} = -\frac{1}{[I]_o}\frac{d[M]}{dt} = k_p[M] \tag{4.2.6}$$

In order to obtain the distribution of chain lengths, we need to do a bit more work. We begin by writing an explicit equation for the rate of consumption of $[P_1^*]$:

$$-\frac{d[P_1^*]}{dt} = k_p[P_1^*][M] \tag{4.2.7}$$

We could insert eq 4.2.4 into eq 4.2.7 to replace [M], and thereby obtain an equation that can be solved. However, a simpler approach turns out to be to invoke the chain rule, as follows:

$$\frac{d[P_1^*]}{dt} = \frac{d[P_1^*]}{d\bar{\nu}}\frac{d\bar{\nu}}{dt} = \frac{d[P_1^*]}{d\bar{\nu}}k_p[M] \tag{4.2.8}$$

If we now compare eqs 4.2.7 and 4.2.8 we can see that

$$-\frac{d[P_1^*]}{d\bar{\nu}} = [P_1^*] \tag{4.2.9}$$

and this equation is easily solved:

$$[P_1^*] = [P_1^*]_o e^{-\bar{\nu}} = [I]_o e^{-\bar{\nu}} \tag{4.2.10}$$

Now we repeat this process for $[P_2^*]$, beginning with the rate law. This is slightly more complicated, because $[P_2^*]$ grows by the reaction of $[P_1^*]$ as well as decreases by reaction with [M]:

$$\begin{aligned}\frac{d[P_2^*]}{dt} &= k_p[P_1^*][M] - k_p[P_2^*][M] \\ &= k_p[M]\left([P_1^*] - [P_2^*]\right) = \frac{d\bar{\nu}}{dt}\left([P_1^*] - [P_2^*]\right)\end{aligned} \tag{4.2.11}$$

By invoking the chain rule once more

$$\frac{d[P_2^*]}{dt} = \frac{d[P_2^*]}{d\bar{\nu}}\frac{d\bar{\nu}}{dt} \tag{4.2.12}$$

and comparing with eq 4.2.11 we obtain

$$\frac{d[P_2{*}]}{d\bar{\nu}} + [P_2{*}] = [P_1{*}] = [I]_o e^{-\bar{\nu}} \qquad (4.2.13)$$

This equation has the solution

$$[P_2{*}] = \bar{\nu}[I]_o e^{-\bar{\nu}} \qquad (4.2.14)$$

We can go through this sequence of steps once more, considering the concentration of trimer $[P_3{*}]$:

$$\begin{aligned} \frac{d[P_3{*}]}{dt} &= k_p[P_2{*}][M] - k_p[P_3{*}][M] \\ &= k_p[M]\big([P_2{*}] - [P_3{*}]\big) = \frac{d\bar{\nu}}{dt}\big([P_2{*}] - [P_3{*}]\big) \end{aligned} \qquad (4.2.15)$$

leading to

$$\frac{d[P_3{*}]}{d\bar{\nu}} + [P_3{*}] = [P_2{*}] = \bar{\nu}[I]_o e^{-\bar{\nu}} \qquad (4.2.16)$$

which has the solution (check it yourself):

$$[P_3{*}] = \frac{1}{2}\bar{\nu}^2\,[I]_o e^{-\bar{\nu}} \qquad (4.2.17)$$

This pattern continues, and the result for the population of i-mer is

$$[P_i^*] = \frac{1}{(i-1)!}\bar{\nu}^{i-1}[I]_o e^{-\bar{\nu}} \qquad (4.2.18)$$

From this result we can obtain the desired distribution, namely the mole fraction of i-mer among all polymers, x_i, by dividing eq 4.2.18 by the total number of polymers, $[I]_o$:

$$x_i = \frac{\bar{\nu}^{i-1}e^{-\bar{\nu}}}{(i-1)!} \qquad (4.2.19)$$

This particular function, eq 4.2.19, is called the Poisson Distribution. Although we have obtained it from consideration of a specific kinetic scheme, in fact it will describe the situation whenever a larger number of objects (monomers, in this case) are distributed randomly among a small number of boxes (polymers). Once the polymerization reaction has gone to completion, and the polymers terminated by introduction of some appropriate reagent, the resulting molecular weight distribution should obey eq 4.2.19, with $\bar{\nu}$ equal to $[M]_o/[I]_o$.

The following example illustrates some aspects of the kinetics of a living polymerization.

Example 4.1

The following data were reported for the living anionic polymerization of styrene (W. Lee, H. Lee, J. Cha, T. Chang, K. J. Hanley, and T. P. Lodge, *Macromolecules*, 33, 5111 (2000)). The initial monomer concentration was 0.29 M, and the initiator concentration was 0.00048 M. The reactor was sampled at the indicated times, and the resulting polymer was terminated and analyzed for molecular weight and polydispersity. Use these data and eqs 4.2.4 and 4.2.5 to answer the following questions: Does conversion of monomer to polymer follow the expected time dependence? What is the propagation rate constant under these conditions?

t, sec	**M_n, g/mol**	**N_n**	**PDI**	**1 – p**
238	3774	36.3	1.06	0.940
888	20590	198	1.02	0.672
1626	33730	324	1.02	0.463
2296	42970	413	1.01	0.316
3098	49800	479	1.008	0.207
4220	54870	528	1.006	0.127
14345	61690	593	1.005	0.018

Solution

We can equate the conversion of monomer to polymer with the familiar extent of reaction, p, as in Chapters 2 and 3:

$$p = \frac{[M]_o - [M]}{[M]_o} = 1 - \frac{[M]}{[M]_o}$$

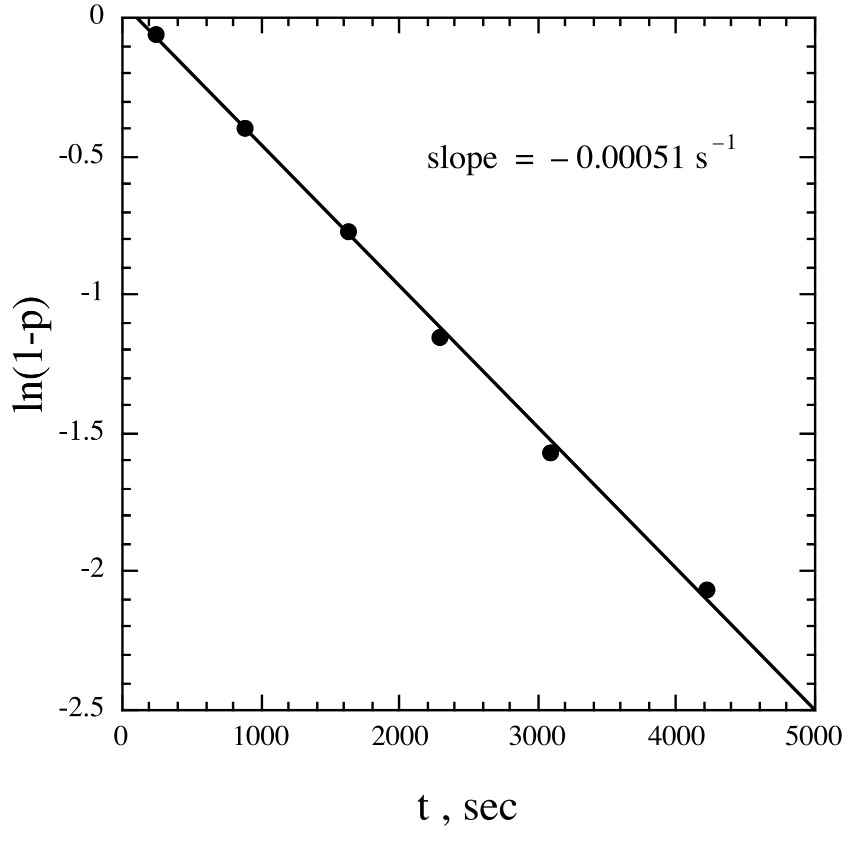
Using eq 4.2.4 we see how p should evolve in time:

$$p = 1 - \exp\{-k_p [I]_o t\}$$

Therefore a plot of ln(1-p) versus t should give a straight line with slope equal to $-k_p[I]_o$. The data provided do not include [M] explicitly, but we can infer [M] and p from M_n. From eq 4.2.5, the kinetic chain length is equal to $p[I]_o/[M]_o$, and it is also equal to N_n ($=M_n/M_o$); thus $(1-p)$ in the table was obtained as

$$1 - p = 1 - \frac{[I]_o}{[M]_o} N_n = 1 - \frac{(0.00048)}{(0.29)} N_n$$

The suggested plot is shown below, and the resulting slope from linear regression implies that $k_p \approx 1$ mol L^{-1} s^{-1}. (This is actually a rather low value, and in fact only an apparent value, due to a phenomenon to be described in Section 4.3 (see also Problem 4.3)). Note that the last point has been omitted from the fit, as it corresponds to essentially complete conversion, and thus is independent of t once the reaction is finished.



4.2B Breadth of the Poisson distribution

Figure 4.1 illustrates the Poisson distribution for values of $\bar{\nu}$ equal to 100, 500, and 1,000. For polystyrene with M_0 = 104, these would correspond to polymers with number average molecular weights of about 10^4, 5 x 10^4, and 10^5, respectively, which are moderate. The width of the distributions, although narrow, increases with $\bar{\nu}$, but as we shall see in a moment, the relative width (i.e., the width divided by $\bar{\nu}$), decreases steadily. It should be clear that these distributions are very narrow compared to the step-growth or free radical polymerizations shown in Figures 2.5 and 3.5, respectively. To underscore this, Figure 4.2 compares the theoretical distributions for free radical polymerization with termination by combination (eq 3.7.26) and for living polymerization, both with $\bar{\nu}$ = 100. The difference is dramatic, and is made even more so when we recall that termination by combination leads to a relatively narrow distribution with M_w/M_n approaching 1.5 rather than 2.

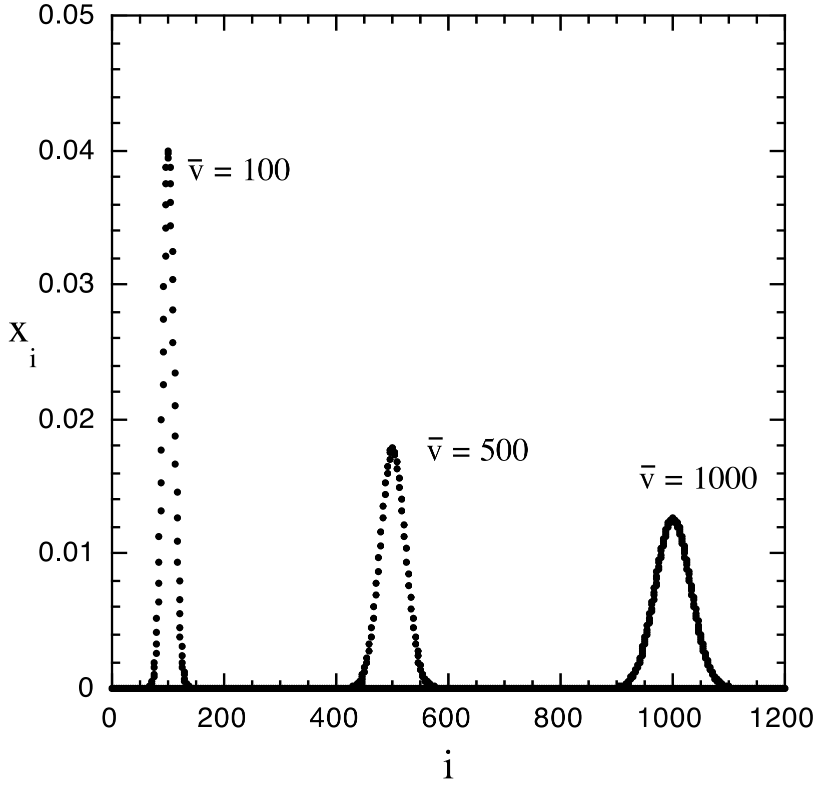


Figure 4.1
Mole fraction of i-mer for the Poisson distribution with the indicated kinetic chain lengths.

For the Poisson distribution the polydispersity index, M_w/M_n, in fact approaches unity as $\bar{\nu}$ increases indefinitely. The explicit relation for the Poisson distribution is

$$\frac{M_w}{M_n} = \frac{N_w}{N_n} = 1 + \frac{\bar{\nu}}{(1+\bar{\nu})^2} \approx 1 + \frac{1}{\bar{\nu}} \tag{4.2.20}$$

where the approximation applies for large $\bar{\nu}$. For $\bar{\nu} = 1{,}000$ eq 4.2.20 indicates that the polydispersity index will be 1.001, which is a far cry from 2!

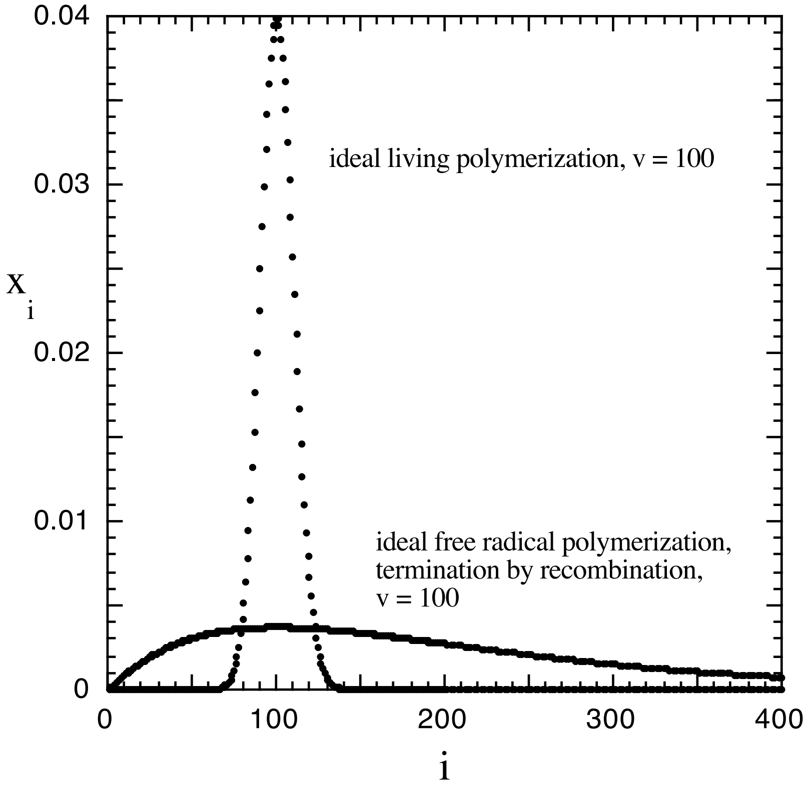


Figure 4.2
Comparison of Poisson distribution and distribution for free radical polymerization with termination by recombination.

The derivation of eq 4.2.20 is not too complicated, but it has a couple of sneaky steps, as we will now show. From eq 1.7.2 we recall the definition of N_n, and insert eq 4.2.19 to obtain

$$N_n = \sum_{i=1}^{\infty} i x_i = \sum_{i=1}^{\infty} \frac{i\bar{\nu}^{i-1}e^{-\bar{\nu}}}{(i-1)!} \tag{4.2.21}$$

To progress further with this, it is helpful to recall the infinite series expansion of e^x (see the Appendix if this is unfamiliar):

$$e^x = \sum_{i=0}^{\infty} \frac{x^i}{i!} = \sum_{i=1}^{\infty} \frac{x^{i-1}}{(i-1)!} \tag{4.2.22}$$

We will use this expansion to get rid of the factorials. Returning to eq 4.2.21, we perform a series of manipulations, recognizing that $e^{-\bar{\nu}}$ does not depend on i and can be factored out of the sum, and that $i\bar{\nu}^{i-1}$ can be written as $d(\bar{\nu}^i)/d\bar{\nu}$:

$$\begin{aligned} N_n &= \sum_{i=1}^{\infty} \frac{i\bar{\nu}^{i-1}e^{-\bar{\nu}}}{(i-1)!} = e^{-\bar{\nu}}\sum_{i=1}^{\infty} \frac{i\bar{\nu}^{i-1}}{(i-1)!} \\ &= e^{-\bar{\nu}}\sum_{i=1}^{\infty} \frac{d}{d\bar{\nu}}\frac{\bar{\nu}^{i}}{(i-1)!} = e^{-\bar{\nu}}\frac{d}{d\bar{\nu}}\sum_{i=1}^{\infty} \frac{\bar{\nu}^{i}}{(i-1)!} \\ &= e^{-\bar{\nu}}\frac{d}{d\bar{\nu}}\sum_{i=1}^{\infty} \bar{\nu}\frac{\bar{\nu}^{i-1}}{(i-1)!} = e^{-\bar{\nu}}\frac{d}{d\bar{\nu}}\left\{\bar{\nu}\sum_{i=1}^{\infty} \frac{\bar{\nu}^{i-1}}{(i-1)!}\right\} = e^{-\bar{\nu}}\frac{d}{d\bar{\nu}}\left\{\bar{\nu}e^{\bar{\nu}}\right\} \end{aligned} \tag{4.2.23}$$

This differentiation is straightforward, recalling the rule for differentiating the product of two functions, and that $d(e^x)/dx = e^x$:

$$e^{-\bar{\nu}}\frac{d}{d\bar{\nu}}\left\{\bar{\nu}e^{\bar{\nu}}\right\} = e^{-\bar{\nu}}\left\{e^{\bar{\nu}} + \bar{\nu}e^{\bar{\nu}}\right\} = 1 + \bar{\nu} \qquad (4.2.24)$$

This relation establishes that $N_n = 1 + \bar{\nu}$. (You may be wondering where the "1" came from. A glance at eq 4.2.5 reveals the answer: before the reaction begins, when $[M] = [M]_o$, then $\bar{\nu} = 0$ when the "degree of polymerization" is actually 1. Of course, for any reasonable value of N_n, the difference between N_n and N_n+1 is inconsequential).

The development to obtain an expression for N_w follows a similar approach, beginning with the definition from eq 1.7.4:

$$N_w = \sum_{i=1}^{\infty} i\,w_i = \frac{\sum_{i=1}^{\infty} i^2 x_i}{\sum_{i=1}^{\infty} i\,x_i} \qquad (4.2.25)$$

We already know that the denominator on the right hand side of eq 4.2.25 is equal to $1+\bar{\nu}$, so we just need to sort out the numerator.

$$\begin{aligned}\sum_{i=1}^{\infty} i^2 x_i &= \sum_{i=1}^{\infty} i^2\frac{\bar{\nu}^{i-1}e^{-\bar{\nu}}}{(i-1)!} = e^{-\bar{\nu}}\sum_{i=1}^{\infty} i^2\frac{\bar{\nu}^{i-1}}{(i-1)!}\\ &= e^{-\bar{\nu}}\frac{d}{d\bar{\nu}}\left\{\sum_{i=1}^{\infty} i\frac{\bar{\nu}^{i}}{(i-1)!}\right\} = e^{-\bar{\nu}}\frac{d}{d\bar{\nu}}\bar{\nu}\left\{\sum_{i=1}^{\infty} i\frac{\bar{\nu}^{i-1}}{(i-1)!}\right\} \qquad (4.2.26)\\ &= e^{-\bar{\nu}}\frac{d}{d\bar{\nu}}\bar{\nu}\frac{d}{d\bar{\nu}}\left\{\sum_{i=1}^{\infty}\frac{\bar{\nu}^{i}}{(i-1)!}\right\} = e^{-\bar{\nu}}\frac{d}{d\bar{\nu}}\bar{\nu}\frac{d}{d\bar{\nu}}\left\{\bar{\nu}e^{\bar{\nu}}\right\}\end{aligned}$$

which leaves us with some more derivatives to take:

$$e^{-\bar{\nu}}\frac{d}{d\bar{\nu}}\bar{\nu}\frac{d}{d\bar{\nu}}\left\{\bar{\nu}e^{\bar{\nu}}\right\} = e^{-\bar{\nu}}\frac{d}{d\bar{\nu}}\bar{\nu}\left\{e^{\bar{\nu}} + \bar{\nu}e^{\bar{\nu}}\right\}$$

$$= e^{-\bar{\nu}}\left\{\bar{\nu}e^{\bar{\nu}} + e^{\bar{\nu}} + 2\bar{\nu}e^{\bar{\nu}} + \bar{\nu}^2 e^{\bar{\nu}}\right\} \tag{4.2.27}$$

$$= 1 + 3\bar{\nu} + \bar{\nu}^2$$

Finally, we can insert eq 4.2.27 into eq 4.2.25 to obtain N_w:

$$N_w = \frac{1 + 3\bar{\nu} + \bar{\nu}^2}{1 + \bar{\nu}} \tag{4.2.28}$$

It is now straightforward to obtain the result for the polydispersity index given in eq 4.2.20, using eqs 4.2.24 and 4.2.28:

$$\frac{N_w}{N_n} = \frac{1 + 3\bar{\nu} + \bar{\nu}^2}{(1 + \bar{\nu})^2} = \frac{(1 + \bar{\nu})^2 + \bar{\nu}}{(1 + \bar{\nu})^2} = 1 + \frac{\bar{\nu}}{(1 + \bar{\nu})^2} \tag{4.2.29}$$

The polydispersity data provided in Example 4.1 are compared with the Poisson distribution result, eq 4.2.29, in Figure 4.3a. The experimental results are consistently larger than the prediction, but actually not by much. And, as the molecular weight increases, the experimental results seem to be approaching the Poisson result; the implications of this observation are considered in Problem 4.2. It is an interesting fact that this experimental test of eq 4.2.29 was only recently made possible by advances in analytical techniques. To measure a polydispersity index below 1.01 would require an accuracy much better than 1% in the determination of M_w and M_n, and this is not yet possible using the standard techniques discussed in Chapters 1, 7, 8 and 9. In Figure 4.3b, the distribution for one particular sample obtained by MALDI mass spectrometry (and shown in Figure 1.7b) is compared with the Poisson distribution with the same mean; the agreement is excellent, with the experimental distribution being only slightly broader than the theoretical one.

