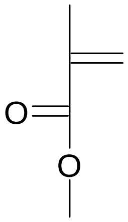
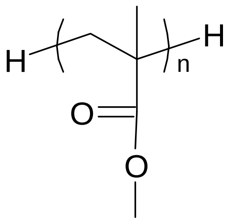
2.3 Poly(methyl methacrylate) [*9011-14-7*]

Rohm and Bauer polymerized methyl methacrylate (MMA) [*80-62-6*] into transparent sheets in 1932.[111] Pure, atactic poly(methyl methacrylate) (PMMA) is an amorphous plastic with a high surface gloss, high brilliance, a clear transparency of 92 % (inorganic glass also has a transparency of 92 %), and a refractive index of 1.49. PMMA is classified as a hard, rigid, but brittle material, with a glass transition temperature of 105°C. PMMA has good mechanical strength, acceptable chemical resistance, and extremely good weather resistance. PMMA has favorable processing properties, good thermoforming, and can be modified with pigments, flame retardant additives, UV absorbent additives, and scratch resistant coatings.[112,113]



Methyl Methacrylate
b.p. = 100°C



Poly(methyl methacrylate)

Because of the excellent optical properties, weather resistance, light weight, impact and shatter resistance (compared to inorganic glass), dimensional stability, heat resistance, and processability, PMMA has many profound and diverse uses that affect our lives every day. The ability to mold PMMA allows for the easy and inexpensive manufacture of complex optics. Complex reflex lenses, used in automobile tail lights, are made from PMMA. PMMA has been used for protection and safety in bank teller windows, as a barrier in police cars, in panels around hockey rinks, in storm doors, bath

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[111] Stickler, M.; Rhein, T., “Polymethacrylates” in *Ullmann’s Encyclopedia of Industrial Chemistry*, 5th ed., Elvers, B.; Hawkins, S.; Schultz, G. Eds., VHS: New York, **1992**, *A21*, 473.

[112] Stickler, M.; Rhein, *ibid*.

[113] Kine, B.B; Novak, R.W., “Acrylic and Methacrylic Ester Polymers” in *Encyclopedia of Polymer Science and Engineering*, Wiley: New York, **1985**, 262.

and shower enclosures, and in showcases.[114,115] For current safety glass applications, however, PMMA has been replaced by polycarbonates such as Lexan® and Merlon®.[116] Lenses, reflectors, and prisms are all made industrially from PMMA, mostly by casting.[117,118]

Health effects are minimal for PMMA.[119] For biomedical grade PMMA, however, there must be no residual monomer. Unlike PMMA, MMA is allergenic, and has health implications. PMMA has many biomedical uses because of its low *in-vivo* immune response. Anecdotically, PMMA was found to be extremely inert to tissues during World War II. Fighter pilots sometimes returned to base with, among other things, PMMA deeply embedded in them. PMMA was found to be very inert to surrounding tissues, even to the human eye, and shards that could not easily be removed were allowed to simply remain in place, coexisting with the surrounding tissue. PMMA is not biodegradable, thus it remained *in situ* throughout these pilots lives.[120]

Today, new derivatives of methacrylates, acrylates and dimethacrylates have biomedical applications in bone cements, dental fillings, and hard and soft contact lenses.[121,122] The biggest biomedical use of PMMA, again due to its excellent optical properties as well as its biomedical inertness, is in the human eye as a permanent implant for the intraocular lens following cataract surgery. Annually, 1.6 million intraocular lens implants are performed in the United States alone.[123] Sixteen million people are blinded

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[114] Stickler, M.; Rhein, T., "Polymethacrylates" in *Ullmann's Encyclopedia of Industrial Chemistry*, 5th ed., Elvers, B.; Hawkins, S.; Schultz, G. Eds., VHS: New York, **1992**, *A21*, 473.

[115] Kine, B.B; Novak, R.W., "Acrylic and Methacrylic Ester Polymers" in *Encyclopedia of Polymer Science and Engineering*, Wiley: New York, **1985**, 262.

[116] Shultz, A., communication, **2001**.

[117] Stickler, M.; Rhein, T., *Op. Cit.*

[118] Kine, B.B; Novak, R.W., *Op. Cit.*

[119] Stickler, M.; Rhein, T., *Op. Cit.*

[120] Chirila, T.; Hicks, C.; Dalton, P.; Vijayasekaran, S.; Lou, X.; Hong, Y.; Clayton, A.; Ziegelaar, B.; Fitton, J.H.; Platten, S.; Crawford, G.; Constable, I., *Prog. Polym. Sci.*, **1998**, *23*, 447.

