The synthesis of macromolecules composed of more than one monomeric repeating unit has been explored as a means of controlling the properties of the resulting material. In this respect, it is useful to distinguish several ways in which different monomeric units might be incorporated in a polymeric molecule. The following examples refer to a two component system, in which one monomer is designated A and the other B.

- **Statistical Copolymers:** Also called random copolymers. Here the monomeric units are distributed randomly, and sometimes unevenly, in the polymer chain: \( \sim \text{ABBBAAAABBBABABABA} \sim \).

- **Alternating Copolymers:** Here the monomeric units are distributed in a regular alternating fashion, with nearly equimolar amounts of each in the chain: \( \sim \text{ABABABABABABABAB} \sim \).

- **Block Copolymers:** Instead of a mixed distribution of monomeric units, a long sequence or block of one monomer is joined to a block of the second monomer: \( \sim \text{AAAAA-BBBBBBBBB} \sim \text{AAAAAAA-BBB} \sim \).

- **Graft Copolymers:** As the name suggests, side chains of a given monomer are attached to the main chain of the second monomer: \( \sim \text{AAAAAAA(BBBBBBB~)AAAAAAA(BBBB~)} \text{AAA} \sim \).

### Addition Copolymerization

Most direct copolymerizations of equimolar mixtures of different monomers give statistical copolymers, or if one monomer is much more reactive a nearly homopolymer of that monomer. The copolymerization of styrene with methyl methacrylate, for example, proceeds differently depending on the mechanism. Radical polymerization gives a statistical copolymer. However, the product of cationic polymerization is largely polystyrene, and anionic polymerization favors formation of poly(methyl methacrylate). In cases where the relative reactivities are different, the copolymer composition can sometimes be controlled by continuous introduction of a biased mixture of monomers into the reaction.

Formation of alternating copolymers is favored when the monomers have different polar substituents (e.g. one electron withdrawing and the other electron donating), and both have similar reactivities toward radicals. For example, styrene and acrylonitrile copolymerize in a largely alternating fashion.

#### Some Useful Copolymers

<table>
<thead>
<tr>
<th>Monomer A</th>
<th>Monomer B</th>
<th>Copolymer</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2\text{C}=\text{CHCl} )</td>
<td>( \text{H}_2\text{C}=\text{CCl}_2 )</td>
<td>Saran</td>
<td>films &amp; fibers</td>
</tr>
<tr>
<td>( \text{H}_2\text{C}=\text{CHC}_6\text{H}_5 )</td>
<td>( \text{H}_2\text{C}=\text{C}-\text{CH}=\text{CH}_2 )</td>
<td>SBR</td>
<td>styrene butadiene rubber</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>tires</td>
</tr>
</tbody>
</table>
A terpolymer of acrylonitrile, butadiene and styrene, called ABS rubber, is used for high-impact containers, pipes and gaskets.

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**Block Copolymerization**

Several different techniques for preparing block copolymers have been developed, many of which use condensation reactions (next section). At this point, our discussion will be limited to an application of anionic polymerization. In the anionic polymerization of styrene described above, a reactive site remains at the end of the chain until it is quenched. The unquenched polymer has been termed a living polymer, and if additional styrene or a different suitable monomer is added a block polymer will form. This is illustrated for methyl methacrylate in the following diagram.

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**Contributors**