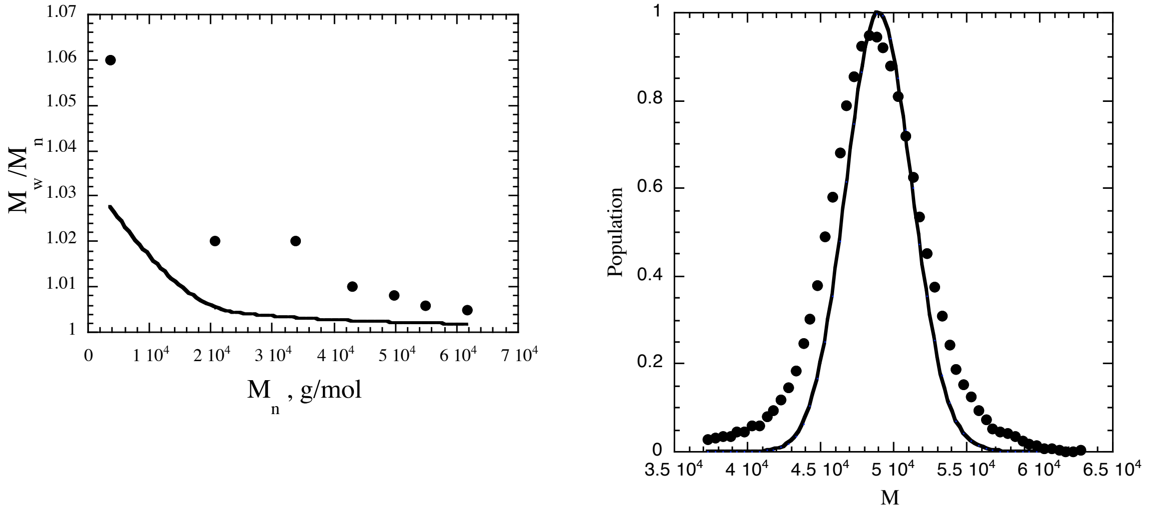


Figure 4.3.
(a) Experimental polydispersities versus molecular weight for anionically polymerized polystyrenes, from the data in Example 4.1. (b) The distribution obtained by MALDI mass spectrometry for one particular sample. The smooth curves represent the results for the Poisson distribution, eq 4.2.29. in (a) and eq 4.2.19 in (b).

We conclude this section with a summary of the requirements for achieving a narrow molecular weight distribution, and thereby draw an important distinction between "livingness" and the Poisson distribution. To recall the basic definition, a living polymerization is one that proceeds in the absence of transfer and termination reactions. Satisfying these two criteria is not sufficient to guarantee a narrow distribution, however. The additional requirements for approaching the Poisson distribution are:

1. All active chain ends must be equally likely to react with a monomer throughout the polymerization. This requires both the principle of equal reactivity, and good mixing of reagents at all times.

2. All active chain ends must be introduced at the same time. In practice this means that the rate of initiation needs to be much more rapid than the rate of propagation, if all the monomer is added to the reaction mixture at the outset.

3. Propagation must be essentially irreversible, i.e., the reverse "depolymerization" reaction does not occur to a significant extent. There are, in fact, cases where the propagation step is reversible, leading to the concept of an equilibrium polymerization, which we will take up in Section 4.8.

4.3 Anionic polymerization

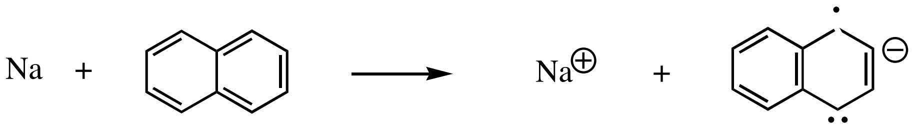
Anionic polymerization has been the most important mechanism for living polymerization, since its first realization in the 1950s.[2] Both modes of ionic polymerization (i.e., anionic and cationic) are described by the same vocabulary as the corresponding steps in the free-radical mechanism for chain-growth polymerization. However, initiation, propagation, transfer, and termination are quite different than in the free-radical case and, in fact, different in many ways between anionic and cationic mechanisms. In particular, termination by recombination is clearly not an option in ionic polymerization, a simple fact that underpins the development of living polymerization. In this section we will discuss some of the factors that contribute to a successful living anionic polymerization, and in the following section we will illustrate the extension of these techniques to block copolymers and controlled architecture branched polymers.

Monomers that are amenable to anionic polymerization include those with double bonds (vinyl, diene, and carbonyl functionality), and heterocyclic rings (See also Table 4.3). In the case of vinyl monomers CH_2=CHX, the X group needs to have some electron withdrawing character, in order to stabilize the resulting carbanion. Examples include styrenes and substituted styrenes, vinyl aromatics, vinyl pyridines, alkyl methacrylates and acrylates, and conjugated dienes. The relative stabilities of these carbanions can be assessed by considering the pK_a of the corresponding conjugate acid. For example, the polystyryl carbanion is roughly equivalent to the conjugate base of toluene. The smaller the pK_a of the corresponding acid, the more stable the resulting carbanion. The more stable the carbanion, the more reactive the monomer in anionic polymerization. In the case of anionic ring-opening polymerization, the ring must be amenable to nucleophilic attack, as well as present a stable anion. Examples include epoxides, cyclic siloxanes, lactones and carbonates. At the same time, there are many functionalities that will interfere with an anionic mechanism, especially those with an acidic proton (e.g., –OH, $–NH_3$, –COOH) or an electrophilic functional group (e.g., O_2, –C=O, CO_2). Anionic polymerization of monomers that include such functionalities can generally only be achieved if the functional group can be protected. As a corollary, the polymerization medium must be rigorously free of protic impurities such as water, as well as oxygen and carbon dioxide.

A wide variety of initiating systems have been developed for anionic polymerization. The first consideration is to choose an initiator that has comparable, or slightly higher reactivity, than the intended carbanion. If the initiator is less reactive, the reaction will not proceed. If, on the other hand, it is too reactive, unwanted side reactions may result. As the pK_as of the conjugate acids for the many possible monomers span a wide range, so too must the pK_as of the conjugate acids of the initiators. Second, the initiator must be soluble in the same solvent as the monomer and resulting polymer. Common classes of initiators include radical anions, alkali metals, and especially alkyllithium compounds. We will illustrate two particular initiator systems: sodium naphthalenide, as an example of a radical anion, for the polymerization of styrene, and *sec*-butyllithium, as an alkyllithium, in the polymerization of isoprene.

The first living polymer studied in detail was polystyrene initiated with sodium naphthalenide in tetrahydrofuran at low temperatures:

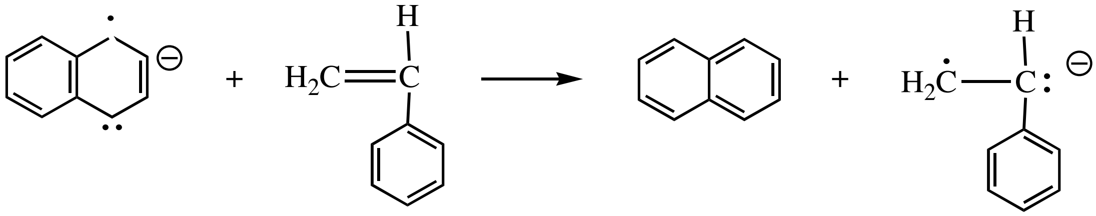
1. The catalyst is prepared by the reaction of sodium metal with naphthalene and results in the formation of a radical ion:



(4.A)

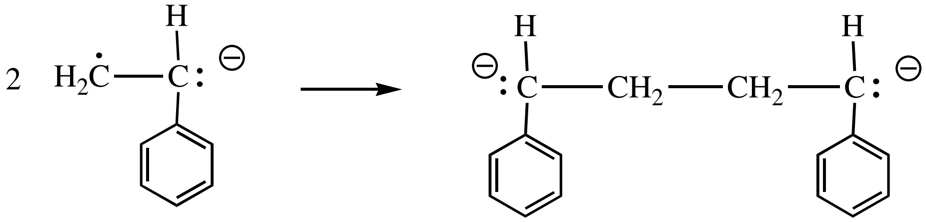
Of course the structure of the radical anion shown is just one of several possible resonance forms.

2. These green radical ions react with styrene to produce the red styryl radical ion:



(4.B)

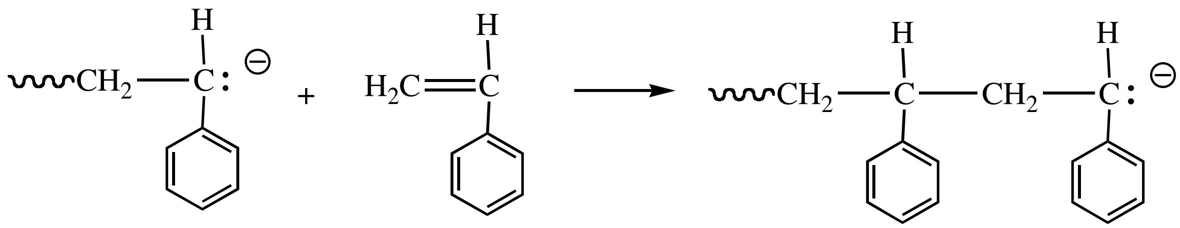
3. The latter undergoes radical combination to form the dianion, which subsequently polymerizes:



(4.C)

In this case the degree of polymerization is $2\overline{\nu}$ because the initiator is difunctional; furthermore there will be a single tail-to-tail linkage somewhere near the middle of each chain.

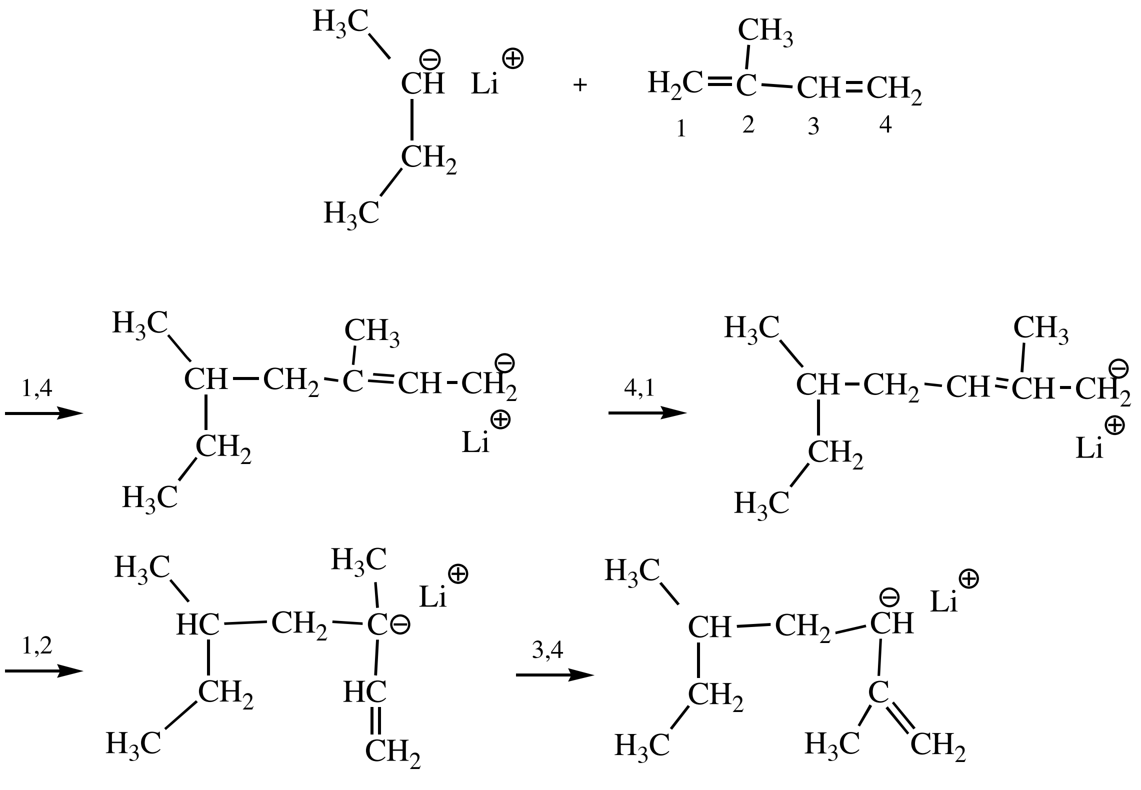
4. The propagation step at either end of the chain can be written as follows:



(4.D)

The carbanion attacks the more electropositive carbon, to regenerate the more stable secondary carbanion. Thus the addition is essentially all head-to-tail in this case. Note also that the sodium counterions have not been written explicitly in reactions 4.B – 4.D, although of course they are present. As we will see below, the counter ion can actually play a crucial role in the polymerization itself.

Now we consider the polymerization of isoprene by *sec*-butyllithium, in benzene at room temperature. In the first step, one monomer is added, but immediately there are many possibilities, as indicated:



(4.E)

Which happens, and why? What happens when the next monomer adds? Is it the same configuration, or not? What does it all depend on? There is no simple answer to these questions, but we can gain a little insight into how to control the microstructure of a polydiene by looking at some data.

Solvent	Counterion	T, °C	1,4 cis	1,4 trans	1,2	3,4
THF	Li	30	12 combined		29	59
dioxane	Li	15	3	11	18	68
heptane[a]	Li	–10	74	18	–	8
heptane[b]	Li	–10	97	–	–	–
none	Li	25	94	–	–	6
none	Na	25	–	45	7	48
none	Cs	25	4	51	8	37

Table 4.1

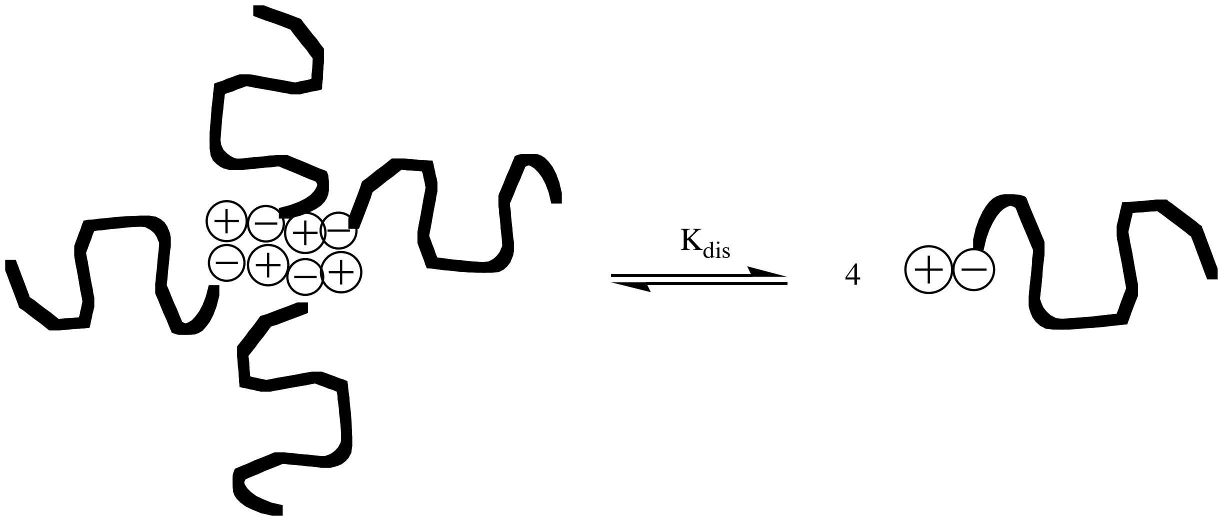
Polymerization of polyisoprene under various conditions, and the resulting microstructure in %. Data collected and discussed in Hsieh and Quirk [3].

a. Initiator concentration 6 x 10^{-3} $\underline{\text{M}}$

b. Initiator concentration 8 x 10^{-6} $\underline{\text{M}}$

Table 4.1 gives the results of chemical analysis of the microstructure of polyisoprene, after polymerization under the stated conditions. In the first two cases there is a strong preference for 3,4 addition, with significant amounts of 1,2; relatively little 1,4 addition is found. The key feature here turns out to be the solvent polarity, as will be discussed below. When switching to heptane, a non-polar solvent, the situation is reversed; now 1,4 cis is heavily favored. Interestingly, decreasing the initiator concentration by a factor of a thousand exerts a significant influence on the 1,4 cis/trans ratio. At first glance this seems strange; the details of an addition step shouldn't depend on the number of initiators. However, the answer lies in kinetics, as the propagation step is not as simple as one might naively expect. Finally, the last three entries show isoprene polymerized in bulk, which also corresponds to a nonpolar medium. In this case we see that changing the counterion has a huge effect. Simply replacing lithium with sodium switches the product from almost all cis 1,4 to a mixture of trans 1,4 and 3,4.

The key factor that comes into play in non-polar solvents is ion-pairing or clustering of the living ends. Ionic species tend to be sparingly soluble in hydrocarbons, as the dielectric constant of the medium is too low. Consequently, the counterion is rather tightly associated with the carbanion, forming a dipole; these dipoles have a strong tendency to associate into a small cluster, with perhaps n = 2, 4, or 6 chains effectively connected as a star molecule. This equilibrium is illustrated in the cartoon below for the case n = 4:



(4.F)

Addition steps occur primarily when the living chain end is not associated. This leads to an interesting dependence of the rate of polymerization, R_p, on living chain concentration, as can readily be understood as follows (recall eq 4.2.3):

$$R_p = -\frac{d[M]}{dt} = k_p[M][P^*]_{free} \tag{4.3.1}$$

where $[P^*]_{free}$ is the concentration of unassociated living chains. This concentration is set by the equilibrium between associated and free chains:

$$K_{dis} = \frac{([P^*]_{free})^4}{[(P^*)_4]} \tag{4.3.2}$$

Inserting eq 4.3.2 into eq 4.3.1 gives

$$R_p = k_p(K_{dis})^{1/4}[M][(P^*)_4]^{1/4} = k_{app}[M][P^*]^{1/4} \tag{4.3.3}$$

where we recognize that $[(P^*)_4] \approx (1/4)[P^*]$, as most of the chains are in aggregates, and that the apparent rate constant $k_{app} = k_p\ (K_{dis}/4)^{\ 1/4}$. The rate of polymerization is therefore first order in monomer concentration, as one should expect, but has a (1/n) fractional dependence on initiator concentration, where n is the average aggregate size. Accurate experimental determination of n is tricky, but a large body of data exist. It should also be noted that there is in all likelihood a distribution of states of association or ion clustering, so that the actual situation is considerably more complicated than implied by reaction (4.F).

Increasing the size of the counterion increases the separation between charges at the end of the growing chain, thereby facilitating the insertion of the next monomer. The concentration of initiator can also influence n, presumably by the law of mass action. The dependence of the cis isomer concentration in heptane indicated in Table 4.1 is actually thought to be the result of a more subtle effect than this, however. It is generally accepted that the cis configuration is preferred immediately after addition of a monomer, but that isomerization to trans is possible, within an aggregate, given time. The rate of isomerization is proportional to the concentration of chains in aggregates, and therefore proportional to [P*], whereas the rate of addition is proportional to a fractional power of [P*]. Increasing the initiator concentration increases both rates, but favors isomerization relative to propagation.

Termination of an anionic polymerization is a relatively straightforward process; introduction of a suitable acidic proton source, such as methanol, will cap the growing chain and produce the corresponding salt, e.g. $Li^+OCH_3^-$. Care must be taken that the termination is conducted under the same conditions of purity as the reaction itself, however. For example, introduction of oxygen along with the terminating agent can induce coupling of two living chains. However, in many cases it is desirable to introduce a particular chemical functionality at the end of the growing chain. One prime example is to switch to a second monomer, which is capable of continued polymerization to form a block copolymer. A second example is to use particular multifunctional terminating agents to prepare star-branched polymers. These cases, and other uses of end-functional chains, are the next subject we take up.

4.4 Block copolymers, end-functional polymers, and branched polymers by anionic polymerization

The central importance of living anionic polymerization to current understanding of polymer behavior cannot be overstated. For example, throughout Chapters 6-13 we will derive a host of relationships between observable physical properties of polymers and their molecular weight. These relationships have been largely confirmed or established experimentally by measurements on narrow molecular weight distribution polymers, which were prepared by living anionic methods. However, it can be argued that even more important and interesting applications of living polymerization arise in the production of elaborate, controlled architectures; this section touches on some of these possibilities.