[121] Stickler, M.; Rhein, T., *Op. Cit.*

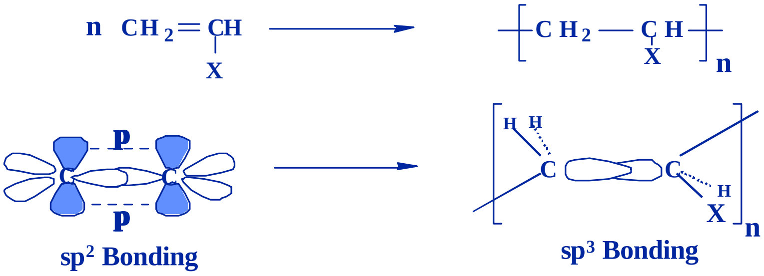
[122] Kine, B.B; Novak, R.W., *Op. Cit.*

[123] Newsletter, *Hospital Materials Management*, **2000**, *25(9)*, 1.

by cataracts worldwide.[124] PMMA is also used to improve vision external to the body, again due to its excellent optical properties and processability, as well as its biomedical inertness when in contact with the eye, as contact lenses are. Hard and soft contact lenses, and optical spectacles for eyeglasses, are all made commercially from homopolymers and copolymers of PMMA.[125,126]

2.3.1 Polymerization of Methyl Methacrylate [*80-62-6*]

PMMA can be produced using a variety of polymerization mechanisms. The most common technique is the free radical polymerization of MMA. The free radical polymerization of acrylates and methacrylates is a chain polymerization across the double bond of the monomer (Figure 2.5). The free radical polymerization of MMA can be performed homogeneously, by bulk or solution polymerization, or heterogeneously, by suspension or emulsion polymerization. Free radical polymerizations can be performed relatively easily. Unlike many types of polymerizations, absolute dryness is not necessary. In order for polymerization to proceed successfully, however, all oxygen must be removed from the polymerization. Oxygen is a radical scavenger, and terminates free radical polymerizations.[127,128]



- Relief of Strain is a Driving Force
- Must be Activated

Figure 2.6 Chain Polymerization for an Acrylate System[129]

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[124] Charters, L., *Ophthalmology Times*, **2000**, *25(15)*, 1.

[125] Stickler, M.; Rhein, T., “Polymethacrylates” in *Ullmann’s Encyclopedia of Industrial Chemistry*, 5th ed., Elvers, B.; Hawkins, S.; Schultz, G. Eds., VHS: New York, **1992**, *A21*, 473.

[126] Kine, B.B; Novak, R.W., “Acrylic and Methacrylic Ester Polymers” in *Encyclopedia of Polymer Science and Engineering*, Wiley: New York, **1985**, 262.

[127] Stickler, M.; Rhein, T., *Op. Cit.*

[128] Kine, B.B; Novak, R.W., *Op. Cit.*

[129] McGrath, J. E.; Wilkes, G.L.; Ward, T., *ACS Polymer Short Course Notes*, **2001**.

Radicals can be generated with radiation, heat, or chemical agents (usually in conjunction with radiation or heat). MMA can be polymerized spontaneously with heat. This polymerization is extremely slow, however, and of no industrial relevance. MMA has been polymerized anionically. The anionic polymerization is not used industrially because the monomer has to be extremely pure, and the polymerization must be performed at very low temperatures. The free radical polymerization of MMA is the predominant industrial mechanism to produce PMMA.[130,131]

2.3.1.1 Radiation Initiated Polymerization of MMA

The polymerization of MMA can be initiated with light or δ-radiation. The photoinitiation of MMA, using ultraviolet or visible light, can be performed without sensitizers. It is still not entirely clear whether the photoinduced polymerization is by a free radical mechanism or by an excited state mechanism.[132] Typically, photochemically labile compounds called sensitizers are added. Some examples of photosensitizers are anthracene, t-butyl peroxide, benzoyl peroxide, 1-hydrocycyclohexyl phenyl ketone, and azoisopropane. Figure 2.6 shows examples of various photoinitiators. The mechanism for the photoinitiation from benzophenone is shown in Figure 2.7. The formation of radicals from 1-hydrocyclohexyl phenyl ketone, also called Irgacure 184™, is shown in Figure 2.8. Upon exposure to light, the sensitizer either forms free radicals directly, or is converted to an excited state before forming free radicals by abstracting a hydrogen atom from the monomer or solvent.[133] Radiation initiated polymerizations of MMA are typically performed as bulk polymerizations.[134,135,136]

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[130] Stickler, M.; Rhein, T., "Polymethacrylates" in *Ullmann's Encyclopedia of Industrial Chemistry*, 5th ed., Elvers, B.; Hawkins, S.; Schultz, G. Eds., VHS: New York, **1992**, *A21*, 473.

[131] Kine, B.B; Novak, R.W., "Acrylic and Methacrylic Ester Polymers" in *Encyclopedia of Polymer Science and Engineering,* Wiley: New York, **1985**, 262.

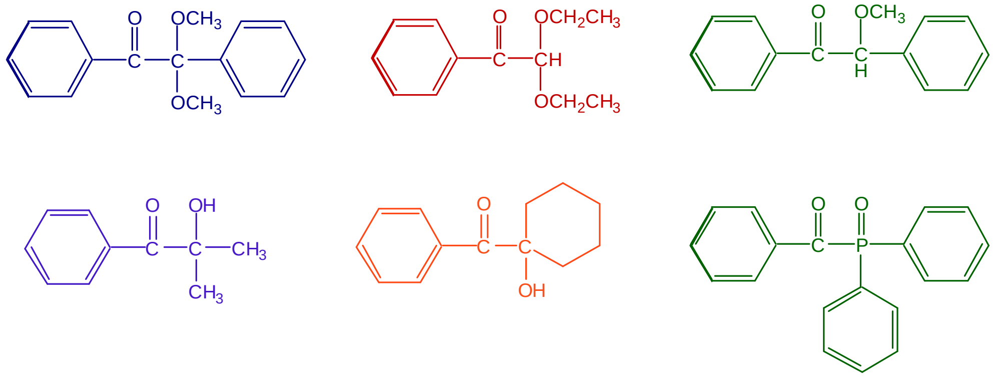
[132] Gruber, H.F., *Prog. Polym. Sci.*, **1992**, *17*, 953.

[133] Gruber, H. F. *ibid.*

[134] Decker, P., *Macromol. Symp.*, **1999**, *143*, 45.

[135] Stickler, M.; Rhein, T., *Op. Cit.*

[136] Kine, B.B; Novak, R.W., *Op. Cit.*



- **•Absence of benzylic radicals - reduces yellowing**
- **•Clear coatings (low Abs. at 300-400 nm)**

Figure 2.7 A. Examples of Photoinitiators and Their Advantages[137]

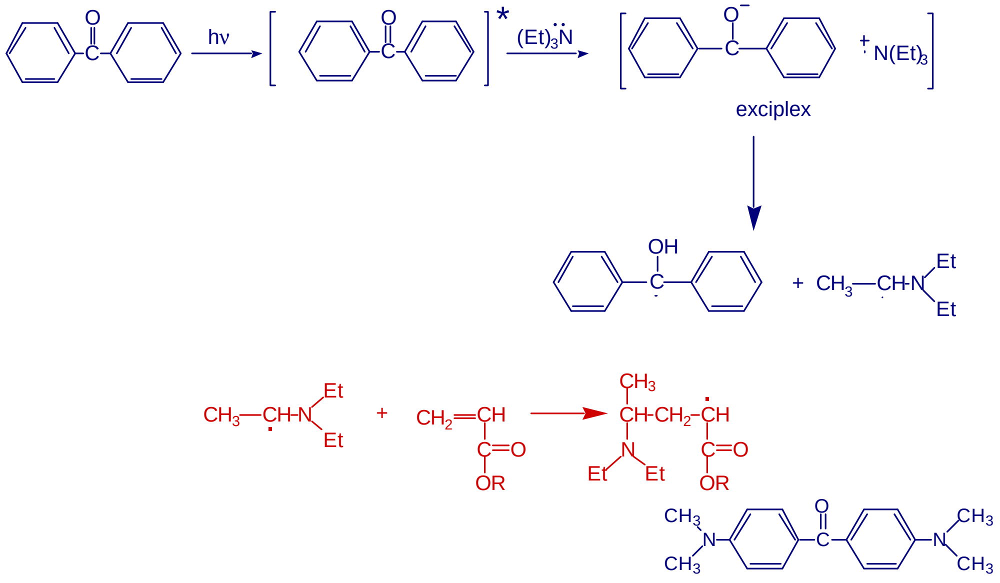


Figure 2.7 B. Photoinitiation Mechanism for Benzophenone[138]

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[137] McGrath, J. E.; Wilkes, G.L.; Ward, T., *ACS Polymer Short Course Notes*, **2001**.

[138] McGrath, J. E.; Wilkes, G.L.; Ward, T., *ibid.*

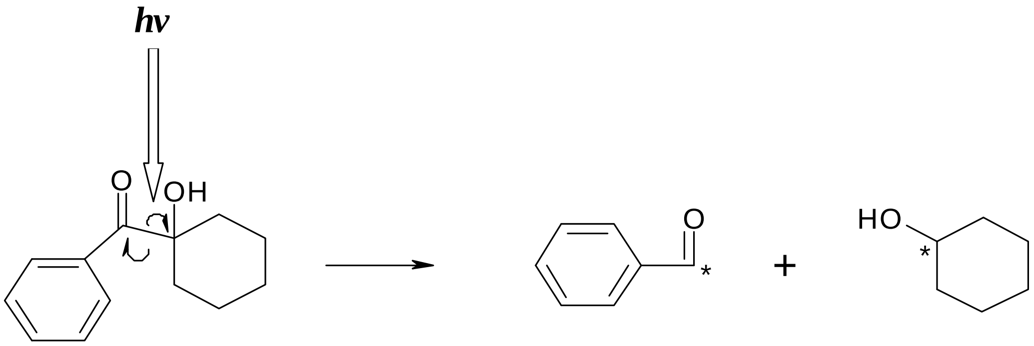

Figure 2.8 Radical Formation of 1–Hydroxycylohexyl Phenyl Ketone by UV Radiation

Light induced polymerization is considered one of the most efficient techniques for rapidly producing polymeric materials with well defined characteristics, particularly for cross-linked polymer networks. Photopolymerization is often the method of choice for rapid, assembly style, through-put polymerizations. Most of the photosensitive resins used in industrial photopolymerizations are made of acrylates rather than methacrylates, due to the much higher reactivity of the acrylate double bond. The propagation rate constant , k_p, is about 15,000 L/mole•second for acrylate monomers, which compares to less than 1,000 L/mole•second for methacrylate monomers.[139]