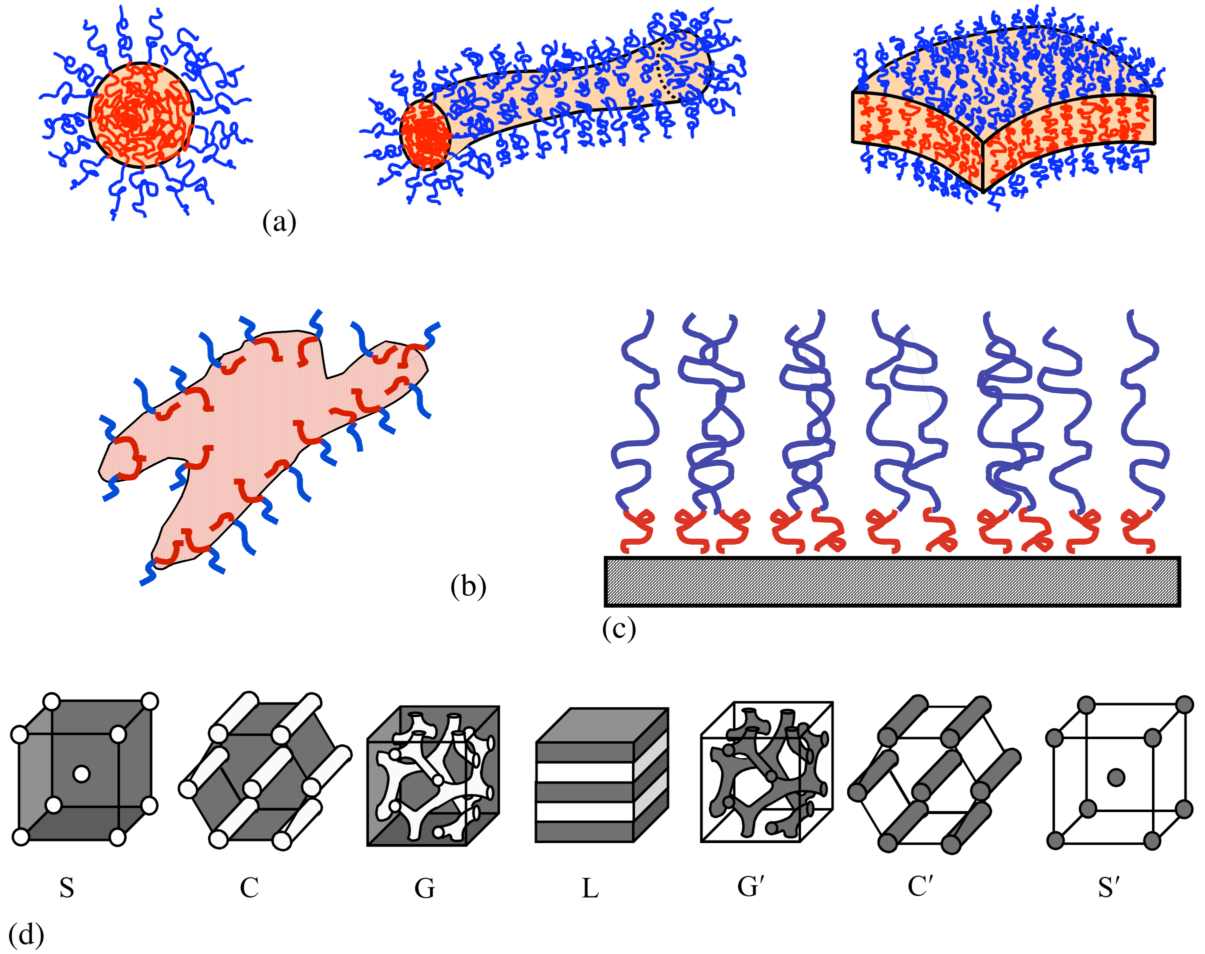


Figure 4.4
Examples of block copolymer self-assembly: (a) as spherical, cylindrical, and bilayer micelles in a selective solvent for one block; (b) as surfactants in a dispersion of one polymer in an immiscible matrix polymer; (c) on surfaces, following adsorption of one block; (d) as bulk, nanostructured materials. Body-centered spherical micelles (S), hexagonally packed cylindrical micelles (C), bicontinuous double gyroid (G), lamellae (L).

4.4A Block copolymers

Before addressing the preparation of block copolymers by anionic polymerization, it is appropriate to consider some of the reasons why block copolymers are such an interesting class of macromolecules. The importance of block copolymers begins with the fact that a single molecule contains two (or more) different polymers, and therefore may in some sense exhibit the characteristics of both components. This offers the possibility of tuning properties, or combinations of properties, between the extremes of the pure components. However, a random or statistical copolymer could also do that, without the effort required to prepare the block architecture. The important difference is that, for reasons that will be explored in Chapter 7, two different polymers will usually not mix; they tend to phase separate into almost pure components. The architecture of a block copolymer defeats this macroscopic phase separation, because of the covalent linkages between the different blocks. The consequence is that block copolymers undergo what is often called *microphase separation*; the blocks of one type segregate into domains that have dimensions on the lengthscale of the blocks themselves, i.e., 5–50 nm. In the current jargon, these polymers undergo *self-assembly* to produce particular *nanostructures*.

There are at least four broad arenas in which the self-assembly of block copolymers is useful, as illustrated in Figure 4.4:

1. *Micelles.* In a solvent that dissolves one block but not the other, copolymers will aggregate into micelles. A typical micelle is roughly spherical, about 20 nm in size, and contains 50–200 molecules. However, under appropriate conditions the micelles can be long, worm-like structures, or even flat bilayers that can curve around to form closed "bags" called vesicles. This behavior is analogous to that of small molecule surfactants or biological lipids. Micelles can be used to sequester, extract or transport insoluble molecules though a solvent.

2. *Macromolecular surfactants*. Extending the analogy to small molecule surfactants, where the amphiphilic character of the molecule can stabilize dispersions of oil droplets in water ("emulsions") or water in oil, an AB block copolymer could stabilize a dispersion of polymer A in a matrix of polymer B. This strategy is used to control the tendency of different polymers to phase separate on a macroscopic scale, and allows preparation of *compatibilized* polymer blends, with dispersed droplets on the micron scale.

3. *Tailored surfaces and thin films*. In a selective solvent, block copolymers can adsorb on a surface with the insoluble block forming a dense film, and the soluble block extending out into the solvent, forming a *brush*. Such brushes can impart colloidal stability to dispersed particles, or prevent protein adsorption in biomedical devices. Or, a thin film of copolymer can be allowed to self-assemble on a surface, forming nanoscale patterns such as stripes and spheres, that are under consideration for lithographic applications.

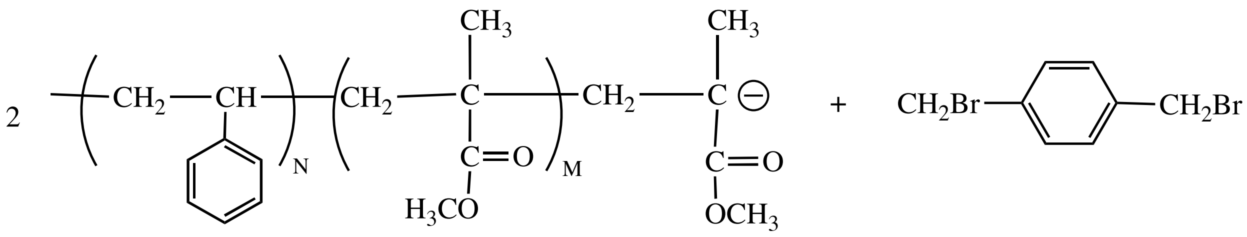
4. *Nanostructured materials*. In the bulk state, or in concentrated solution, the self-assembly process can lead to structures with well-defined long-range order or symmetry. As illustrated in Figure 4.4, an AB diblock tends to adopt one of 7 particular ordered phases, depending primarily on the relative lengths of the two blocks. For example, when the fraction of the chain that is A is small, perhaps 10-20%, the A blocks collect in spherical micelles, and the micelles adopt a body-centered cubic lattice. As the fraction of A is increased, the chains form cylindrical micelles on a hexagonal lattice, and then when the amounts of A and B are roughly equal, flat sheets or lamellae are formed. As A becomes the majority component, the same structures are seen, but now with the B blocks inside the cylinders and spheres. This sequence of interfacial curvature mirrors exactly that seen in micelles. However, one new feature is the presence of a bicontinuous cubic structure, the double gyroid, which intervenes between cylinders and lamellae.

In current commercial practice the most important block copolymer is the ABA triblock, where the A block is usually polystyrene and the B block is an elastomer such as isoprene, butadiene, or their saturated (i.e., hydrogenated) equivalents. Such polymers are known as *thermoplastic elastomers*, because at ambient temperatures they self-assemble in such a way that small styrene domains, which are glassy, act as crosslinks to formed an extended, elastomeric network of the bridging B blocks. (We will discuss network elasticity in detail in Chapter 10, and the nature of the glass transition in Chapter 12). At elevated temperatures (i.e., above 100 ^{o}C) the polystyrene blocks can flow, and the network can be reformed into a new shape. These anionically prepared materials find use in such diverse applications as pressure sensitive adhesives, hot melt adhesives, asphalt modifiers, sports footwear, and drug-releasing stents.

Block copolymers are usually prepared by *sequential* living anionic polymerization. This means that one block is polymerized to completion, but not terminated; the second monomer is then added to the reaction mixture. The living chains act as *macroinitiators* for the polymerization of the second block. After the second block is complete, a terminating agent can be introduced, or the monomer for a third block, and so on. The key requirements for this strategy to be successful include the following:

1. The most important criterion is that the carbanion of the first block be capable of initiating polymerization of the second block. Returning to the discussion in the previous section, this implies that the stability of the second block carbanion is greater than or equal to that of the first block, or equivalently that the pK_a of the conjugate acid is smaller. As an example, if it is desired to prepare polystyrene-*block*-poly(methyl methacylate), the polystyrene block must be prepared first. On the other hand, polystyryl, polybutadienyl, and polyisoprenyl anions can initiate one another, so in principle arbitrary sequences of these blocks are accessible.
2. The solvent system chosen must be suitable for all blocks, or it must be modified for the polymerization of the second block. For example, it is possible to prepare block copolymers of 1,4 polyisoprene and 1,2 polybutadiene, by adding a “polar modifier” in midstream. The first block microstructure calls for a non-polar solvent, whereas the second requires a polar environment. Rather than switching solvents entirely, a polar modifier associates with the carbanion active site and directs the regiochemistry of addition in a similar fashion to a polar solvent. Examples of modifiers include Lewis bases such as triethylamine, N,N,N’N’-tetramethylethylenediamine (“TMEDA”), and 2,2’-Bis(4,4,6-trimethyl-1,3-dioxane) (“DIPIP”).
3. The counterion must also be suitable for the polymerization of both blocks.

These requirements, and especially the first, might appear to be rather limiting. For example, how could either poly(methyl methacrylate)-*block*-polystyrene-*block*-poly(methyl methacrylate) or polystyrene-*block*-poly(methyl methacrylate)-*block*-polystyrene triblocks be prepared? The answer in both cases is actually rather straightforward. In the first case a difunctional initiator such as sodium naphthalenide could be used; then the triblock would be grown from the middle out. In the second case a *coupling agent* can be used, which would link two equivalent living polystyrene-*block*-poly(methyl methacrylate) diblocks together. The coupling agent is usually a difunctional molecule, in which each functional group is equally capable of terminating an anionic polymerization. This is illustrated by *α,α*'-dibromo-*p*-xylene in the following reaction:

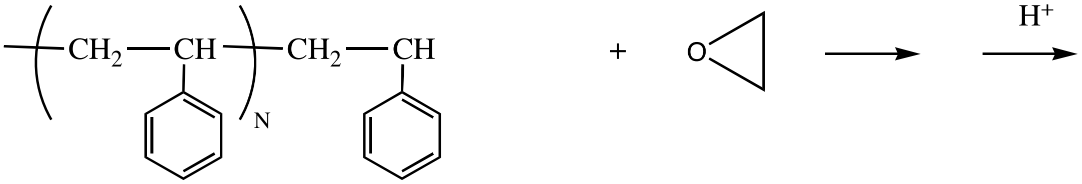


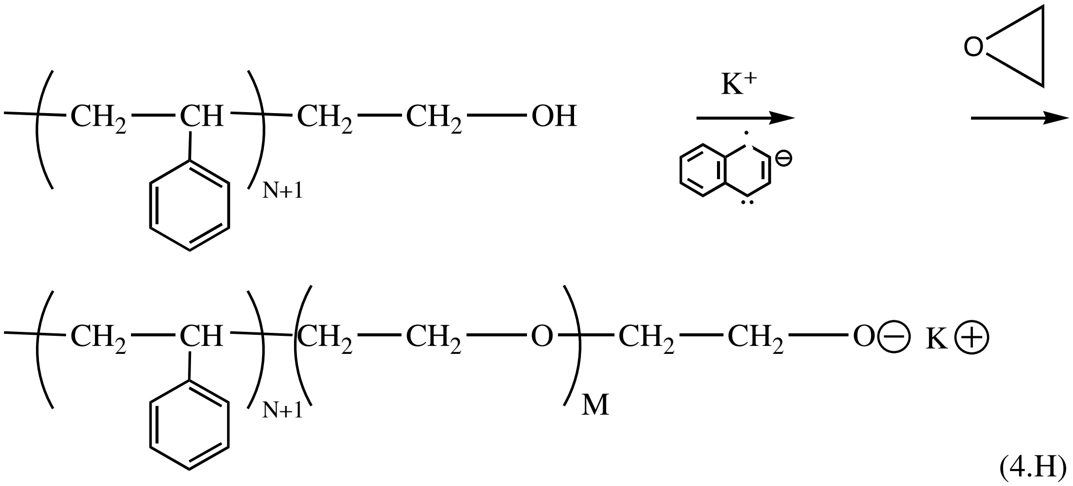
$$\longrightarrow \quad (\text{Styrene})_N\text{–}(\text{Methylmethacrylate})_{2M}\text{–}(\text{Styrene})_N \quad + \quad 2\ \text{Li Br}$$

(4.G)

Note that the resulting methyl methacrylate midblock will have one phenyl linkage in the middle. This coupling strategy has several potential advantages over sequential monomer addition. In addition to achieving otherwise inaccessible block sequences, the total polymerization time is roughly cut in half. Furthermore the second "crossover" step is avoided, which is desirable in that each addition of monomer brings with it the possibility of contamination or less than complete initiation of the subsequent blocks. The primary limitation of coupling is the inevitability of incomplete conversion of diblock to triblock. If reaction 4.G is run with either excess living chain or coupling agent, there will be some remaining diblock. If run under stoichiometric conditions, incomplete coupling is still probable. Any excess diblock can be removed by fractionation, if necessary.

There are still many block copolymers, even diblocks, that simply cannot be prepared by sequential monomer addition: the conditions required for the polymerization of one block are not compatible with the other. In this case one general strategy is to prepare batches of the two homopolymers, each functionalized at one end with a reactive group that can couple to the other. This potentially enables preparation of any conceivable diblock, and each block could be prepared by any suitable living polymerization scheme, not just the anionic one. However, this approach is usually the last resort, because polymer-polymer coupling reactions are notoriously inefficient, even assuming a common solvent can be found. Coupling reactions are practical in the anionic triblock case because the two reacting chains are already present in the reactor, and the carbanions are highly reactive; this might not be the case with say, a hydroxyl-terminated polymer A and a carboxylic acid-terminated polymer B. A more efficient strategy is to terminate the polymerization of the first block in such a way as to leave a functional group that can subsequently be used to initiate living polymerization of the second monomer; this is the *macroinitiator* approach, but where the reaction conditions are completely changed in midstream. As an example, polystyrene and poly(ethylene oxide) are both amenable to living anionic polymerization, but not under the same conditions. If ethylene oxide monomer is introduced to the polystyryl anion with a lithium counterion, it turns out that one monomer adds but no propagation occurs. Termination with a proton therefore generates a polystyrene molecule with a terminal hydroxyl group. This can then act as a macroinitiator; titration of the endgroup with the strong base potassium naphthanelide produces the terminal alkoxide with a potassium counterion, which can initiate ethylene oxide polymerization.





(4.H)

4.4B End-functional polymers

The previous illustration of the macroinitiator approach is an excellent example of the utility of an end-functional polymer, by which we mean a polymer with a well-defined, reactive chemical functionality at one end. A subset of this class are polymers with reactive groups at both ends; such polymers are said to be *telechelic*. It should be apparent that most condensation polymers have reactive groups at each end, and thus fall in this class. However, we are concerned here with polymers that have narrow molecular weight distributions as a result of a living polymerization. In essence, an end-functional polymer is a macromolecular reagent. It can be carefully characterized, and then stored on the shelf until needed for a particular application. The following is a list of a few of the many examples of possible uses for end-functional polymers:

1. *Macroinitiators.* As illustrated in the previous section, a macroinitiator is an end-functional polymer in which the functional group can be used to initiate polymerization of a second monomer. In this way block copolymers can be prepared that are not readily accessible by sequential monomer addition. Indeed, the second block could be polymerized by an entirely different mechanism than the first; other living polymerization schemes will be discussed in subsequent sections.

2. *Labeled polymers*. It is sometimes desired to attach a “label” to a particular polymer, such as a fluorescent dye or radioactive group, which will permit subsequent tracking of the location of the polymer in some process. By attaching the label to the end of the chain, the number of labels is well-defined, and labeled chains can be dispersed in otherwise equivalent unlabeled chains in any desired proportion.

3. *Chain coupling*. Both block copolymers and regular branched architectures can be accessed by coupling reactions between complementary functionalities on different chains.

4. *Macromonomers*. If the terminal functional group is actually polymerizable, such as a carbon-carbon double bond, polymerization through the double bond can produce densely branched comb or “bottlebrush” copolymers.

5. *Grafting to surfaces*. As mentioned in the context of copolymer adsorption to a surface, a densely packing layer of polymer chains emanating from a surface forms a brush. Such brushes can also be prepared by grafting of end-functional chains, where the functionality is tailored to react with the surface. High grafting densities are hard to achieve by this strategy, however, due to steric crowding; the first chains anchored to the surface make it progressively harder for further chain ends to react.

6. *Controlled branched and cyclic architectures*. Examples of branched structures will be given in the following section. Cyclic polymers can be prepared by intramolecular reaction of an “α,ω-heterotelechelic” linear precursor, where the two distinct end groups can react. Such ring-closing reactions have to be run at extreme dilution, to suppress interchain end-linking.

7. *Network precursors*. Telechelic polymers can serve as precursors to network formation, when combined with suitable multifunctional linkers or catalysts. For example, some silicone adhesives contain poly(dimethyl siloxane) chains with vinyl groups at each end.

In the unreacted form, these polymers form a low viscosity fluid which can easily be mixed with catalyst and spread on the surfaces to be joined; the subsequent reaction produces an adhesive, three-dimensional network *in situ*.

8. *Reactive compatibilization.* As noted previously, block copolymers can act as macromolecular surfactants to stabilize dispersions of immiscible homopolymers. However, direct mixing of block copolymers during polymer processing is not always successful, as the copolymers have a tendency to aggregate into micelles and never reach the interface between the two polymers. One effective way to overcome this is to form the block copolymer at the targeted interface, by *in situ* reaction of suitably functional chains. Note that in this case it is not absolutely necessary that the reactive groups be at the chain ends.

There are two general routes to end-functional chains: use a functional initiator or use a functional terminating group. For a telechelic polymer, both strategies must be employed (unless a difunctional initiator is used). The use of a functional terminating agent proves to be the more flexible strategy, for a rather straightforward reason. Any functional group present in the initiator must be inert to the polymerization, which can be problematic in the case of anionic polymerization. Thus the functional group in the initiator must be protected in some way. In contrast, for the terminating agent all that is required are two functionalities: the desired one, and another electrophilic one to terminate the polymerization. However, the functionality that is designed to terminate polymerization must be substantially more reactive to carbanions than the other functionality, or more than one chain end structure will result. Consequently, in most cases a protection strategy is also employed for the terminating agent. Nevertheless in the termination case the demands on the protecting group are much reduced relative to initiation; in the former, the protecting group only needs to be significantly less reactive than the electrophile, whereas in the latter the protective groups must be substantially less reactive than the monomer.

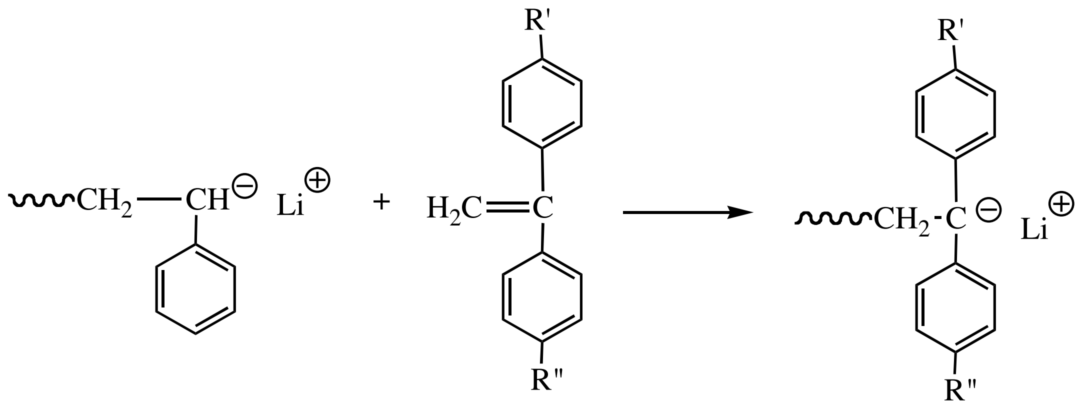
For the living anionic polymerization of styrene, butadiene, and isoprene, an effective terminating strategy is to use alkanes that have an iodo- or bromo-functionality at one end, and the protecting group at the other. The halide is very reactive to the carbanion, readily eliminating the LiBr or LiI salt as the chain is terminated. Of course, the protecting group must then be removed in a separate step. Examples of protecting groups and the desired functionalities are given in Table 4.2. Some of the same protective groups illustrated in Table 4.2 can also be used in functional initiators. For example, the *tert*-butyl dimethylsilyl moiety used to protect the thiol group can also be used to protect a hydroxyl group in the initiator, as in the commercially available (3-(*t*-butyl dimethylsilyloxy-1-propyllithium).

Functional Group	**Protected Functionality**
–OH	–O–$Si(CH_3)_3$
$–NH_2$	$–N(Si(CH_3)_3)_2$
–SH	$–S–Si((CH_3)_2$t-Bu)
–COOH	$–C(OCH_3)_3$
–C≡CH	–C≡C–Si $(CH_3)_3$

Table 4.2

Examples of protection strategies for preparing end-functional polymers by living anionic polymerization of styrenes and dienes. Termination by short alkanes with a halide at one end and the protected functionality at the other. Adapted from A. Hirao and M. Hoyashi, *Acta Polymerica* 50, 219 (1999).

Another powerful strategy for preparing end-functional polymers by anionic polymerization was implicitly suggested in the previous section, where addition of a nominally polymerizable monomer (ethylene oxide in that instance) to a growing polystyryl anion resulted in the addition of only one new monomer. It turns out that 1,1-diphenylethylene and derivatives thereof will only react with organolithium salts to form the associated relatively stable carbanion; no further propagation occurs.