PMMA can also be produced by initiation with δ-radiation, typically from a ^{60}Co source, and by electron beams. γ-Radiation initiated polymerization is useful when the addition of an initiator is undesirable, or if the polymerization batch absorbs light too strongly, because of pigments or because of the monomer being impregnated into porous materials, such as wood or stone.[140] γ-Radiation is also used for sterilization purposes. γ-Radiation may be the polymerization mechanism of choice for polymers that must also be microbially sterile.

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[139] Decker, P., *Macromol. Symp.*, **1999**, *143*, 45.

[140] Stickler, M.; Rhein, T., "Polymethacrylates" in *Ullmann's Encyclopedia of Industrial Chemistry,* 5th ed., Elvers, B.; Hawkins, S.; Schultz, G. Eds., VHS: New York, **1992**, *A21*, 473.

2.3.1.2 Heat Initiated Polymerization of MMA

The polymerization of MMA is most commonly initiated by thermally labile compounds, such a 2,2'-azobisisobutyronitrile (AIBN). The time for the concentration of initiator to decrease to one half of its original concentration is called the initiator half-life. A wide range of thermal initiators are available with appropriate half-lives at various polymerization temperatures. For example, AIBN has a half-life of 74 hours at 50°C, 4.8 hours at 70°C, and 7.2 minutes at 100°C.[141,142] t-Butyl peroxide has a half-life of 218 hours at 100°C, 34 hours at 115°C, and 6.4 hours at 130°C.[143,144] Upon heating, the thermal initiator forms free radicals, which initiate the polymerization. Figure 2.9 shows the generation of free radicals for benzoyl peroxide and AIBN. The equations for determining initiator half-life are shown in Figure 2.10. Scheme 2.1 shows initiation, propagation, and termination for the AIBN initiated polymerization of MMA.[145]

Free radical polymerization is a chain polymerization, and produces high molecular weight PMMA at low conversion. At all points in the conversion, only monomer, high polymer, and initiating species are detected. Allowing time for the polymerization to complete increases the overall polymer percent yield.[146]

Termination occurs through two mechanisms, combination and disproportionation (Scheme 2.1). With termination by combination, the resulting polymer has a head–to-head linkage, and the molecular weight roughly doubles. With termination by disproportionation, in which a proton is abstracted from one propagating chain end to another, two different types of polymers are produced with about the same molecular weight. Combination predominates at lower temperatures. Disproportionation becomes more significant at higher temperatures. The free radical polymerization of MMA at

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[141] Odian, G., *Principles of Polymerization*, 2nd ed., Wiley: New York, **1981**, 196.
[142] Brandrup, J.; Immergut, E.H.; Grulke, E.A. Eds., *Polymer Handbook*, 4th ed., Wiley: New York, **1999**, *II*, 3.
[143] Odian, G., *Op. Cit.*, 196.
[144] Brandrup, J.; Immergut, E.H.; Grulke, E.A. Eds., *Op. Cit.*, *II*, 25.
[145] Odian, G., *Op. Cit.*, 179-242.
[146] Odian, G., *ibid.*

60° C has 79 % termination by disproportionation and 21 % termination by combination.[147] At higher temperatures, the incidence of chain transfer increases as well. With chain transfer, the propagating polymer radical reacts with another molecule by proton abstraction rather than by addition. When a proton is abstracted from another polymer molecule, this leads to branching and possible cross-linking.[148] Chain transfer to polymer is discussed in more detail in Section 2.3.2.

Thermally initiated polymerizations of MMA are performed as bulk polymerizations, solution polymerizations, suspension polymerizations, and emulsion polymerizations. The polymerization method used is determined by the application of the final polymer. Bulk polymerizations of MMA are still the predominant method for producing high quality acrylic glass, such as Plexiglas®. Solution polymerizations of MMA are used commercially to produce adhesives, paint resins, and additives. Suspension polymerizations of MMA produce PMMA beads, which can then be molded. Emulsion polymerizations of MMA are used to produce paint resins, paper coating agents and paper processing agents, textile binders, and additives.[149,150]

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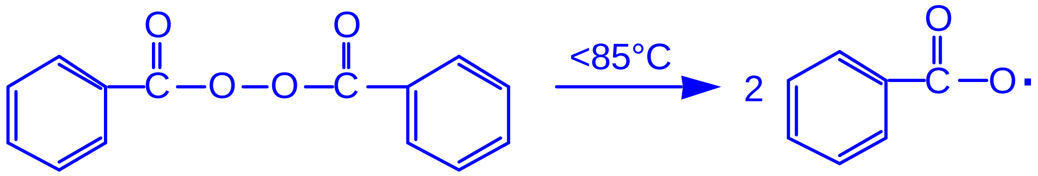
[147] Allcock, H.R.; Lampe, F.W., *Contemporary Polymer Chemistry*, 2nd ed., Prentice Hall: Englewood Cliffs, NJ, **1981**, 61.

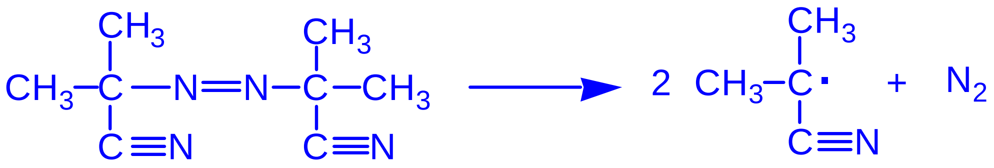
[148] Allcock, H.R.; Lampe, F.W., *ibid*, 59.

[149] Stickler, M.; Rhein, T., "Polymethacrylates" in *Ullmann's Encyclopedia of Industrial Chemistry*, 5th ed., Elvers, B.; Hawkins, S.; Schultz, G. Eds., VHS: New York, **1992**, *A21*, 473.

[150] Kine, B.B; Novak, R.W., "Acrylic and Methacrylic Ester Polymers" in *Encyclopedia of Polymer Science and Engineering*, Wiley: New York, **1985**, 262.

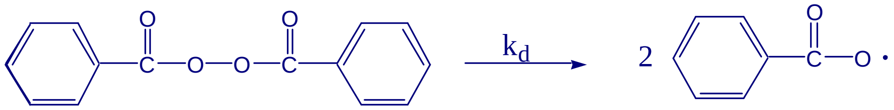


benzoyl peroxide



AIBN (“VAZO 64”)

Figure 2.9 Generation of Free Radicals from Some Thermal Initiators



$$\frac{-d\,[I]}{dt} = k_d\,[I]$$

$$\frac{-d\,[I]}{[I]} = k_d\ dt$$

$$-\ln \frac{[\,I_t\,]}{[\,I_0\,]} = k_d\,t$$

$$\ln \frac{[\,I_0\,]}{[\,I_t\,]} = k_d\,t$$

$$\ln\ 2 = k_d\,t_{1/2}$$

$$0.693 = k_d\,t_{1/2}$$

$$\frac{0.693}{k_d} = t_{1/2}$$

Half-life: The amount of time necessary for the initiator concentration to decrease to half its original value.

$[I_t]$ = initiator concentration at time t
$[I_o]$ = initial initiator concentration
k_d = disassociation rate constant

Figure 2.10 Rate of Free Radical Initiation[151]

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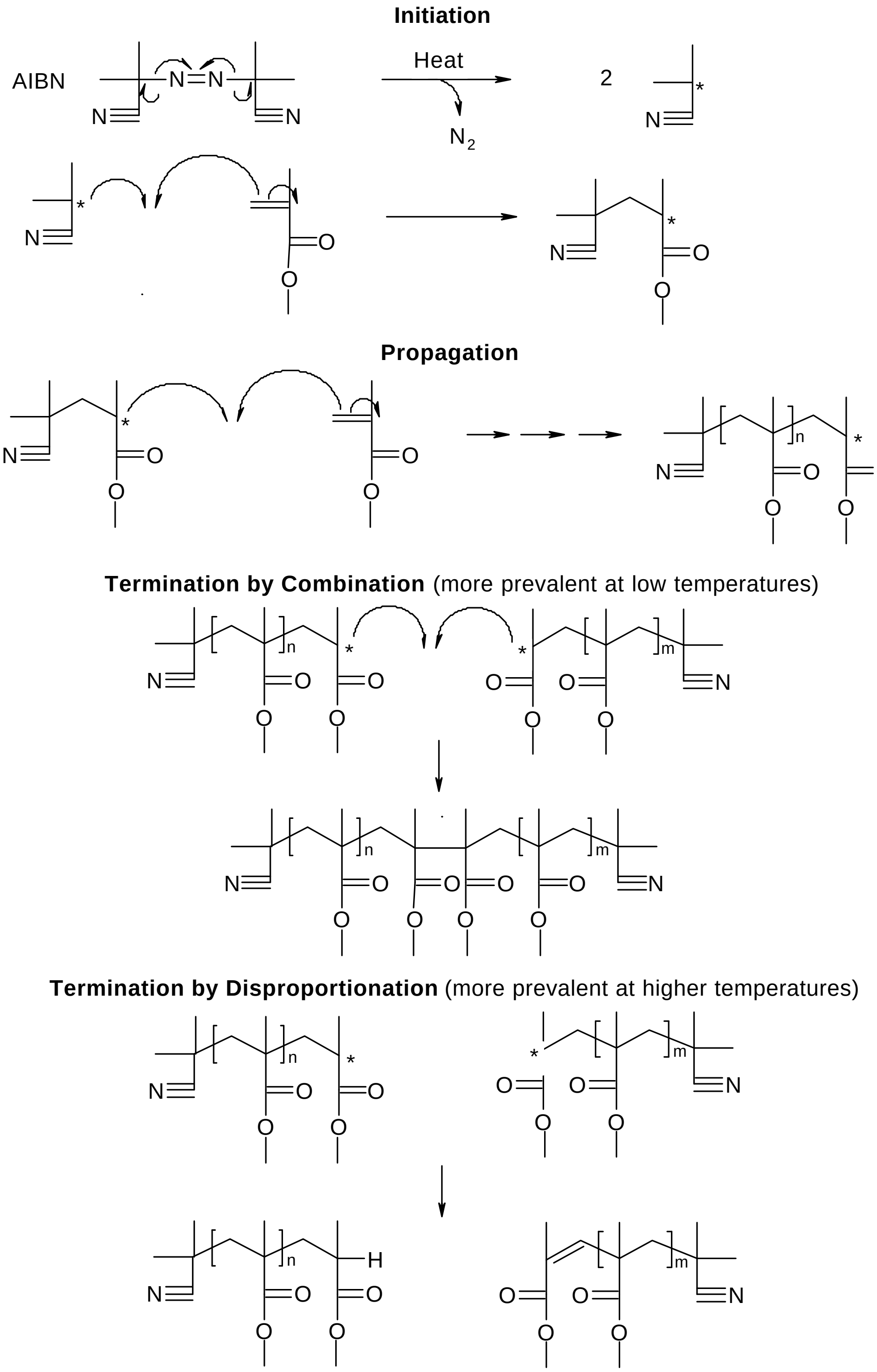
[151] McGrath, J. E.; Wilkes, G.L.; Ward, T., *ACS Polymer Short Course Notes*, **2001**.