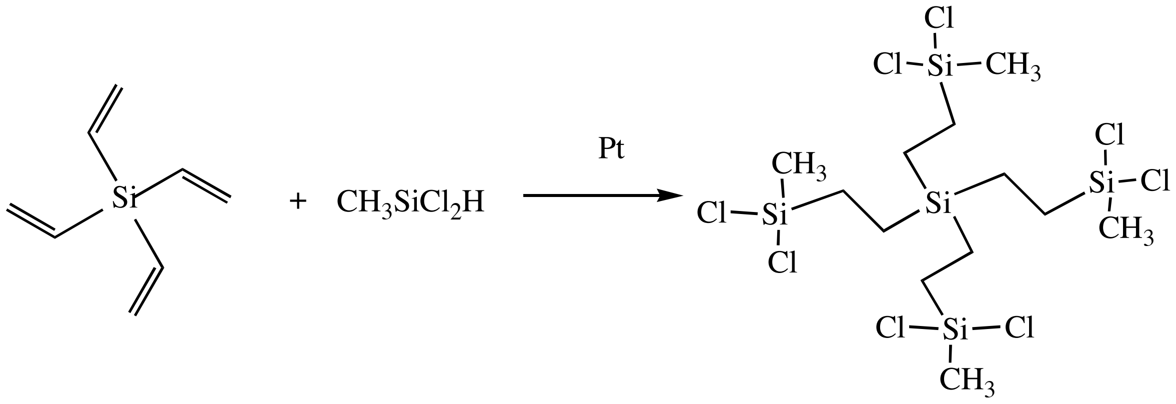
(4.I)

In this structure R' and R" could be any of a variety of protected or even unprotected functionalities. Even more interesting is the fact that this carbanion can be used to initiate anionic polymerization of a new monomer (such as methyl methacrylate, dienes, etc.) or even to re-initiate the polymerization of styrene. In this way diphenylethylene derivatives can be used to place particular functional groups at desired locations along a homopolymer or copolymer, not just at the terminus.

4.4C Regular branched architectures

The kinds of synthetic methodology suggested in the previous section have been adapted to the preparation of a wide range of polymer structures with controlled branching. [4] The first architecture to consider is that of the *regular star*, in which a predetermined number of equal length arms are connected to a central core. There are two general strategies to prepare such a polymer by living anionic polymerization: use a multifunctional initiator, and grow the arms outwards simultaneously, or use a multifunctional terminating agent to link together premade arms. The first route is an example of an approach known as *grafting from,* whereas the second is termed *grafting to*. Or, in anticipation of the discussion of dendrimers in Section 4.9, grafting from and grafting to are analogous to *divergent* and *convergent* synthetic strategies. Although both have been used extensively, grafting to is more generally applicable to anionic polymerization, due to the difficulty in preparing and dissolving small molecules with multiple alkyllithium functionalities. Furthermore, in order to achieve uniform arm lengths, it is essential that each initiation site be equally reactive and equally accessible to monomers in the reaction medium. If it is desired to terminate each star arm with a functional group, however, then grafting from may be preferred. Should the anionic polymerization be initiated by a potassium alkoxide group, as for example with the polymerization of ethylene oxide suggested in the context of reaction 4.H, then preparation of initiators with multiple hydroxyl groups is quite feasible (see Reaction 4.EE for a specific example). Similarly, if other living polymerization routes are employed, such as controlled radical polymerization to be discussion in Section 4.6, then grafting from is more convenient than in the anionic case.

The preparation of an 8-arm polystyrene star by grafting to is illustrated in the following scheme. The most popular terminating functionality in this context is a chlorosilane, which reacts rapidly and cleanly with many polymeric carbanions, and which can be prepared with functionalities up to at least 32 without extraordinary effort. An octafunctional chlorosilane can be prepared starting with tetravinylsilane and dichloromethylsilane, using platinum as a catalyst:

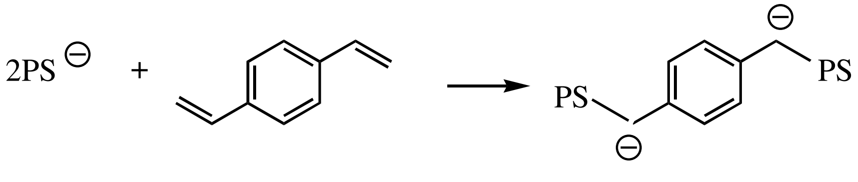


(4.J)

This multifunctional terminating agent is then introduced directly into the reaction vessel containing the living polystyryl chains. The chains should be in stoichiometric excess, to minimize the formation of a mixture of stars with different numbers of arms. This will necessitate separation of the unattached arms from the reaction mixture, but this is feasible. Moreover, an additional advantage of the grafting to approach is thus exposed: the unattached arms can be characterized (for molecular weight, polydispersity, etc.) *independently of the stars themselves*, a desirable step that is not possible when grafting from.

The scheme just outlined is not quite as straightforward as it might appear. A key issue is to make all 8 terminating sites accessible to the polystyryl chains. As the number of attached arms grows, it becomes harder and harder for new chain ends to find their way into the reactive core. In order to reduce these steric effects, more methylene groups can be inserted into the terminating agent, to spread out the chlorosilanes. In some cases, polystyryl chains have been capped with a few butadienyl units to reduce the steric bulk of the chain end. Clearly, all of these issues grow in importance as the number of arms increases. Note, however, that it is not necessary that all the chlorosilanes be equally reactive in order to preserve a narrow molecular weight distribution; it is only necessary that the attachment of the narrowly-distributed arms be driven to completion (which may take some time).

As the desired number of arms increases, it is practical to surrender some control over the exact number of arms in favor of a simpler method for termination. A scheme that has been refined to a considerable extent is to introduce a difunctional monomer, such as divinyl benzene, as a polymerizable linking agent. The idea is illustrated in the following reaction:

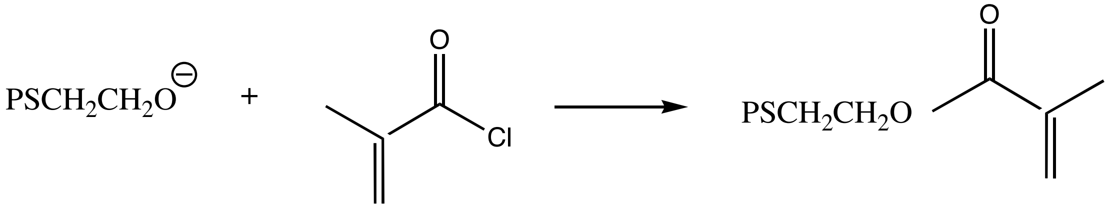


(4.K)

One divinylbenzene molecule can thus couple two polystyryl chains, and leave two anions for further reaction. Each anion might add one more divinylbenzene, each of which could then add one more polystyryl chain. At that point the growing star molecule would have four arms, emanating from a core containing three divinylbenzene moieties and four anions. This process can continue until the divinyl benzene is consumed, and the anions terminated. Clearly there is potential for a great deal of variation in the resulting structures, both in the size of the core and in the number of arms. However, by carefully controlling the reaction conditions, and especially the ratio of divinylbenzene to living chains, reasonably narrow distributions of functionality can be obtained, with average numbers of arms even exceeding 100.

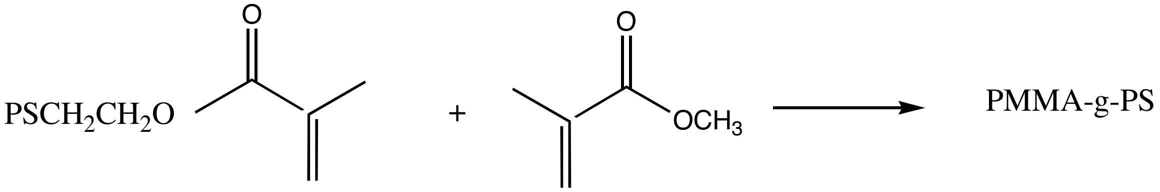
The preceding strategy can actually be classified as *grafting through*, a third approach that is particularly useful for the preparation of comb polymers. A comb polymer consists of a backbone, to which a number of polymeric arms are attached; combs can be prepared by grafting from, grafting to, and grafting through. In the first case the backbone must contain reactive sites that can used to initiate polymerization. The backbone can be characterized independently of the arms, but the arms themselves cannot. In grafting to, the backbone must contain reactive sites such as chlorosilanes that can act to terminate the polymerization of the arms. Clearly in this case, as with stars, the arms and the backbone can be characterized independently. The grafting through strategy takes advantage of what we previously termed macromonomers: the arms are polymers terminated with a polymerizable group. These groups can be co-polymerized with the analogous monomers to generate the backbone. By varying the ratio of macromonomer to comonomer, the spacing of the "teeth" of the comb can be tuned. Note that this process is not necessarily straightforward. In Chapter 5 we will consider copolymerization in great detail, but a key concept is that of *reactivity ratio*. This refers to the relative probability of adding one monomer to a growing chain, depending on the identity of the previous monomer that attached. It is generally the case that there are significant preferences (i.e., the reactivity ratios of the two monomers are not unity), which means that the two monomers will not add completely randomly. These factors need to be understood before regular comb molecules with variable branching density can be prepared by grafting through.

The grafting through approach can be illustrated through the following sequence.[5] Polystyryl chains can be capped with one ethylene oxide unit (Reaction 4.H) followed by termination with methacryloyl chloride.



(4.L)

This macromonomer can them be copolymerized with methyl methacrylate, to produce a comb or graft copolymer, with a poly(methyl methacrylate) backbone and polystyrene arms.



(4.M)

This last example reminds us that the variety of possible controlled branched architectures is greatly enhanced when different chemistries are used for different parts of the molecule. If we confine ourselves to the case of stars, a molecule in which any two arms differ in a deliberate and significant way has been termed a *miktoarm star*, from the Greek word for mixed [4]. A whole host of different structures have been prepared in this manner. For example, an A_2B miktoarm star contains two equal length arms of polymer A and one arm of polymer B. Among the structures that have been reported are A_2B, A_3B, A_2B_2, A_4B_4, and a variety of ABC miktoarm terpolymers. It is even possible to produce asymmetric stars, in which the arms consist of the same polymer but differ in length.

4.5 Cationic polymerization

Just as anionic polymerization is a chain-growth mechanism that shares important parallels with the free radical route, so too cationic polymerizations can be discussed within the same framework: initiation, propagation, termination, and transfer. However, there are important differences between anionic and cationic polymerization that have direct impact on the suitability of the latter for living polymerization. The principal differences between the two ionic routes are the following:

1. A single initiator species is often not sufficient in cationic polymerizations; frequently a cocatalyst is required.
2. Total dissociation of the cationic initiator is rather rare, which has implications for the ability to start all the chains growing at the same time.
3. Although both ionic mechanisms clearly eliminate termination by direct recombination of growing chains, cationic species are much more prone to transfer reactions than their anionic counterparts. Consequently, living cationic polymerization is much less prevalent than living anionic polymerization.
4. Most monomers that can be readily polymerized by anionic mechanisms are also amenable to free radical polymerization. Thus, in commercial practice the rather more demanding anionic route is only employed when the higher degree of control is required, e.g., in the preparation of styrene-diene block copolymers.
5. Although most monomers that can be polymerized by cationic mechanisms are also amenable to free radical polymerization, there are important exceptions. The most significant from a total production point of view is polyisobutylene (“butyl rubber”), which is produced commercially by (both living and non-living) cationic polymerization.

A brief summary of the applicability of the three chain growth mechanisms – radical, anionic, cationic – to various monomer classes is presented in Table 4.3. In the remainder of this section we describe general aspects of cationic polymerization, and introduce some of the transfer reactions that inhibit living polymerization. Then we conclude by discussing the strategies that have been used to achieve living cationic polymerization.

Monomer	**Radical**	**Anionic**	**Cationic**
Ethylene	✓	✓	×
1-Alkyl alkenes	×	✓	×
1,1-Dialkyl alkenes	×	×	✓
Halogenated alkenes	✓	×	×
1,3-Dienes	✓	✓	✓
Styrenes	✓	✓	✓
Acrylates, methacrylates	✓	✓	×
Acrylonitrile	✓	✓	×
Acrylamide, methacrylamide	✓	✓	×
Vinyl esters	✓	×	✓
Vinyl ethers	×	×	✓
Aldehydes, ketones	×	✓	×

Table 4.3

General summary of polymerizability of various monomer types by the indicated chain growth modes. Adapted from Odian. [10]

4.5A Aspects of cationic polymerization

In cationic polymerization the active species is the ion formed by the addition of a proton from the initiator system to a monomer (partly for this reason the initiator species is often called a catalyst, because it is not incorporated into the chain). For vinyl monomers the substituents which promote this type of polymerization are electron donating, to stabilize the carbocation; examples include alkyl, 1,1-dialkyl, aryl, and alkoxy. The aforementioned isobutylene, α-methylstyrene, and vinyl alkyl ethers are examples of monomers commonly polymerized via cationic intermediates.

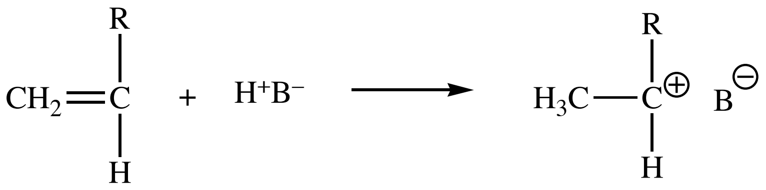
The initiator systems are generally Lewis acids, such as BF_3, $AlCl_3$, and $TiCl_4$, or protonic acids, such as H_2SO_4, $HClO_4$, and HI. In the case of the Lewis acids, a proton donating cocatalyst such as water or methanol is often used:

$$\begin{aligned} &BF_3 + H_2O \Leftrightarrow F_3BOH^- + H^+ \\ &AlCl_3 + H_2O \Leftrightarrow Cl_3AlOH^- + H^+ \\ &TiCl_4 + CH_3OH \Leftrightarrow Cl_4TiOCH_3^- + H^+ \end{aligned} \tag{4.N}$$

With insufficient cocatalyst these equilibria lie too far to the left, while excess cocatalyst can terminate the chain or destroy the catalyst. Thus the optimum proportion of catalyst and cocatalyst varies with the specific monomer and polymerization solvent. In the case of protonic acids, the concentration of protons depends on the position of the standard acid-base equilibria, but in the chosen organic solvent:

$$\begin{aligned} &H_2SO_4 \Leftrightarrow H^+ + HSO_4^- \\ &HClO_4 \Leftrightarrow H^+ + ClO_4^- \\ &HI \Leftrightarrow H^+ + I^- \end{aligned} \tag{4.O}$$

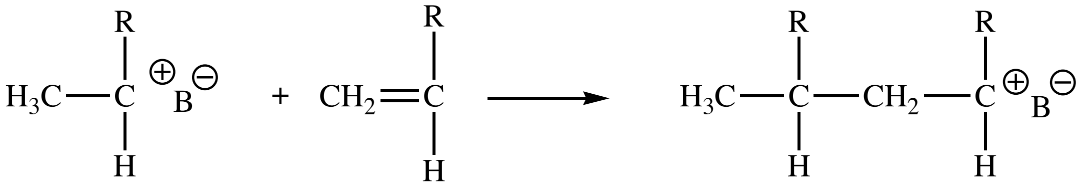
If we write the general formula for the initiator system as H^+B^-, then the initiation and propagation steps for a vinyl monomer $CH_2{=}CHR$ can be written as follows. The proton adds to the more electronegative carbon atom in the olefin to initiate chain growth:



$$\mathrm{CH_2{=}\underset{H}{\overset{R}{C}}} + \mathrm{H^+B^-} \longrightarrow \mathrm{H_3C{-}\underset{H}{\overset{R}{C}}{}^{\oplus}\;B^{\ominus}}$$

(4.P)

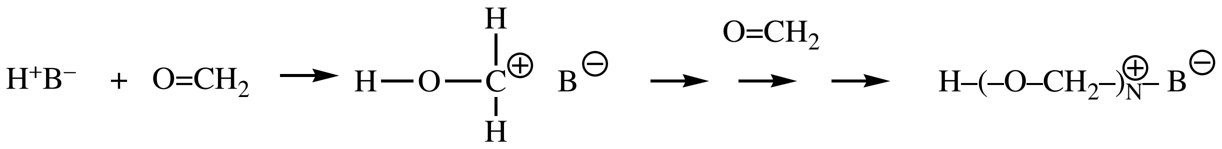
The electron donating character of the R group helps to stabilize this cation. As with anionic polymerization, the separation of the ions and the possibility of ion pairing play important roles in the ease of subsequent monomer insertion. The propagation proceeds in a head-to-tail manner:



$$\mathrm{H_3C{-}\underset{H}{\overset{R}{C}}{}^{\oplus}\,B^{\ominus}} + \mathrm{CH_2{=}\underset{H}{\overset{R}{C}}} \longrightarrow \mathrm{H_3C{-}\underset{H}{\overset{R}{C}}{-}CH_2{-}\underset{H}{\overset{R}{C}}{}^{\oplus}\,B^{\ominus}}$$

(4.Q)

Aldehydes can also be polymerized in this fashion, with the corresponding reactions for formaldehyde being



$$\mathrm{H^+B^-} + \mathrm{O{=}CH_2} \longrightarrow \mathrm{H{-}O{-}\underset{H}{\overset{H}{C}}{}^{\oplus}\;B^{\ominus}} \xrightarrow{\mathrm{O=CH_2}} \longrightarrow \longrightarrow \mathrm{H{-}({-}O{-}CH_2{-})_N^{\oplus}{-}\,B^{\ominus}}$$

(4.R)

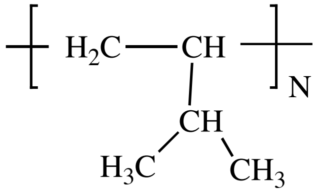
One of the side reactions that can complicate cationic polymerization is the possibility of the ionic repeat unit undergoing rearrangement during the polymerization. The following example illustrates this situation.

Example 4.2

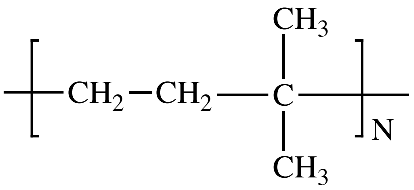
It has been observed that poly(1,1-dimethyl propane) is the product when 3-methylbutene-1 CH_2=CH–CH(CH_3)$_2$ is polymerized with $AlCl_2$ in ethyl chloride at –130 °C (J. P. Kennedy and R. M. Thomas, *Makromol. Chem.* 53, 28 (1962)). Draw structural formulas for the "expected" and observed repeat units, and propose an explanation.

Solution

The structures expected and found are sketched here:

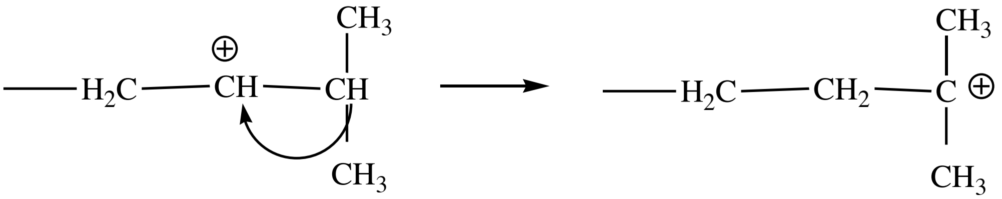


Expected



Found

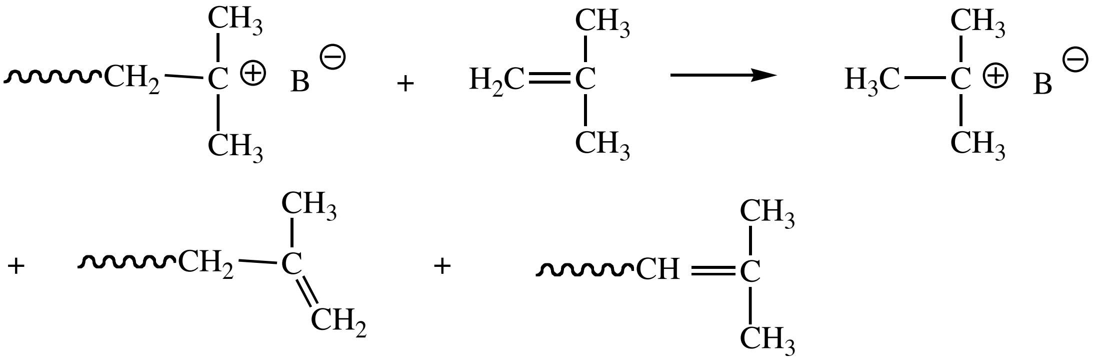
The conversion of the cationic intermediate of the monomer to the cation of the product occurs by a *hydride shift* between adjacent carbons:



This is a well-known reaction which is favored by the greater stability of the tertiary compared to the secondary carbocation.

The preceding example illustrates one of the potential complications encountered in cationic polymerization, but it is not in itself an impediment to living polymerization. There are several other potential transfer reactions, however, that collectively do interfere with achieving a living cationic polymerization. Four of these are the following.

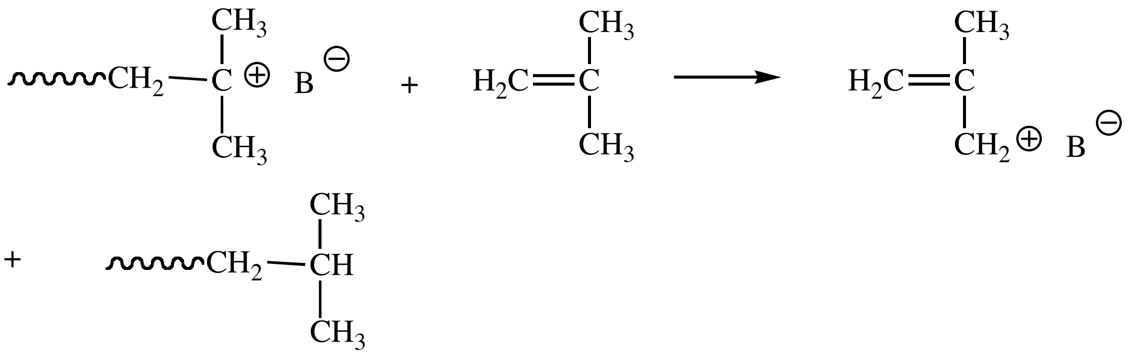
1. *β-proton transfer.* This is exemplified by the case of polyisobutylene. Protons on carbons adjacent ("beta") to the carbocation are electropositive, due to a phenomenon known as *hyperconjugation*; we can view this as partial electron delocalization through sigma bonds, in contrast to resonance, which is delocalization through pi bonds. Consequently there is a tendency for β-protons to react with any base present, such as a vinyl monomer.



(4.S)

The activated monomer can now participate in propagation reactions, whereas the previous chain is terminated. Note that in isobutylene there are two distinct β-protons, and thus two possible structures for the terminal unsaturation of the chain. There is also the possibility that these double bonds can react subsequently.

2. *Hydride transfer from monomer.* In this case the transfer proceeds in the opposite direction, but has the same detrimental net effect from the point of view of achieving a living polymerization.

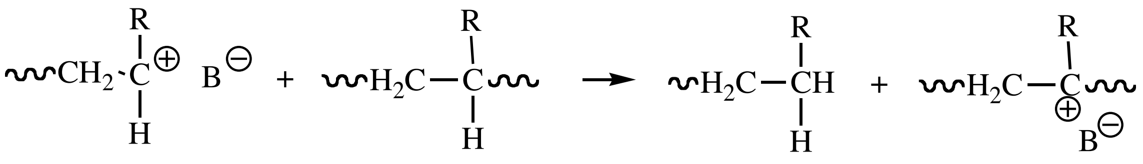


$$\sim CH_2-C^{\oplus}(CH_3)_2\ B^{\ominus} + H_2C{=}C(CH_3)_2 \longrightarrow H_2C{=}C(CH_3)CH_2^{\oplus}\ B^{\ominus} + \sim CH_2-CH(CH_3)_2$$

(4.T)

In the particular case of isobutylene the resulting primary carbocation is less stable than the tertiary one on the chain, so reaction (4.T) is less of an issue than reaction (4.S).

3. *Intermolecular hydride transfer*. This is an example of transfer to polymer, and can be written generally as



$$\sim CH_2-C^{\oplus}(R)H\ B^{\ominus} + \sim H_2C-C(R)(H)\sim \longrightarrow \sim H_2C-CH(R)H + \sim H_2C-C^{\oplus}(R)\sim\ B^{\ominus}$$

(4.U)

4. *Spontaneous termination.* This process, also known as chain transfer to counterion, is essentially a reversal of the initiation step, as a β-proton is transferred back to the anion (e.g., as in reaction 4.P, but with a growing chain rather than the first monomer).

4.5B Living cationic polymerization

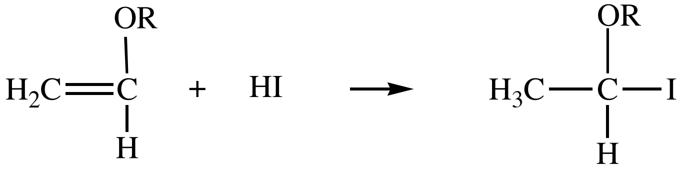
The preceding discussion provides some insight into the obstacles to achieving a living cationic polymerization. Nevertheless, living cationic polymerization is by now a relatively common tool, and many of the controlled architectures (block copolymers, end-functional chains, regular branched molecules) that we discussed in the context of anionic polymerization have been accessed.[6] In this section we briefly describe the general strategy behind living cationic polymerization; recall that the essential elements are the absence of termination or transfer reactions.

1. Clearly, the reaction must be conducted in the absence of nucleophilic species that are capable of irreversible termination of the growing chain.
2. Similarly, the reaction should be conducted in the absence of bases that can participate in β-proton transfer. As discussed above, the monomer itself is such as base, and therefore cationic polymerization always has a "built-in" transfer reaction. The key step, therefore, is to choose reaction conditions to maximize the rate of propagation relative to transfer, given that transfer probably cannot be completely eliminated.
3. Generally, both propagation and transfer are very rapid reactions, with transfer having the higher activation energy. Lower temperatures therefore favor propagation relative to transfer, as well as having the advantage of bringing both reactions under better control.
4. Cationic polymerization is often highly exothermic, and thus it is important to slow down the rate of polymerization in order to remove the excess heat. Low temperature is the first option in this respect, followed by lower concentrations of growing chains.
5. Another way to view control in this context is to aim to extend the lifetime of the growing chain. As a point of reference, a living polystyryl carbanion can persist for months in a sealed reaction vessel; a polyisobutyl carbocation will probably not last for an hour under equivalently pristine conditions. While low temperature certainly aids in increasing the lifetime, another useful strategy is to make the growing center inactive or dormant for a significant fraction of the elapsed reaction time. This is done via the process of *reversible termination*, as illustrated by the reaction sequence 4.V:

$$\begin{aligned}
&\mathrm{HCl} + \mathrm{TiCl_4} \Leftrightarrow \mathrm{TiCl_5}^- + \mathrm{H}^+ \\
&\mathrm{H}^+ + \mathrm{M} \rightarrow \mathrm{P_1}^+ \\
&\mathrm{P_i}^+ + \mathrm{M} \rightarrow \mathrm{P_{i+1}}^+ \qquad (4.V) \\
&\mathrm{P_i}^+ + \mathrm{TiCl_5}^- \Leftrightarrow \mathrm{P_iCl} + \mathrm{TiCl_4}
\end{aligned}$$

In this sequence, the first reaction generates the initiating proton, and the second and third reactions correspond to standard irreversible initiation and propagation steps involving monomer M. The fourth reaction is the key. The growing cationic i-mer P_i^+ is converted to a dormant, covalent species P_iCl by a reversible reaction. While the growing chain is in this form, it does not undergo transfer or propagation reactions, thereby extending its lifetime. The reversible activation/deactivation reaction must be sufficiently rapid to allow each chain to have many opportunities to add monomer during the polymerization, and the relative length of time spent in the active and dormant states can be controlled by the position of the associated equilibrium. This, in turn, offers many opportunities to tune a particular chemical system. For example, decreasing the polarity of the solvent or adding an inert salt that contains a common ion (chloride in this case) both push the equilibrium towards the dormant state.

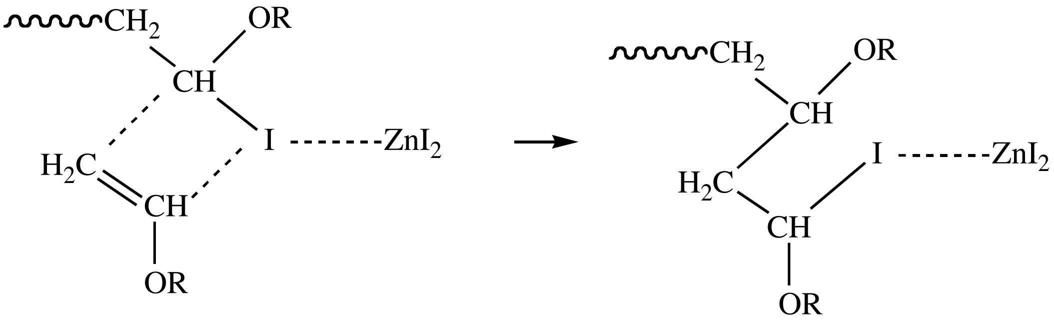
We will revisit this idea of a dormant reactive species in the next section on living radical polymerization, where it plays the central role. We conclude this section with a specific example of a successful living cationic polymerization scheme. Isobutyl vinyl ether (and other vinyl ethers) can be polymerized by a combination of HI and ZnI_2.[7] The hydrogen iodide "initiator" adds across the double bond, but forms an essentially unreactive species:



$$\mathrm{H_2C{=}CH(OR)} + \mathrm{HI} \longrightarrow \mathrm{H_3C{-}CH(OR){-}I}$$

(4.W)

The carbon-iodide bond is then activated by the relatively weak Lewis acid ZnI_2, to allow insertion of the next monomer. The transition state for propagation may be represented schematically as



(4.X)

Experimentally, the system exhibits many of the characteristics associated with a living polymerization: polydispersities consistently below 1.1; M_n increasing linearly with conversion; the ability to resume polymerization after addition of a new charge of monomer. These aspects are illustrated in Figure 4.5. The mechanism implied by reactions 4.W and 4.X is consistent with the experimental observation that M_n is inversely proportional to the concentration of HI, but independent of the concentration of ZnI_2. On the other hand, the polymerization rate increases with added ZnI_2. The ZnI_2 is apparently sufficiently mild an activator that the polymerization is still living at room temperature when conducted in toluene, whereas in the more polar solvent methylene chloride lower temperatures are required.

4.6 Living radical polymerization

In this section we take up the topic of living radical polymerization, which represents one of the most active fields in polymer synthesis in recent years. The combination of the general advantages of radical polymerization (a wide range of suitable monomers, tolerance to many functional groups, characteristically rapid reactions, relatively relaxed polymerization conditions) with the unique features of a living polymerization (narrow molecular weight distributions, controlled molecular weights, end-functionality, block copolymers and other complex architectures) has tremendous appeal in many different areas of polymer science. In this section we outline first in general terms how this combination is achieved, and then give some specific examples of the mechanistic details.

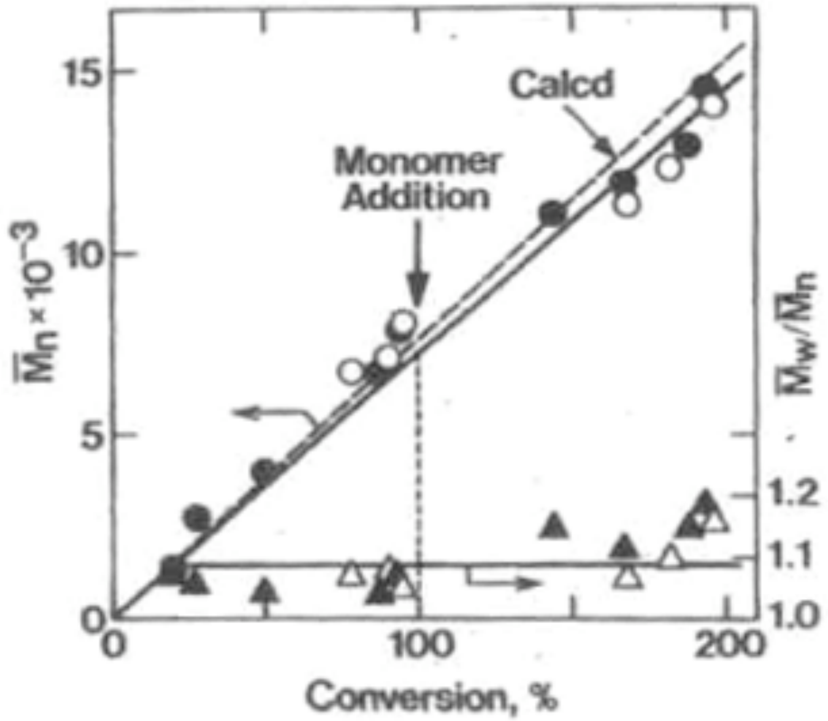


Figure 4.5
Living cationic polymerization of isobutyl vinyl ether in methylene chloride at –40 ºC. The calculated curve indicates the expected molecular weight assuming 100% initiator (HI) efficiency. After 100% conversion a new charge of monomer was added, demonstrating the ability of the chain ends to resume propagation. Figure reproduced from [7], with permission.

4.6A General principles of living radical polymerization

The first task is to resolve the apparent paradox: given that radicals can always combine to undergo termination reactions, how do we approximate a living radical polymerization? To develop the answer, it is help to start by summarizing once again the essence of a chain-growth polymerization in terms of initiation, propagation, and termination rates:

$$R_i = k_i[I][M] \tag{4.6.1}$$

$$R_p = k_p[P\bullet][M] \tag{4.6.2}$$

$$R_t = k_t[P\bullet][P\bullet] \tag{4.6.3}$$

where as before [I] is the concentration of initiating species, [M] is the concentration of unreacted monomer, and [P•] is the total concentration of radicals of any length. The key to a living polymerization is that $R_t \rightarrow 0$, or equivalently in practice, that $R_p >> R_t$. From Tables 3.3 and 3.4, we can see that typical values of k_t are about 4 orders of magnitude larger than k_p. Therefore if we want R_p to be, say, 10^4 times larger than R_t we will need [M] to be 10^8 times larger than [P•]. Given that [M] could be on the order of 1–10 M (i.e., in bulk or concentrated solution), that means the concentration of radicals, and therefore growing chains, will have to be $10^{-7} - 10^{-8}$ M. This is quite small, but from the calculations in Chapter 3.4C we know that it is quite feasible.

We can do even better than this, however, by a nifty trick already suggested in the context of living cationic polymerization. Suppose that the absolute concentration of radical forming species is not that small, but that each molecule spends the vast majority of its time in an unreactive, dormant form. This is illustrated schematically below:

$$PX \Leftrightarrow P\bullet + X \tag{4.Y}$$

where PX is the dormant species and X is a group (atom or molecular fragment) that can leave and re-attach to the radical rapidly. (Note that radical species are apparently not conserved in the way reaction 4.Y is expressed, but as we will see subsequently this is not actually the case. Usually either X or PX is also a radical species, but one that is not capable of propagating). If the equilibrium constant for the activation process, K_{act}, is small, then the instantaneous [P•] will be small even if [PX] is reasonably large:

$$[\mathrm{P}\bullet] \quad = \quad K_{act}\frac{[\mathrm{PX}]}{[\mathrm{X}]} \tag{4.6.4}$$

The process of living radical polymerization can now be seen to take place as follows. The dormant species PX spontaneously dissociates into the active radical and the inert partner X. The exposed radical may then undergo propagation steps, or simply recombine with X so that no net reaction takes place. If each radical spends most of its time in the dormant state, the instantaneous concentration of radicals is small, and termination is very unlikely (but never impossible). During an average active period a given radical may add many new monomers, about one new monomer, or essentially no new monomers. It is actually the last situation that is most desirable, because it means that over time all radicals are equally likely to propagate, one monomer at a time. We can understand this concept in the following way. After the polymerization has proceeded for a reasonable time, so that each chain on average has experienced many active periods, the number of active periods per chain will follow the Poisson distribution (eq 4.2.19). That is because we are randomly distributing a large number of items (active periods) into a smaller number of boxes (growing chains). In the limit where the likelihood of adding a monomer per active period is small, the average number of monomers added per chain will be directly proportional to the number of active periods, and thus follow the Poisson distribution as well. Of course, we are neglecting any termination and transfer reactions.

In contrast, if radicals tend to add monomers in a burst during each active period, the molecular weight distribution will not be as narrow unless the total degree of polymerization involves many such bursts. In fact, the length distribution of the "bursts" will be the most probable distribution, which (recall eqs 2.4.10 and 3.7.19) has a polydispersity approaching 2. We can actually rationalize an approximate expression for the polydispersity of the resulting polymers, based on what we already know. Suppose the mean number of monomers added per active period is $Q \geq 1$. The distribution of active periods from chain to chain still follows the Poisson distribution, so it is almost as though we were adding one Q-length block per active period. Thus the polydispersity index becomes that for the Poisson distribution (recall eq 4.2.20) with a new "effective monomer" of molecular weight QM_o:

$$\frac{M_w}{M_n} \approx 1 + \frac{Q\,M_o}{M_n} \qquad (4.6.5)$$

Equation 4.6.5 suggests that even if Q is 10, a polydispersity of 1.1 is achievable if the total degree of polymerization exceeds 100. A more detailed analysis yields equations similar to eq 4.6.5, when the average degree of polymerization is sufficiently large.[8] It is worth noting that there are several complications to this analysis, such as the fact that the value of Q will actually change during the polymerization, as [M] decreases.

It should be evident from the preceding discussion that termination processes are not rigorously excluded in living radical polymerization, only significantly suppressed. Nevertheless, polydispersities $M_w/M_n < 1.1 - 1.2$ are routinely obtained by this methodology. It should also be evident that the higher the average chain length, the more likely termination steps become. This can be seen directly from eqs 4.6.2 and 4.6.3; as time progresses, R_t remains essentially constant, whereas R_p decreases because [M] decreases with time. Consequently, the relative likelihood of a termination event increases steadily as the reaction progresses. In fact, there is really a three-way competition in designing a living radical polymerization scheme, among average molecular weight, polydispersity, and "efficiency", where we use efficiency to denote a combination of practical issues. For example, the higher the desired molecular weight, the broader the distribution will become, due to termination reactions. This could be mitigated to some extent by running at even higher dilution, but this costs time and generates large volumes of solvent waste. Or, the reaction vessel could be replenished with monomer, to keep [M] high even as the reaction progresses, but this wastes monomer, or at least necessitates a recovery process.

4.6B Particular realizations of living radical polymerization

A rich variety of systems that fall under the umbrella of reaction 4.Y have been reported. Three general schemes have so far emerged as the most prevalent, although there is no *a priori* reason why others may not become more popular in the years ahead. Each has particular advantages and disadvantages relative to the others, but for the purposes of this discussion we are really only interested in their evident success.

Atom transfer radical polymerization (ATRP)

In this approach the leaving group X in reaction 4.Y is a halide, such as a chloride or bromide, and it is extracted by a suitable metal, such as copper or nickel. The metal is chelated by ligands such as bipyridines and trialklyphosphines that can stabilize the metal in different oxidation states. A particular example of the activation/deactivation equilibrium using copper bromide/2,2'-bipyridine ("bipy") can thus be written:

$$P_i\mathrm{Br} + \mathrm{CuBr(bipy)_2} \Leftrightarrow P_i\bullet + \mathrm{CuBr_2(bipy)_2} \qquad (4.Z)$$

where the copper atom is oxidized from Cu(I)Br to Cu(II)Br_2. Reaction 4.Z suggests that the polymerization could be initiated by the appropriate halide of the monomer in question, such as 1-phenylethyl bromide when styrene is the monomer. Alternatively, a standard free radical initiator such as AIBN could be employed (recall Chapter 3.3). A particularly appealing aspect of ATRP is the wide variety of monomers that are amenable to this approach: styrene and substituted styrenes, acrylates and methacrylates, dienes, and other vinyl monomers. The following example illustrates some of the quantitative aspects of ATRP of styrene.

Example 4.3

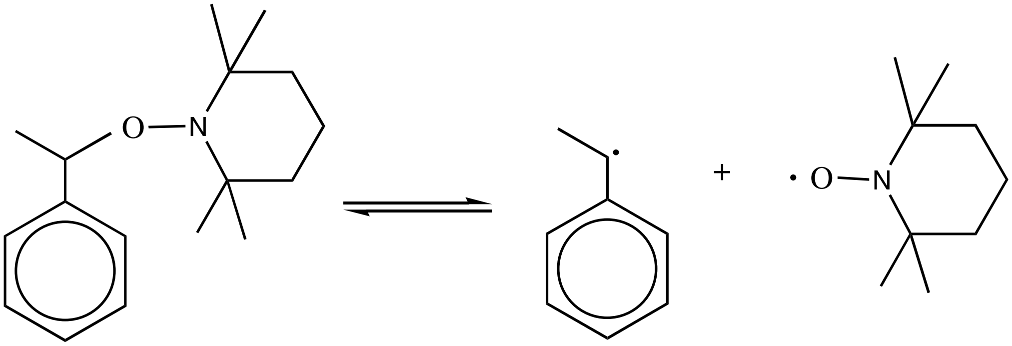
From a linear plot of ln ($[M]_o/[M]$) versus time, it has been reported that *apparent* propagation rate constant for the ATRP of styrene in bulk is on the order of 10^{-4} sec^{-1}, where the apparent rate constant k_p^{app} is defined by $R_p = k_p^{app}$ [M] (K. Matyjaszewski, T. E. Patten, and J. Xia, *J. Am. Chem. Soc.* 119, 674 (1997)). What is the order of magnitude of the concentration of active radicals at any time?

Solution

From eq 4.6.2 we can see that k_p^{app} thus defined is actually equal to k_p [P•]. From Table 3.4 in Chapter 3 we know that a typical value for k_p for free radical polymerization is $10^2 - 10^3$ $\underline{M}^{-1}$ sec^{-1}, and on this basis direct substitution tells us that [P•] is about 10^{-4} sec^{-1} / 10^{2-3} $\underline{M}^{-1}$ sec^{-1} = $10^{-6} - 10^{-7}$ $\underline{M}$. This is in line with the estimate given in the previous section, of the target concentration of active radicals needed to make the rate of termination small with respect to the rate of propagation.

Stable free radical polymerization (SFRP)

In this variant, the leaving group X in reaction 4.Y is a free radical, but one sufficiently stable that it does not initiate polymerization. The prime example of this class is the nitroxide radical, usually embedded in the (2,2,6,6-tetramethylpiperidinyloxy) “TEMPO” group.[9] When attached to a monomer analog or a growing polymer chain terminus through the alkoxyamine C–ON bond, homolytic cleavage of the C–O bond produces the stable TEMPO radical and an active radical species. This reaction is illustrated below for the case of styrene:



(4.AA)

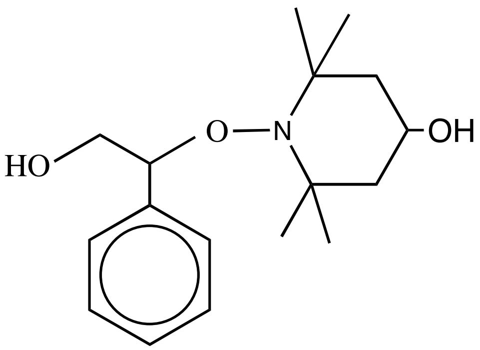
The adduct of styrene and TEMPO on the left hand side of reaction 4.AA can be prepared rather readily, purified, and stored indefinitely. In contrast to other living radical polymerization schemes, this approach is based on a single initiating species; no co-catalyst or transfer agent is needed. Even in the presence of a large excess of styrene monomer, it is not until the system is brought to an elevated temperature such as 125 ^{o}C that polymerization proceeds directly. The reaction can be run under nitrogen, and the rigorous purification necessary for living ionic polymerizations is not required. Molecular weights well in excess of 10^5, with polydispersities in the range of 1.1 to 1.2, have been achieved. The range of accessible monomers is so far more restricted than with ATRP or RAFT, with styrene, acrylate, and methacrylate derivatives being the monomers of choice. However, the polymerization is relatively tolerant of functional groups, and many functionalized initiators with TEMPO adducts have been designed. This makes SFRP an appealing alternative to living ionic polymerization for the production of end-functional polymers (recall Section 4.4), and by extension block copolymers and branched architectures.