Scheme 2.1 Free Radical Polymerization of MMA Using AIBN[152,153]

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[152] Odian, G., *Principles of Polymerization*, 2nd ed., Wiley: New York, **1981**, 179-242.

[153] Allcock, H.R.; Lampe, F.W., *Contemporary Polymer Chemistry*, 2nd ed., Prentice Hall: Englewood Cliffs, NJ, **1981**, 61.

2.3.1.3 Bulk Free Radical Polymerization and the Trommsdorf Effect

In bulk polymerizations, the monomer and initiator are combined undiluted. In large batches, exotherms due to autoacceleration are a concern. For most (non-radical) polymerizations, the reaction rate decreases with time. For the polymerization of MMA and other acrylic and vinylic monomers to high conversion, particularly in bulk polymerizations, the reaction rate can be governed by the gel effect, also called the Trommsdorf effect.[154,155,156]

In the first stage of the polymerization, Stage I, the polymerization rate is constant or declining with time. As the polymerization progresses to Stage II, the rate of polymerization increases with time, which can lead to dramatic autoacceleration, known as the gel or Trommsdorf effect. In the last stage of the polymerization, Stage III, the rate of polymerization is either constant or often declining. In bulk polymerizations, the extremely large increase in the viscosity of the reaction during Stage III can hinder the diffusion of the propagating polymer radicals. Even with these safety and viscosity drawbacks, bulk polymerizations are used commercially to produce high-gloss, optically clear acrylic glasses from MMA.[157,158,159]

2.3.1.4 Solution Free Radical Polymerization

By polymerizing MMA in a solvent, many of the disadvantages of the bulk polymerizations are overcome. The solvent acts as a diluent and aids in the transfer of heat of polymerization. Thermal control is much better in solution polymerizations

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[154] Stickler, M.; Rhein, T., “Polymethacrylates” in *Ullmann’s Encyclopedia of Industrial Chemistry*, 5th ed., Elvers, B.; Hawkins, S.; Schultz, G. Eds., VHS: New York, **1992**, *A21*, 473.
[155] Kine, B.B; Novak, R.W., “Acrylic and Methacrylic Ester Polymers” in *Encyclopedia of Polymer Science and Engineering*, Wiley: New York, **1985**, 262.
[156] Odian, G., *Principles of Polymerization*, 2nd ed., Wiley: New York, **1981**, 271.
[157] Stickler, M.; Rhein, T., *Op. Cit.*
[158] Kine, B.B; Novak, R.W., *Op. Cit.*
[159] Odian, G., *Op. Cit.*, 286-287.

compared to bulk polymerizations. Additionally, the viscosity of the reaction mixture is decreased.[160,161]

The solvent must be chosen with care, however. Many organic solvents acts as chain transfer agents for free radical reactions, thus lowering the polymer molecular weight. Aromatic solvents can accept and stabilize a free radical, in effect inhibiting the polymerization.[162] For solution polymerizations of MMA, N,N-dimethylacetamide and dimethylformamide are examples of acceptable solvents. Chain transfer is discussed in detail in Section 2.3.2.