Example 4.4

An interesting question arises upon examination of reaction 4.AA: does each TEMPO radical remain associated with the same chain during the polymerization, or does it migrate freely through the reaction medium? In the case of anionic polymerization in a nonpolar solvent the counterion is certainly closely associated with the chain end, due to the requirement of electrical neutrality. In the case of conventional free radical polymerization, we considered the "caging effect" that can severely limit the efficiency of an initiator (see Section 3.3). In this case the relatively high temperature should enhance both the mobility of the individual species, and the ability to escape from whatever attractive interaction would hold the two radical species in proximity. How could one test this intuition experimentally?

Solution

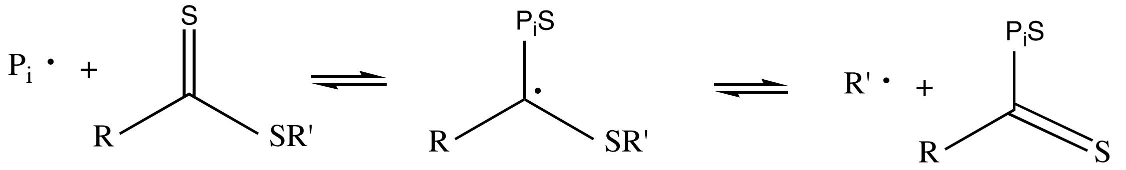
The unimolecular nature of the TEMPO-based initiator, plus its susceptibility to functionalization, offer a convenient solution, as has been demonstrated (C. J. Hawker, G. G. Barclay, and J. Dao, *J. Am. Chem. Soc.* 118, 11467 (1996)). These authors prepared the styrene-TEMPO adduct shown in reaction 4.AA, plus a dihydoxy functionalized variant:



A 1:1 mixture of the two initiators was added to styrene monomer and heated to the polymerization temperature. At various times the reaction mixture could be cooled, and analyzed. If the exchange of TEMPO groups was rapid, then one would expect four distinct chain populations, with roughly equal proportions: one with no hydroxyls, one with a hydroxyl at each end, one with a hydroxyl at the terminus, and one with a hydroxyl at the initial monomer. On the other hand, if there was little exchange, there should be just two populations: one with no hydroxyls, and one with two. Liquid chromatographic analysis gave results fully consistent with the former scenario.

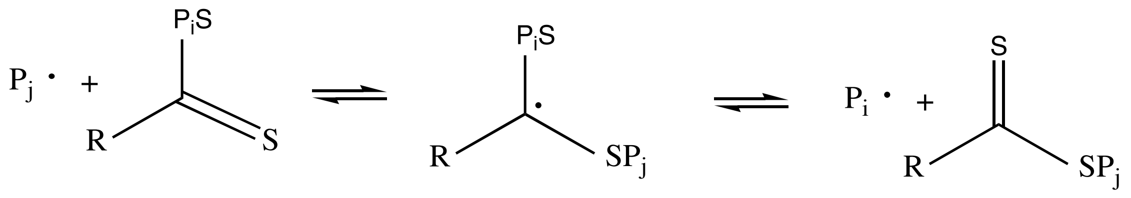
Reversible addition fragmentation polymerization (RAFT)

The principal distinction between RAFT on the one hand and ATRP or SFRP on the other is that RAFT involves a reversible chain transfer, whereas the other two involve reversible chain termination. The key player in the RAFT process is the chain transfer agent itself; the radicals are generally provided by conventional free radical initiators such as AIBN. Dithioesters (RCSSR') such as cumyl dithiobenzoate are often used; in this instance R is a phenyl ring and R' is a cumyl group. The growing radical chain P_i• reacts with the transfer agent, and the cumyl group departs with the radical:



(4.BB)

A different growing radical P_j• can also react in the analogous manner:



(4.CC)

In this way the dithioester end-group is transferred from chain to chain. An important feature of this reaction scheme which is important for achieving narrow molecular weight distributions is that the ease of transfer of the dithioester is essentially independent of the length of the associated chain, or between chains and the R' group.

There is an important feature of this scheme, that is different from the other two living radical approaches. Namely, the number of chains is not determined by the number of initiators, but by the combination of conventional initiators (e.g., AIBN) and those from the RAFT agent, e.g., cumyl radicals (R'• in reaction 4.BB). In fact, given that the decomposition of AIBN cannot be controlled, it is advantageous to use an excess of the RAFT agent, thereby dictating the number of chains via R'• which in turn is proportional to the concentration of RCSSR'. This process is facilitated by the fact that such dithioesters have very large chain transfer constants (recall Chapter 3.8), and thus a chain initiated by AIBN or by R'• is rapidly transformed into a dormant form, before achieving a significant degree of polymerization. The RAFT approach has been successful with a very wide variety of different monomers, wider even that ATRP.

4.7 Polymerization equilibrium

Up to this point we have tended to write chain-growth propagation steps as one-way reactions, with a single arrow pointing to the product:

$$P_i^* + M \xrightarrow{k_p} P_{i+1}^* \tag{4.DD}$$

In fact, as a chemical reaction, there must be a reverse "depropagation" or depolymerization step, and the possibility of chemical equilibrium:

$$P_i^* + M \xleftrightarrow{K_{poly}} P_{i+1}^* \tag{4.EE}$$

This equilibrium constant for polymerization K_{poly} can be written as the ratio of the forward and reverse rate constants, and as the appropriate ratio of species concentrations *at equilibrium*:

$$K_{poly} = \frac{k_p}{k_{dep}} = \frac{[P_{i+1}^*]}{[P_i^*][M]} \approx \frac{1}{[M]_{eq}} \tag{4.7.1}$$

The last term indicates that the equilibrium constant is the inverse of the equilibrium monomer concentration, because the concentrations of i-mer and (i+1)-mer must be nearly equal (recall eq 3.7.3). The reason we have not emphasized the possibility of equilibrium so far is that almost all polymerization reactions are run under conditions where the equilibrium lies far to the right, in favor of products; the residual monomer concentration is very small. This is not always the case, however, as we shall now discuss.

The state of equilibrium is directly related to the Gibbs free energy of polymerization:

$$\Delta G_{poly} = \Delta G^{o}_{poly} + RT \ln Q \tag{4.7.2}$$

where the *reaction quotient*, Q, is the same ratio of product and reactant concentrations as K, but not necessarily at equilibrium. The free energy of polymerization is the difference between the free energies of the products and the reactants, in kJ/mol, where for polymeric species we consider moles of repeat units. The superscript o indicates the standard quantity, where all species are at some specified standard state (e.g, pure monomer and repeat unit, or perhaps at 1 M concentration in solution). For the polymerization reaction to proceed spontaneously, $\Delta G_{\text{poly}} < 0$. When the reaction is allowed to come to equilibrium, Q = K, and $\Delta G_{\text{poly}} = 0$. Thus we have the well-known relation

$$\Delta G^{o}_{\text{poly}} = -RT \ln K \qquad (4.7.3)$$

The free energy change per repeat unit upon polymerization may be further resolved into enthalpic (H) and entropic (S) contributions

$$\Delta G^{o}_{\text{poly}} = \Delta H^{o}_{\text{poly}} - T\,\Delta S^{o}_{\text{poly}} \qquad (4.7.4)$$

From eq 4.7.3 we can see that the statement that K is large, favoring products, is equivalent to saying that $\Delta G^{o}_{\text{poly}}$ is large and negative. From eq 4.7.4 we can see that facile polymerization requires that either ΔH_{poly} is large and negative, i.e. the reaction is exothermic, or that ΔS_{poly} is large and positive. In fact, ΔS_{poly} is usually negative; the monomers lose a lot of translational entropy when bonded together in a polymer. However, ΔH_{poly} is exothermic, because the extra energy of a carbon-carbon double bond relative to a single bond is released. In fact, we could have anticipated this conclusion from the outset: polymers would not be made inexpensively in large quantities if we had to put in energy for each propagation step.

Table 4.4 provides examples of the enthalpy and entropy of polymerization for a few common vinyl monomers. In all cases both the enthalpy and the entropy changes are negative, as expected; furthermore, ΔG_{poly} is negative at room temperature (300 K). Starting with ethylene as the reference, the relative enthalpies of polymerization can be understood in terms of two general effects. The first is the possibility of resonance stabilization of the double bond in the monomer, that is lost upon polymerization. This results in lower exothermicity for butadiene, isoprene, styrene, and α-methylstyrene, for example. The second is steric hindrance in the resulting polymer. For example, di-substituted carbons in the polymer can lead to significant interactions between substituents on every other carbon, that therefore destabilize the polymer, as in the case of isobutylene, α-methyl styrene, and methyl methacrylate. Tetrafluoroethylene, with its unusually large exothermicity, is included in this short table in part to remind us that there are examples where we simply do not have a simple explanation!

Monomer	**ΔH_{poly} kJ/mol**	**ΔS_{poly} J/K mol**	**ΔG_{poly} at 300 K**
ethylene	–93	–155	–47
propylene	–84	–116	–49
isobutylene	–48	–121	–12
1,-3 butadiene	–73	–89	–46
isoprene	–75	–101	–45
styrene	–73	–104	–42
α-methylstyrene	–35	–110	–2
tetrafluoroethylene	–163	–112	–130
vinyl acetate	–88	–110	–55
methyl methacrylate	–56	–117	–21

Table 4.4.

Values of the enthalpy and entropy of polymerization, as reported in Odian [10]. The enthalpy corresponds to the conversion of liquid monomer (gas in the case of ethylene) to polymer, and is not sensitive to concentration. The entropy corresponds to conversion of a 1 M solution of monomer to polymer.

Equation 4.7.4 indicates that as the polymerization temperature increases, the relative importance of entropy increases as well. As ΔS favors depolymerization, it is possible to reach a temperature above which polymerization will not be spontaneous under standard conditions. This special temperature is referred to as the *ceiling temperature*, T_c. From eq 4.7.4 we have

$$\Delta G^o_{poly} = 0 = \Delta H^o_{poly} - T_c \, \Delta S^o_{poly} \tag{4.7.5}$$

and combining this relation with eqs 4.7.1, 4.7.2, and 4.7.3 we find

$$T_c = \frac{\Delta H^o_{poly}}{\Delta S^o_{poly} + R \ln[M]_{eq}} \tag{4.7.6}$$

Using this relation, the data in Table 4.3, and assuming [M] =1 $\underline{M}$, the ceiling temperature is 45 ^oC for poly(α-methyl styrene) and 206 ^oC for poly(methyl methacrylate). Note the important fact that according to eq 4.7.6, T_c will depend on the monomer concentration, and will therefore be different for a polymerization in dilute solution compared to one in bulk monomer.

Interestingly, there are a few instances in which polymerization is driven by an *increase* in entropy, and where the enthalpy gain is almost negligible. Examples include the polymerization of cyclic oligomers of dimethylsiloxane, such as the cyclic trimer and tetramer, which we will discuss in the next section. In this case the bonds that are broken and reformed are essentially the same, hence $\Delta H_{poly} \approx 0$. On the other hand, possibly because of the greater conformational freedom in the linear polymer versus the small cycles, ΔS_{poly} is positive. In such a case when ΔH_{poly} is slightly positive, it is possible in principle to have a *floor temperature*, below which polymerization cannot occur at equilibrium. Furthermore, for the living polymerization of poly(dimethyl siloxane), for example using an anionic initiator and the cyclic trimer, the ΔG_{poly} is never particularly favorable, compared to the typical vinyl monomer case. Consequently one has to be aware of the law of mass action, just as in a polycondensation. In other words the reaction cannot be allowed to go to completion, because rather than achieve essentially 100% conversion to polymer, the reaction mixture stabilizes at the equilibrium monomer concentration. Then, random propagation and depropagation steps will degrade the narrow molecular weight distribution that was initially sought. This problem can be circumvented by adding more monomer than is necessary to achieve the target molecular weight, and using trial and error to determine the time (and fractional conversion) at which the desired average molecular weight has been achieved.

4.8 Ring-opening polymerization (ROP)

4.8A General aspects

Cyclic molecules in which the ring contains a modest number of atoms, say 3–8, can often be polymerized by a *ring-opening reaction*, in which a particular bond in the cycle is ruptured, and then reformed between two different monomers in a linear sequence. This process is illustrated in the following schematic reaction:

(4.DD)

In this instance the ring contains four atoms, and the A-B bond is the one that is preferentially cleaved. The propagating chain is shown with B containing the active center; it is often the case that ROP proceeds by an ionic mechanism. Comparison of monomer and repeat unit structures in reaction 4.DD reveals that the bonding sequence is the same in both cases, in marked contrast to either a chain-growth polymerization through, e.g., a carbon-carbon double bond, or a step-growth polymerization through, e.g., condensation of acid and alcohol groups. In light of the previous section, where we considered the thermodynamics of polymerization, a basic question immediately arises: if the bonding is the same in monomer and polymer, what is the primary driving force for polymerization? The answer is *ring strain.* The linkage of the atoms into a ring generally enforces distortion of the preferred bond angles and even bond lengths, effects that are grouped together under the title ring strain. The amount of ring strain is a strong function of the number of atoms in the ring, r. For example, ethylene oxide, with $r = 3$, is a quite explosive gas at room temperature. On the other hand, cyclohexane, with $r = 6$, is almost inert. In fact, $r = 6$ represents a special case, at least for all carbon rings, as the “natural” sp^3 bond angles and lengths can be almost perfectly matched. The following example illustrates the effect of r on the thermodynamics of polymerization, for cyclic alkanes.

Example 4.5

The following values of ΔH^o_{lc} and ΔS^o_{lc} per methylene unit have been estimated at room temperature (as reported in [10]), for the process

$$-(CH_2)_r- \text{ (liquid ring) } \Leftrightarrow -(CH_2)_N- \text{ (crystalline linear polymer)}$$

The subscript lc denotes the liquid-to-crystal aspect of the process; as we will see in Chapter 13, high molecular weight linear polyethylene, the product of the hypothetical polymerization reaction, is crystalline at equilibrium at room temperature. Evaluate ΔG^o_{lc} and K for this process, and interpret the results.

r	ΔH^o_{lc} (kJ mol^{-1})	ΔS^o_{lc} (J mol^{-1} K^{-1})
3	–113	–69.1
4	–105	–55.3
5	–21.2	–42.7
6	+2.9	–10.5
7	–21.8	–15.9
8	–34.8	–3.3

Solution

We use the relationships $\Delta G^o = \Delta H^o - T\,\Delta S^o$ (eq 4.7.4) and $\Delta G^o = -RT \ln K$ (eq 4.7.3), with T = 298 K and R = 8.314 J mol^{-1} K^{-1}, to obtain the following table:

r	ΔG^o_{lc} (kJ mol^{-1})	K
3	–92	2×10^{16}
4	–89	3×10^{15}
5	–8.5	30
6	+6.0	0.09
7	–17	10^3
8	–34	8×10^5

The results indicate that for all but r = 6, polymerization is favored, consistent with the known stability of six-membered carbon rings. From the point of view of polymerization, the driving force should be ranked according to r = 3, 4 > r = 8 > r = 5,7. These are general trends, and different substituents or heteroatoms within the ring can change the numerical values significantly. Finally, while ΔH^o shows a distinct maximum at r = 6, ΔS^o decreases monotonically with r, while remaining consistently negative. However, we need to recognize that these values incorporate the relief of the ring strain, the incorporation of monomer into polymer, and the changes associated with crystallization of the liquid polymer. The opening of the ring affords more degrees of freedom to the molecule, increasing the entropy, but both subsequent polymerization and crystallization reduce it. Consequently, it is dangerous to read too much into particular values of ΔS

The preceding example nicely illustrates the importance of ring strain, but the fact is the primary utility of ROP is not to produce polyethylene from cyclic alkanes. Rather, it is to produce interesting polymer structures from readily accessible cyclic monomers, structures that cannot be prepared more conveniently by "classical" step-growth or chain–growth polymerization. Examples of seven different classes of cyclic monomers, and the resulting polymer structures, are given in Table 4.5. In all cases the ring contains one or more heteroatoms, such as O, N, and Si. These participate in the bond-breaking process that is essential to ROP; in contrast, it is actually rather difficult in practice to polymerize cyclic alkanes, even when free energy considerations favor it. In Chapter 1 we suggested that the presence of a heteroatom in the backbone was often characteristic of a step-growth polymerization. One of the beauties of ROP is that it is a chain-growth mechanism, enabling the ready preparation of high molecular weight materials. For example, entry 5 (a polyamide, poly(ε-caprolactam)) and entry 6 (a polyester, polylactide) are polymers that could be prepared by condensation of the appropriate AB monomer. However, by using the cyclic monomer, the condensation step has already taken place, and the small molecule byproduct removed. Thus the law of mass action that typically limits the molecular weight of a step-growth polymerization is overcome. (This is not to say that polymerization equilibrium won't be an issue. In fact, entries 6 and 7 both indicate 6-membered rings, and the correspondingly lower ring strain does bring equilibration into play).

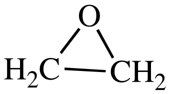
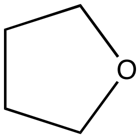
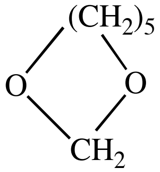
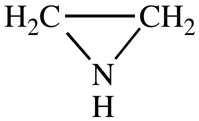
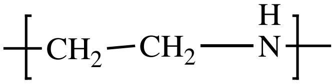
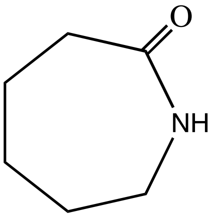
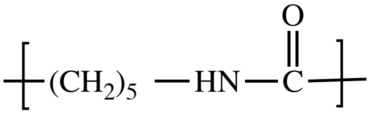
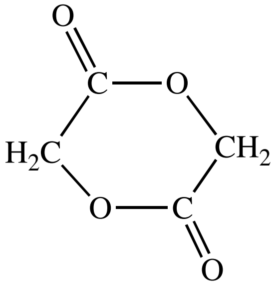
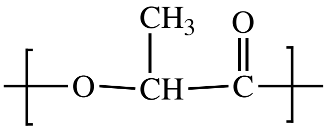
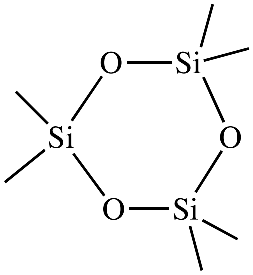
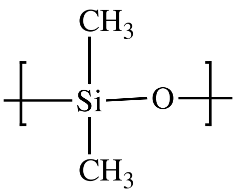
Monomer class	**Example**	**Repeat unit**
1. Epoxides		$\left[-CH_2-CH_2-O-\right]$
2. Cyclic ethers		$\left[-(CH_2)_4-O-\right]$
3. Cyclic acetals		$\left[-O-CH_2-O-(CH_2)_5-\right]$
4. Imines (cyclic amines)		 $\left[-CH_2-CH_2-\overset{H}{N}-\right]$
5. Lactams (cyclic amides)		 $\left[-(CH_2)_5-HN-\overset{O}{\overset{\|}{C}}-\right]$
6. Lactones (cyclic esters)		 $\left[-O-\overset{CH_3}{\overset{\vert}{CH}}-\overset{O}{\overset{\|}{C}}-\right]$
7. Siloxanes		 $\left[-\underset{CH_3}{\underset{\vert}{\overset{CH_3}{\overset{\vert}{Si}}}}-O-\right]$

Table 4.5

Examples of monomers amenable to ring-opening polymerization.

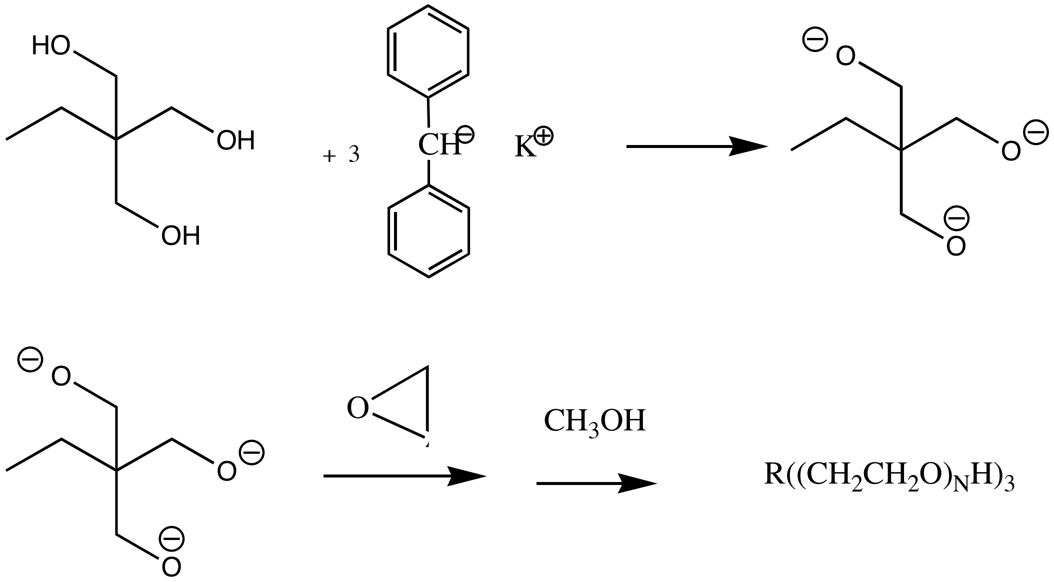
From the perspective of this chapter the main point of ROP is not just the chain-growth character, but the fact that in many cases living polymerization systems have been designed. As indicated above, most ROPs proceed via an ionic mechanism, which certainly invites attempts to achieve a living polymerization. We will briefly present three specific examples of such systems, for three disparate but rather interesting and important polymers in Table 4.4: polyethylene oxide (entry 1), polylactide (entry 6) and polydimethylsiloxane (entry 7). We will also consider a class of ROP that can produce all carbon backbones, via olefin metathesis.

4.8B Specific examples of living ring-opening polymerizations

Poly(ethylene oxide)

Poly(ethylene oxide) represents one of the most versatile polymer structures for both fundamental studies and in commercial applications. It is readily prepared by living anionic polymerization, with molecular weights ranging all the way up to several millions. It is water soluble, a highly desirable yet relatively unusual characteristic of non-ionic, controlled molecular weight polymers. Furthermore, it appears to be more or less benign in humans, thereby allowing its use in many consumer products, biomedical formulations, etc. In fact, a grafted layer of short chain poly(ethylene oxide)s (see Section 4.4) can confer long-term stability against protein adsorption or deposition of other biomacromolecules. In the biochemical arena short chain poly(ethylene oxide)s (with hydroxyl groups at both ends) are more commonly referred to as poly(ethylene glycol)s or PEGs. The grafting of PEG molecules onto a biomacromolecule or other substrate has become such a useful procedure that it has earned a special name: *PEGylation*. Poly(ethylene oxide) crystallizes rather readily, with a typical melting temperature near 65 ^{o}C, which has led to its use in many fundamental studies of polymer crystallization (see Chapter 13). The first block copolymers to become commercially available were the so-called *polyoxamers*, diblocks and triblocks of poly(ethylene oxide) and poly(propylene oxide). Historically, it was the polymerization of ethylene oxide that Flory used as an example in proposing the Poisson distribution for chain-growth polymers prepared from a fixed number of initiators with rapid propagation.[11]

In practice, the living anionic polymerization of ethylene oxide has been achieved by a variety of initiator systems, following the general principles laid out in Section 4.3. Examples include metal hydroxides, alkoxides, alkyls, and aryls. In contrast to styrenes and dienes, however, lithium is not an effective counter ion in this case. (As noted in the context of reaction (4.H), this feature is actually convenient when it is desired to use ethylene oxide to end-functionalize such polymers). The following scheme represents a an example of a three-arm star prepared by grafting from; the initiator is trimethylol propane, which has three equivalent primary alcohols that can be activated by diphenylmethyl potassium. The addition of ethylene oxide monomer is straightforward, and the resulting polymer is terminated with acidic methanol to yield a terminal hydroxyl functionality on each arm.



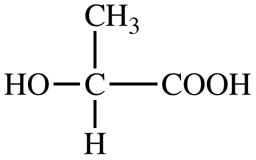
(4.EE)

An interesting feature of this reaction is that it can be carried out in THF, which like ethylene oxide is a cyclic ether. This illustrates again the importance of ring strain in facilitating, or, in this case suppressing, polymerization. In fact cyclic ethers including THF are usually polymerized only by a cationic ring-opening mechanism; the high ring strain of ethylene oxide makes it the exception to this rule.

Polylactide

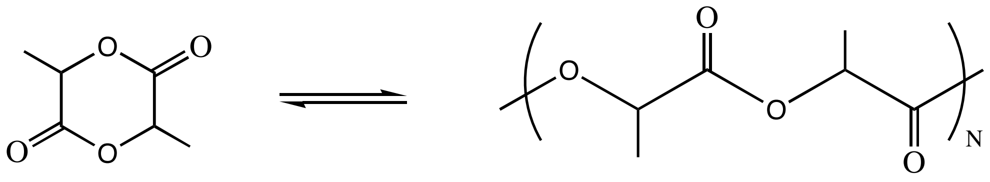
Polylactide is biodegradable, and preparable from biorenewable feedstocks such as corn husks. The former feature enables a longstanding application as resorbable sutures; after a period of days to weeks, the suture degrades and is metabolized by the body. The latter property underscores recent interest in the large scale commercial production of polylactide for a wide variety of thermoplastic applications.

The structure of lactic acid is:



$$\mathrm{HO{-}\overset{\displaystyle CH_3}{\underset{\displaystyle H}{C}}{-}COOH}$$

Clearly, as it contains both a hydroxyl and a carboxylic acid, it could be polymerized directly to the corresponding polyester via condensation. However, if the starting material is lactide, the cyclic dimer of the corresponding ester, then ROP produces the same polymer structure but by a chain growth process:



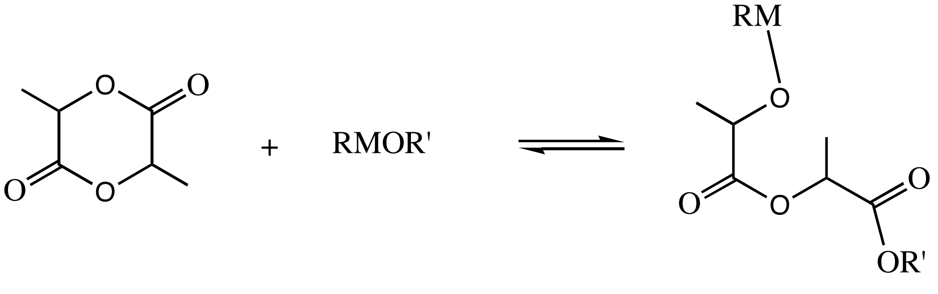
(4.FF)

Note that the central carbon in lactic acid is chiral, and that therefore the corresponding two carbons in both lactide and the polylactide repeat unit are stereocenters. Consequently there are three possibilities for the lactide monomer, according to the configuration of these carbons: D,D;

L,L; and D,L. Polymerization of either of the first two leads to the corresponding stereochemically pure PDLA and PLLA, which are crystallizable; the meso dyad leads to an atactic polymer. In this case, therefore, the responsibility of producing a particular tacticity is transferred from the catalyst (see Chapter 5) to the purification of the starting material. Of course, the catalyst has to guide the polymerization in such a way that the stereochemistry is not scrambled or *epimerized*.

From the point of view of designing a living polymerization of polylactide, there are two general issues to confront. First, as polylactide is a polyester, it is susceptible to transesterification reactions. This constraint favors lower reaction temperatures, conditions that are neither too basic nor acidic, and acts against the normal desire to make the catalyst more "active". Ironically, the advantageous degradability of polylactide through the hydrolysis of the ester linkage is thus a disadvantage from the point of view of molecular weight control. The second problem is equilibration. Recall from Example 4.5 that for cyclic alkanes, the 6-membered ring has no ring strain to speak of, and is therefore not polymerizable. Although lactide is a 6-membered ring, it does possess sufficient ring strain, but not a lot. Consequently, narrow molecular weight distributions are usually obtained only before the reaction has been allowed to approach completion.

A typical catalyst is based on a metal alkoxide, such as RMOR', where R and R' are small alkyl groups. The initiation step can be written



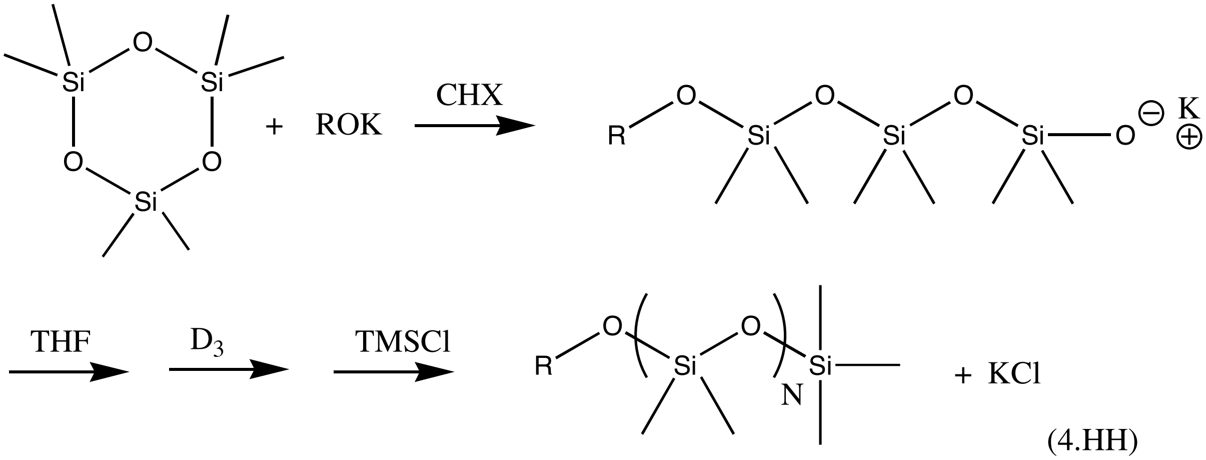
(4.GG)

where the lactide ring is cleaved at the bond between the oxygen and the carbonyl carbon. The subsequent propagation steps involve the same bond cleavage, with addition of the new monomer into the oxygen-metal bond at the growing chain end. In fact, this kind of polymerization has been classified as “anionic coordination”, in distinction to anionic polymerization, as the crucial step is coordination of the metal with the carbonyl oxygen, followed by insertion of the alkoxide into the polarized C–O bond. The most commonly employed catalyst for polylactide is tin ethylhexanoate, but more success in terms of achieving living conditions has been realized with aluminum alkoxides. Interestingly, these aluminum species have a tendency to aggregate in solution, with the result that the reaction kinetics can become rather complicated; different aggregation states can exhibit very different propagation rates. This situation is somewhat analogous to the aggregation of carbanions in anionic polymerization in non-polar solvents discussed in Section 4.3.

Poly(dimethyl siloxane)

Poly(dimethyl siloxane) has one of the lowest glass transition temperatures (T_g, see Chapter 12) of all common polymers. This is due in part to the great flexibility of the backbone structure (see Chapter 6), which reflects the longer Si–O bond compared to the C-C bond, the larger bond angle, and the absence of substituents on every other backbone atom. It is also chemically quite robust. It is used in any number of lubrication and adhesive applications (“silicones”), as well as a variety of rubber materials. Living anionic polymerization of the cyclic trimer hexamethylcyclotrisiloxane, D_3, has been achieved by a number of routes. Given that this monomer is a 6-membered ring, we can anticipate that the polymerization is not strongly favored by thermodynamics. Consequently, narrow molecular weight distributions are achieved by terminating the reaction well before consumption of all the monomer.

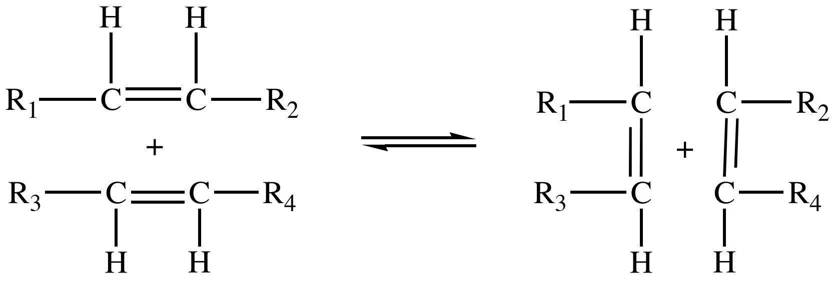
An example of a successful protocol is the following. A modest amount of cyclic trimer is initiated with potassium alkoxide, in cyclohexane solution. Under these conditions initiation is rather slow, but propagation is almost nonexistent, thereby allowing for complete initiation. Presumably the lack of propagation is due to ion clustering as discussed in Section 4.3. The addition of THF, as a polar modifier, plus more monomer allows propagation to proceed for an empirically determined time interval. Termination is achieved with trimethylchlorosilane (TMSCl).



(4.HH)

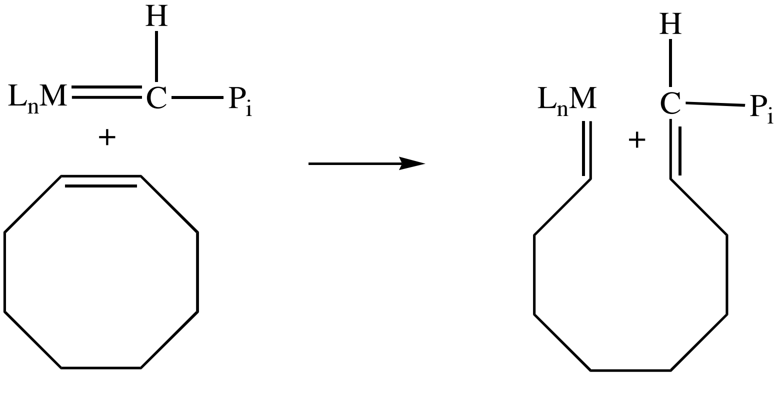
Ring-opening metathesis polymerization (ROMP)

Reactions in this class of ROP are distinct from those previously considered, both in the fact that the mechanism does not involve ionic intermediates, and in the creation of all carbon backbones (albeit ones that contain double bonds). An *olefin metathesis* reaction is one in which two carbon-carbon double bonds are removed, and two new ones are created. Generically this can be represented by the following scheme, whereby $R_1HC{=}CHR_2$ reacts with $R_3HC{=}CHR_4$ to produce, for example, $R_1HC{=}CHR_3$ and $R_2HC{=}CHR_4$.



(4.II)

Although reaction 4.II illustrates the net outcome, it says nothing about the mechanism. Metathesis reactions are catalyzed by transition metal centers, with the associated ligand package providing tunability of reaction characteristics such as rate, selectivity, and stereochemistry of addition. In the case of ROMP, the metal forms a double bond with a carbon at one end of the chain; thus in reaction 4.II the R_1CH group would be replaced by the metal and its ligands (ML_n). For a propagation step, R_2 would denote a previously polymerized chain, P_i. In the monomer to be inserted into the chain, between the metal and the end of the previously chain, R_3 and R_4 are replaced by the ring. Thus the ring plays two key roles: the ring-strain provides the driving force for polymerization, and the ring structure provides the permanent connectivity between the two carbon atoms whose double bond is broken. The ROMP analog to reaction 4.II can thus be described schematically as

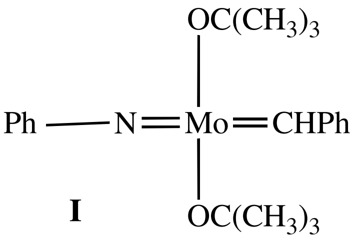


(4.JJ)

In this case the monomer is cyclooctene. After the monomer insertion or propagation step, an active metal carbene remains at the chain terminus, and one carbon-carbon double bond remains in the backbone for each repeat unit.

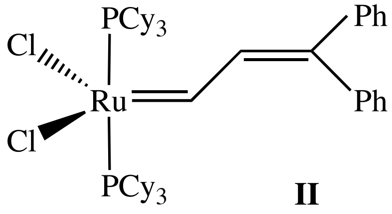
There is a large literature on metathesis catalysts and associated mechanisms, many of which incorporate multiple components beyond the active metal. However, for the purposes of controlled ROMP, there are currently two families of single species catalysts that are highly successful. One, based on tungsten or molybdenum, is known as a Schrock catalyst [I], and the other, based on ruthenium, is a Grubbs catalyst [II]. These investigators were co-recipients of the 2005 Nobel Prize in Chemistry (with Y. Chauvin) for their work on metathesis catalysts. The structures of representative examples are given below, where the symbols Ph and Cy denote phenyl and cyclohexyl rings, respectively:

:



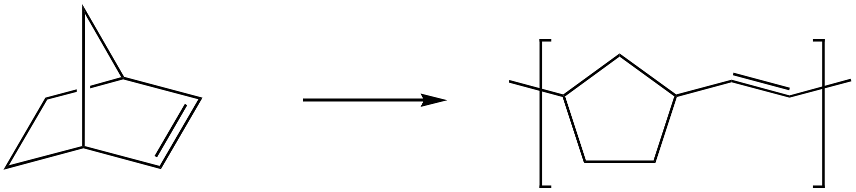
$$\mathrm{Ph{-}N{=}\overset{OC(CH_3)_3}{\underset{OC(CH_3)_3}{Mo}}{=}CHPh}$$

I



II

Note that the substituent on the metal carbene will become attached to the non-propagating terminus of the chain. Collectively, catalysts in these two families have proven capable of achieving controlled polymerization of a wide variety of cyclic olefins, including those containing functional groups. In particular, while the Schrock catalysts tends to be more active, the Grubbs catalysts are more tolerant of functional groups, oxygen, and protic solvents. Reaction conditions are often mild, i.e. near room temperature, and in some cases the polymerization can be conducted in water. Although polydispersities rarely approach those achievable by living anionic polymerization, overall control is nevertheless quite good, and many block copolymers have been prepared by ROMP. Some ROMP systems have even been commercialized, including the polymerization of norbornene:



(4.KK)

4.9 Dendrimers

Denrimers are an interesting, unique class of polymers with controlled structures. For example, they can have precisely defined molecular weights, even though the elementary addition steps are usually of the condensation variety. From an applications point of view it is the structure of the dendrimer, rather than its molecular weight *per se*, that is the source of its appeal. A cartoon example of a dendrimer was provided in Figure 1.2. The term itself comes from the Greek word *dendron*, or tree, and indeed a dendrimer is a highly branched polymer molecule. In particular, a dendrimer is usually an approximately spherical molecule with a radius of a few nanometers. Thus a dendrimer is both a covalently assembled molecule and also a well-defined nanoparticle. The outer surface of the dendrimer is covered with a high density of functional groups that govern the interactions between the dendrimer and its environment. These exterior groups have the advantages of being numerous, and readily accessible for chemical transformation. The interior of the dendrimer can incorporate a distinct kind of functionality, that can endow the molecule with desirable properties. For example, the dendrimer might incorporate a highly absorbing group, for "light harvesting", or a fluorophore, for efficient emission. Other possibilities include catalytic centers or electrochemically active groups. By being housed within the dendrimer, this functional unit can be protected from unwanted interactions with the environment. The functional unit may be covalently bound within the dendrimer, or it may simply be encapsulated. The possibility of controlling uptake and release of specific agents by the dendrimer core also makes them appealing as possible delivery vehicles for pharmaceuticals or other therapeutic agents. As nanoparticles, dendrimers share certain attributes with other objects of similar size, such as globular proteins, surfactant and block copolymer micelles, hyperbranched polymers, and colloidal nanoparticles. Although beyond the scope of this chapter, it is interesting to speculate on the possible advantages and disadvantages of these various structures (see Problem 4.16).

There are two distinct, primary synthetic routes to prepare a dendrimer, termed *divergent* and *convergent*. In a divergent approach, the dendrimer is built up by successive additions of monomers to a central, branched core unit, whereas in the convergent approach branched structures called *dendrons* are built up separately, and then ultimately linked together to form the dendrimer in a final step. The divergent approach was conceived first, and is the more easily visualized. The process is illustrated schematically in Figure 4.6. The core molecule in this case has three functional groups denoted by the open circles. These are reacted with three equivalents of another three-functional "monomer", but in this case two of the functional groups are protected (filled circles). After this reaction is complete, the growing molecule has six functional groups, that are then deprotected. At this stage the molecule is termed a *first generation* (G1) dendrimer. Another addition reaction is then performed, but now six equivalents of the protected monomer are required to complete the next generation. After deprotection the resulting G2 dendrimer has 12 functional groups. It is straightforward to see that the number of functional groups on the surface grows geometrically with the number of generations, g,

$$\text{Number of functional groups} = 3 \times 2^{g} \tag{4.9.1}$$

Thus a perfect G5, G6, and G7 dendrimer would have 96, 192, and 384 functional groups, respectively. Note that eq 4.9.1 would need to be modified in the case of, for example, a tetrafunctional core. We have introduced the term "perfect" here to emphasize that it is certainly possible for a dendrimer molecule to have defects, or missing functional groups, which will propagate through all subsequent generations. For the first few generations it is usually not too difficult to approach perfection, but for G5 and above the functional groups become rather congested, which makes complete addition of the next generation difficult. It also becomes harder to separate out defective structures. It is typically not practical to go beyond G8.

Further consideration of the divergent approach in Figure 4.6 reveals that, as polymerization reactions go, it is rather labor intensive. For example, the addition of each generation requires both an addition step and a deprotection step. The addition will typically be conducted in the presence of a substantial excess of protected monomer, to drive the completion of the new layer. The resulting products will need to be separated, in order to isolate the perfect dendrimer structure from all other reaction products and reagents. Similarly, the deprotection step needs to be driven to completion, and the pure product isolated. Thus in the end there are two reaction steps and two purification steps required for each generation. This requires a significant amount of time, and it is challenging to prepare commercial scale quantities of perfect, high generation products.