2.3.1.5 Suspension Polymerization

Small beads of PMMA can be readily produced using suspension polymerization. The monomer is stirred with approximately twice its volume of water and dispersants. This forms a droplet like suspension of the monomer phase in the aqueous phase. Dispersants stabilize the polymerization and prevent the droplets from adhering to one another. Dispersants are water soluble compounds such as gelatin, cellulose derivatives, or water soluble polymers like poly(vinyl alcohol). Dispersants can also be finely suspended inorganic compounds, such as kaolin, magnesium carbonate, or aluminum hydroxide. The bead or particle size can be controlled by choosing appropriate stirring conditions and dispersants, to produce beads ranging from 50 μm to 1000 μm.[163]

Suspension polymerization is initiated with free radical initiators that favor the monomer phase, such as benzoyl peroxide. Suspension polymerization provides for the removal of heat from the polymerization by the aqueous phase, while allowing for high polymerization rates in the monomer phase (Figure 2.11). After completion of the

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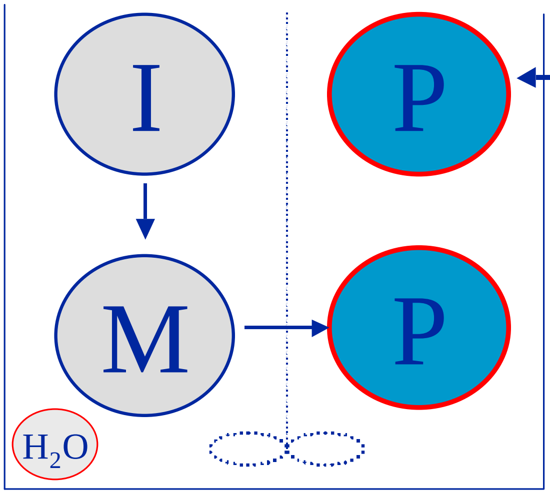
[160] Stickler, M.; Rhein, T., "Polymethacrylates" in *Ullmann's Encyclopedia of Industrial Chemistry*, 5th ed., Elvers, B.; Hawkins, S.; Schultz, G. Eds., VHS: New York, **1992**, *A21*, 473.

[161] Kine, B.B; Novak, R.W., "Acrylic and Methacrylic Ester Polymers" in *Encyclopedia of Polymer Science and Engineering*, Wiley: New York, **1985**, 262.

[162] Odian, G., *Principles of Polymerization*, 2nd ed., Wiley: New York, **1981**, 242-243.

[163] Stickler, M.; Rhein, T., *Op. Cit.*

polymerization, the PMMA polymer beads are easily separated from the aqueous phase by filtration, washed with water, and dried.[164]



Suspending Agent,
e.g., H_2O Sol.
PVA
T° ~ 50-90°C

- Initiator directly dissolved in monomer
- Rp is proportional to M, $I^{1/2}$
- Polymer beads formed directly
- Stirring necessary
- Polymer Tg should be equal to, or higher than reaction temperature

- **ADVANTAGES**
  - Can easily recover polymer by filtration of beads
  - Water normally used as the medium: environmentally friendly, inexpensive, good head transfer
  - Bead size is controllable
  - Viscosity is not a problem
- **DISADVANTAGES**
  - Can only be used effectively for glassy materials (not low Tg materials)

Figure 2.11 Suspension Polymerization[165]

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[164] Stickler, M.; Rhein, T., "Polymethacrylates" in *Ullmann's Encyclopedia of Industrial Chemistry*, 5th ed., Elvers, B.; Hawkins, S.; Schultz, G. Eds., VHS: New York, **1992**, *A21*, 473.

[165] McGrath, J. E.; Wilkes, G.L.; Ward, T., *ACS Polymer Short Course Notes*, **2001**.

2.3.1.6 Emulsion Polymerization

Emulsion polymerization is used to make colloidal dispersions of PMMA. Emulsion polymerization involves the free radical polymerization of monomers that are in a colloidal suspension. Surfactants are added to the (typically) aqueous phase to form micelles. The free radical initiators used are water soluble, such as potassium persulfate. Monomer, including a fraction of free radical initiated monomer, migrates to the micelles. Within the micelles, the monomer concentration is very high, and this is where the polymerization takes place. Under optimal conditions, theoretically, there is one propagating chain end per micelle. Emulsion polymerization provides for high conversion and very high molecular weight polymer within the micelles. Figure 2.12 depicts an emulsion polymerization. The dispersed PMMA particles produced are very small, ranging from 0.001 μm to 0.100 μm.[166,167] Emulsion polymerizations of MMA are used to produce paint resins, paper coating agents and paper processing agents, textile binders, and additives.[168]