As a specific example of a divergent synthesis, we will consider the formation of the polyamidoamine (PAMAM) system. In this case there are two monomers to be added sequentially in each generation, rather than one addition and one deprotection step. The core molecule and one of the monomers is typically ethylene diamine, and the other monomer is methyl acrylate. The first step is addition of four methyl acrylate molecules to ethylene diamine in a solvent such as methanol. The Michael addition-type mechanism involves nucleophilic attack of the electron pair on the nitrogen to the double bond of the acrylate, which is activated by the electron withdrawing character of the ester group:

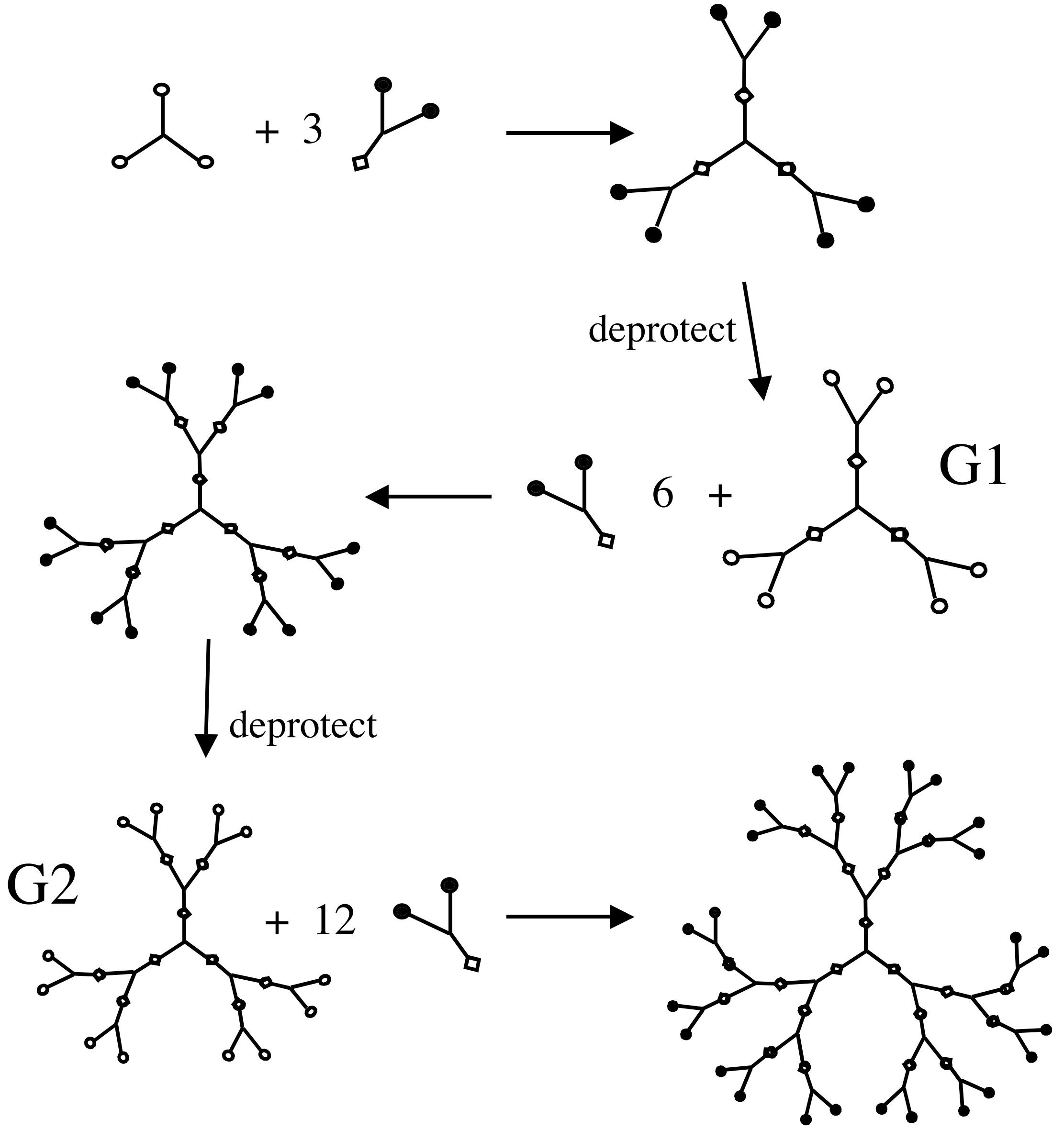
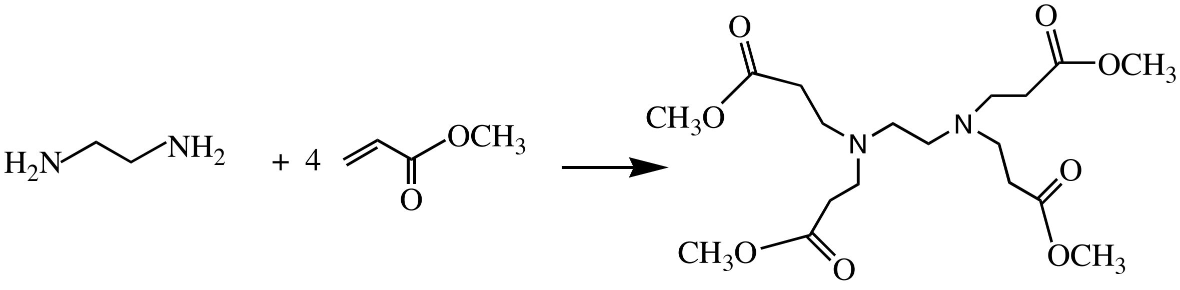


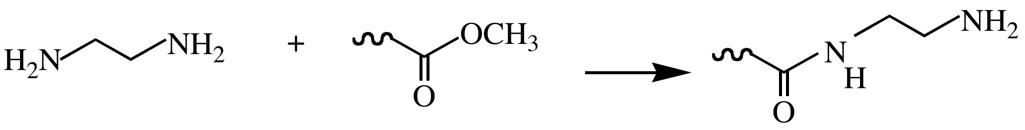
Figure 4.6.

Schematic illustration of the divergent synthesis of a third generation dendrimer from a trifunctional core. The open circles denote reactive groups, and the filled circles protected groups.



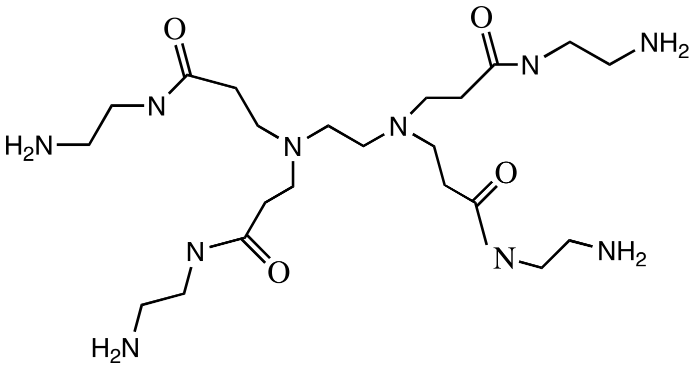
(4.LL)

The next second step involves amidation of each ester group by nucleophilic attack of the nitrogen on the electropositive carbonyl carbon, with release of methanol:



(4.MM)

The structure of the resulting G1 PAMAM dendrimer is therefore the following:



An alternative general strategy for preparing dendrimers and dendritic fragments, or "dendrons", is the so-called *convergent* approach. This is illustrated schematically in Figure 4.7. As the name implies, these molecules are made "from the outside in", that is, the eventual surface group, denoted x in Figure 4.7, is present in the initial reactants. The first reaction products a molecule with two surface groups and one protected reactive group. The second step, after deprotection, doubles the number of surface groups, and so on. At any stage, a suitable multifunctional core molecule can be used, to stitch the appropriate number of dendrons (usually 3 or 4) together. Each growing wedge-shaped dendron possesses only one reactive group, which presents a significant advantage in terms of purification. At each growth step, a dendron either reacts or it doesn't, but the product and reactant are significantly different in molecular weight. By contrast, in the divergent approach, the surface of the dendrimer has many reactive groups, and it may not be easy to separate a G3 dendrimer with 24 newly added monomers from one with only 23. Furthermore, because there are so many more reactive groups on the dendrimer than on the added monomers, the monomer must be present in huge molar excess to drive each reaction to completion. In the convergent approach shown, there are only twice as many dendrons as new coupling molecules at stoichiometric equivalence, so a large excess of dendrons is not necessary.

The initial demonstration of this approach was based on the following scheme. The building blocks were 3,5 dihydroxybenzyl alcohol and a benzylic bromide. The first reaction, conducted in acetone in the presence of potassium carbonate and a crown ether scavenger, coupled two of the bromides with one alcohol. The surviving benzylic alcohol was then transformed back to a bromide functionality with carbon tetrabromide in the presence of triphenyl phosphine. Introduction of more 3,5 dihydroxybenzyl alcohol began the formation of the next generation dendron, and the process continued.

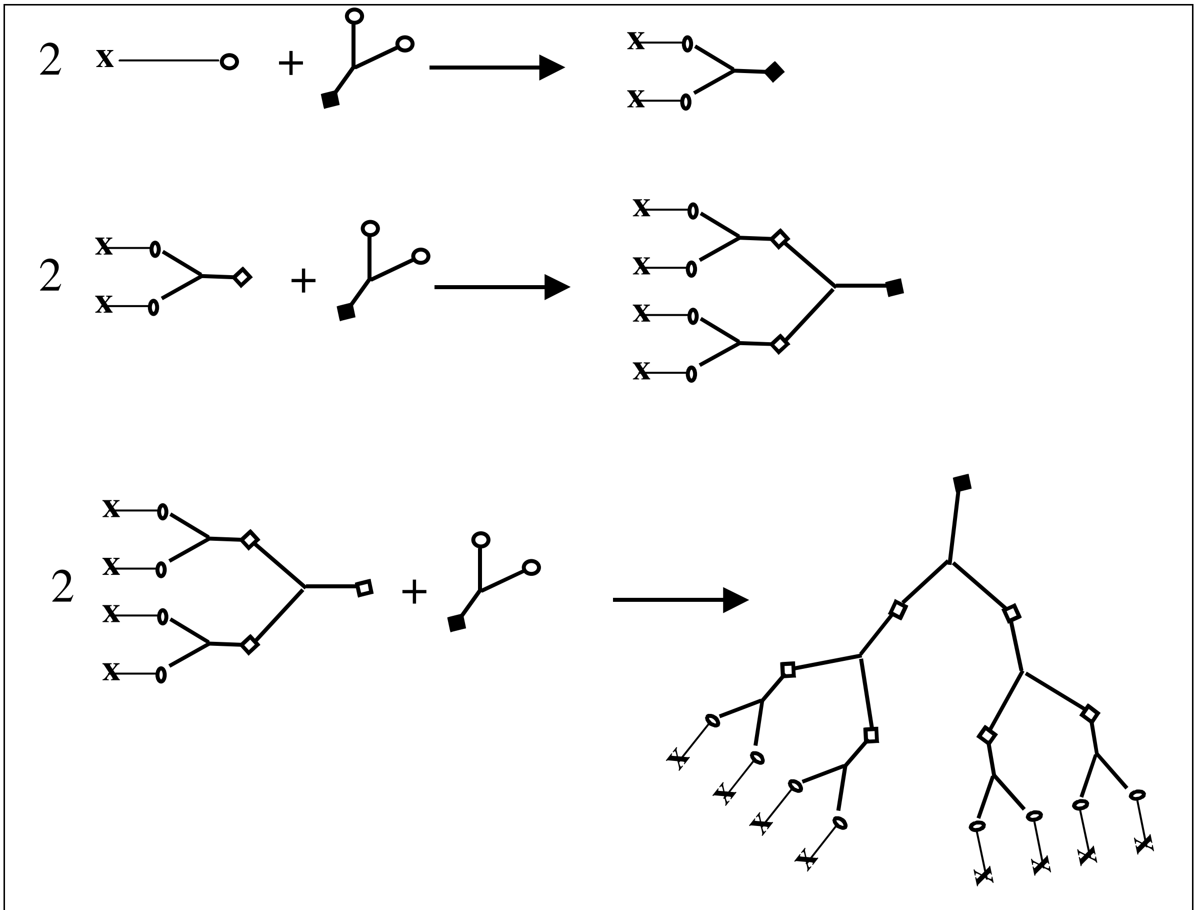
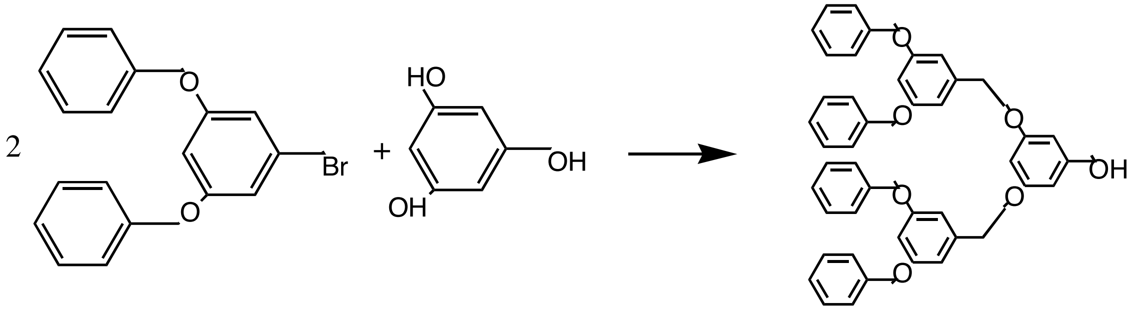


Figure 4.7
Illustration of the convergent approach to dendrimer synthesis. Each dendron is built up by successive 2:1 reactions, before the final coupling step.



(4.NN)

CHAPTER SUMMARY

In his chapter we have considered a wide variety of synthetic strategies to exert greater control over the products of a polymerization, compared to the standard step-growth and chain-growth approaches. Although access to much narrower molecular weight distributions has been the primary focus, production of block copolymers, end-functional polymers, and controlled branched architectures has also been explored. The central concept of the chapter is that of a *living polymerization*, defined as a chain growth process that proceeds in the absence of chain termination or chain transfer.

1. When a living polymerization is conducted such that the rate of initiation is effectively instantaneous compared to propagation, it is possible to approach a Poisson distribution of molecular weights, where the polydispersity is $1 + (1/N_n)$.
2. Anionic polymerization is the most established method for approaching the ideal living polymerization, and effective protocols for a variety of monomers have been established.
3. Cationic polymerization can also be living, although it is generally harder to do so than for the anionic case, in large part due to the prevalence of transfer reactions, including transfer to monomer.
4. Using the concept of a reversibly dormant or inactive species, free radical polymerizations have also been brought under much greater control. Three general flavors of controlled radical polymerization, known as ATRP, SFRP, and RAFT, are currently undergoing rapid development.
5. Living polymerization in general, and anionic polymerization in particular, can be used to produce block copolymers, end-functional polymers, and well-defined star and graft polymers, for a variety of possible uses.
6. Through basic thermodynamic considerations the concepts of equilibrium polymerization, ceiling temperature, and floor temperature have been explored.

7. The utility of ring-opening polymerizations has been established, where the thermodynamic driving force for chain growth relies on ring strain. Specific systems of nearly living ring-opening polymerizations have been introduced, including important metal-catalyzed routes such as ring-opening metathesis.
8. A particular class of highly branched, precisely controlled polymers called dendrimers can be prepared by either of two step-growth routes, referred to as convergent and divergent, respectively.

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Suggestions for further reading on various aspects of controlled polymerization:

H. L. Hsieh and R. P. Quirk, *Anionic Polymerization, Principles and Practical Applications*, Marcel Dekker, Inc., New York, NY (1996).

G. Odian, *Principles of Polymerization*, 4th Edition, Wiley-Interscience, Hoboken, NJ (2004).

Rempp and Merrill

Problems

1. The experimental data cited in Example 4.1 for the anionic polymerization of styrene do not really test the relationship between conversion, p and time; why not? What additional experimental information should have been obtained if that were the object?

2. Although the polydispersities described in Example 4.1 are very low, they consistently exceed the theoretical Poisson limit. List four assumptions that are necessary for the Poisson distribution to apply, and then identify which one is most likely not satisfied. Justify your answer, based on the data provided.

3. For the living anionic polymerization of styrene discussed in Example 4.1, the solvent used was cyclohexane, and the kinetics are known to be 0.5 order with respect to initiator. What is the predominant species in terms of ion pairing, and what is the approximate dissociation constant for this cluster if k_p is actually 1000 mol L^{-1} s^{-1}?

4. One often-cited criterion for judging whether a polymerization is living is that M_n should increase linearly with conversion. Why is this not, in fact, a robust criterion?

5. A living polymerization of 2-vinyl pyridine was conducted using benzyl picolyl magnesium as the initiator (A. Soum and M. Fontanille, in *Anionic Polymerization*, J. E. McGrath, Ed., ACS Symposium Series, Vol 166, 1981). Values of M_n were determined for polymers prepared with different initiator concentrations and different initial concentrations of monomer, as shown below. Calculate the expected M_n assuming complete conversion and 100% initiator efficiency; how well do the theoretical and experimental values agree?

[I] (mmol L^{-1})	$[M]_o$ (mmol L^{-1})	M_n (kg mol^{-1})
0.48	82	20
0.37	85	25
0.17	71	46
0.48	71	17
0.58	73	14
0.15	150	115

6. The following table shows values of ΔH^o at 298 K for the gas phase reactions $X(g) + H^+(g) \rightarrow HX^+(g)$, where X is an olefin. (P. H. Plesch, Ed., *Cationic Polymerization*, Macmillan, New York, 1963). Use these data to comment quantitatively on each of the following points.

(a) The cation is stabilized by electron-supplying alkyl substituents.

(b) The carbonium ion rearrangement of *n*-propyl ions to *i*-propyl ions is energetically favored.

(c) With the supplementary information that ΔH_f^o of 1-butene and cis-2-butene are + 1.6 and –5.8 kJ mol^{-1}, respectively, evaluate the ΔH for the rearrangement n-butyl to sec-butyl ions, and compare with the corresponding isomerization for the propyl cation.

(d) Of the monomers shown, only isobutene undergoes cationic polymerization to any significant extent. Criticize or defend the following proposition: the above data explain this fact by showing that this is the only monomer listed which combines a sufficiently negative ΔH for protonation, with the freedom from interfering isomerization reactions.

X	**HX^+**	**ΔH^o at 298 K (kJ mol^{-1})**
$CH_2{=}CH_2$	$CH_3\,CH_2^+$	–640
$CH_3CH{=}CH_2$	$CH_3\,CH_2\,CH_2^+$	–690
$CH_3CH{=}CH_2$	$CH_3\,C^+H\,CH_3$	–757
$CH_3\,CH_2CH{=}CH_2$	$CH_3\,CH_2\,CH_2\,CH_2^+$	–682
$CH_3CH{=}CHCH_3$	$CH_3\,CH_2\,C^+H\,CH_3$	–782
$(CH_3)_2C{=}CH_2$	$(CH_3)_2\,CH\,CH_2^+$	–695

7. In the study discussed in Example 4.3, a solution ATRP of styrene gave an apparent propagation rate constant of 3.9 x 10^{-5} s^{-1}. Given that the initial monomer concentration was 4.3 M, and that the initial concentrations of initiator and CuBr were 0.045 M, estimate the equilibrium constant K for activation of the chain end radical.

8. For the solution polymerization of L-lactide with [M] = 1 M, Duda and Penczek determined $\Delta H^o = -22.9$ kJ mol^{-1} and $\Delta S^o = -41.1$ J mol^{-1} K^{-1} (*Macromolecules* 23, 1636 1990)). What is the associated ceiling temperature for an equilibrium monomer concentration of 1 M? Does the value you obtain suggest that equilibration is an issue in controlled polymerization of polylactide? Compare these thermodynamic quantities with those for the cyclic alkanes in Table 4.4; how do you account for the differences between the 6-membered alkane and lactide?

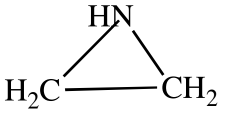
9, For the polymerization system in Problem 4.8, calculate the equilibrium monomer concentration that would actually be obtained, and the conversion to polymer, at 80 °C and 120 °C.

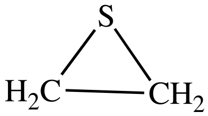
10. *TBD One about kinetic control of PDMS*

11. Given that ring-opening polymerization is often conducted under conditions in which reverse reactions are possible, do we need to worry about cyclization of the entire growing polymer? Why or why not?

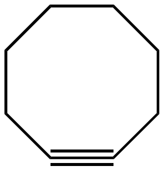
12. Suggest a scheme to test the hypothesis that in lactide polymerization it is the acyl carbon-oxygen bond that is cleaved, rather than the alkyl carbon-oxygen bond.

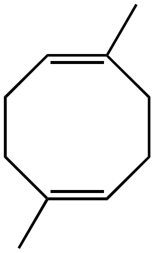
13. Both ethyleneimine and ethylene sulfide are amenable to ROP. The former proceeds in the presence of acid, whereas the latter can follow either anionic or cationic routes. Propose structures for the three propagating chain ends, and the resulting polymers.

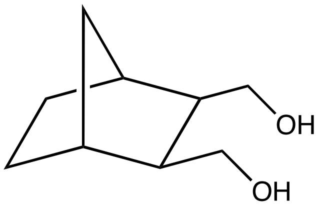




14. Draw repeat unit structures for polymers made by ROMP of the following three monomers:

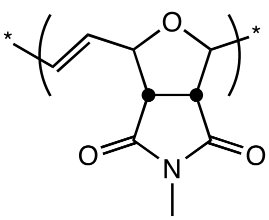






15. Suggest monomer structures that will lead to the following repeat unit structures following ROMP:

$*\!\left(\mathrm{CH{=}CH}\right)\!*$ $*\!-\!\left(\mathrm{CH{=}CHCH_2CH_2CH_2}\right)\!-$



16. Compare and contrast dendrimers with block copolymer micelles, globular proteins, inorganic nanoparticles in terms of attributes and likely utility in the following applications: (i) drug delivery; (ii) homogenous catalysis; (iii) solubilization.

17. In an ideal living polymerization, how should M_n and M_w/M_n vary with conversion of monomer to polymer? How should M_n of the formed polymer vary with time? Compare these to a radical polymerization with termination by disproportionation, and no transfer.

18. The following criteria have all been suggested and/or utilized as diagnostics for whether a polymerization is living or not. For each one, explain why it might be useful, and then decide whether or not it is a robust criterion, i.e., can you think of a situation in which the criterion is satisfied but the polymerization is not living? (See also Problem 4.4).
    (a) Polymerization proceeds until all monomer is consumed. Polymerization continues if more monomer is then added.
    (b) The number of polymer molecules is constant, and independent of conversion.
    (c) Narrow molecular weight distributions are produced.
    (d) The concentration of monomer decreases to zero, exponentially with time.