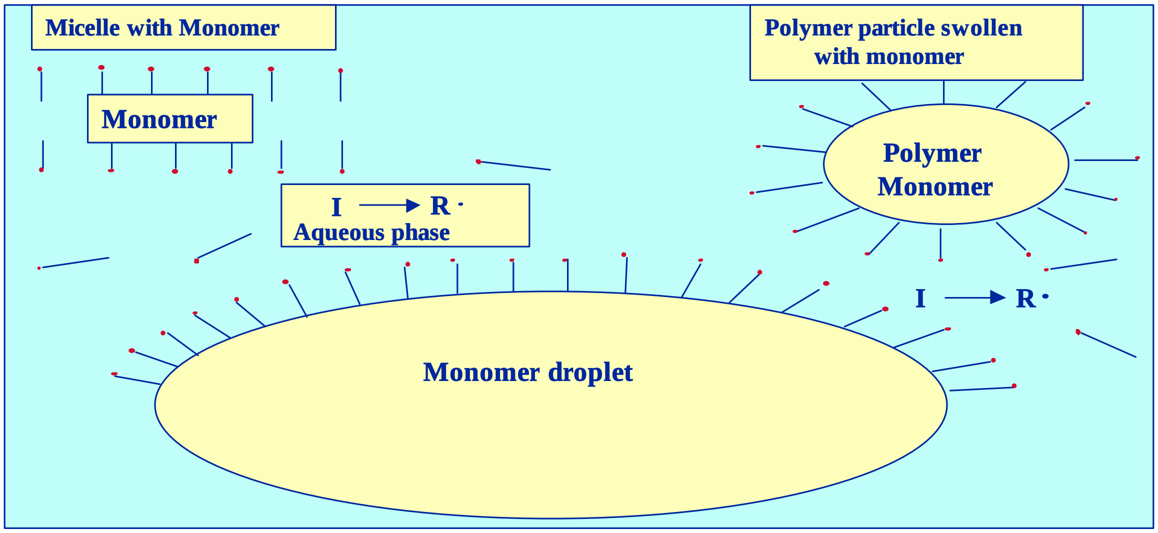

Figure 2.12 Emulsion polymerization[169]

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[166] Stickler, M.; Rhein, T., “Polymethacrylates” in *Ullmann’s Encyclopedia of Industrial Chemistry*, 5th ed., Elvers, B.; Hawkins, S.; Schultz, G. Eds., VHS: New York, **1992**, *A21*, 473.
[167] Odian, G., *Principles of Polymerization*, 2nd ed., Wiley: New York, **1981**, 334-335.
[168] Stickler, M.; Rhein, T., *Op. Cit.*
[169] McGrath, J. E.; Wilkes, G.L.; Ward, T., *ACS Polymer Short Course Notes*, **2001**.

2.3.2 Chain Transfer

Chain transfer is the premature termination of a growing polymer chain and the initiation of another polymer chain by the transfer of a hydrogen, or other atom or species, to the growing polymer chain from some compound present in the system, which could be the monomer, initiator, solvent, or polymer. The radical displacement reaction, shown below, is called a chain transfer reaction.[170,171] Chain transfer to the initiator is referred to as induced initiator decomposition.[172]

$$M_n^{\bullet} + XA \xrightarrow{k_{tr}} M_n\text{—}X + A^{\bullet}$$

where XA = monomer, initiator, solvent, or other species

X = atom or species transferred

k_{tr} = chain transfer rate constant

The new free radical $A^{\bullet}$, reinitiates the free radical polymerization. This causes the polymer molecular weight to be lower than predicted. Chain transfer is a chain breaking reaction, which leads to a decrease in the length of the polymer chains. The number of propagating chain ends remains constant, however.[173]

$$A\bullet + M \xrightarrow{k_a} M\bullet$$

where k_a = rate constant for reinitiation of polymerization

When reinitiation is rapid, with no change in the polymerization rate, in other words, the chain reinitiation rate constant k_a is approximately equal to the propagation rate constant k_p, then two different scenarios can occur. In the first case, when the chain transfer rate constant is much slower than the propagation rate constant ($k_p >> k_{tr}$), this is

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[170] Odian, G., *Principles of Polymerization*, 2nd ed., Wiley: New York, **1981**, 226.

[171] Allcock, H.R.; Lampe, F.W., *Contemporary Polymer Chemistry*, 2nd ed., Prentice Hall: Englewood Cliffs, NJ, **1981**, 61.

[172] Odian, G., *Op. Cit.*, 226.

[173] Odian, G., *ibid.*

considered the normal mode of chain transfer, where the molecular weight of the polymer chains is decreased. In the second case, when the chain transfer rate constant is much larger than the propagation rate constant ($k_p << k_{tr}$), the molecular weight is drastically reduced, and the resulting polymers are referred to as telomers. In both cases, the overall rate of polymerization remains constant.[174]

When reinitiation is slow compared to propagation ($k_a < k_p$), there is a decrease in both the molecular weight and the rate of polymerization. When the chain transfer rate constant is much slower than the propagation rate constant ($k_p >> k_{tr}$), then this effect is called retardation.[175,176] When the chain transfer rate constant is much larger than the propagation rate constant ($k_p << k_{tr}$), then there is a large decrease in the molecular weight and in the rate of polymerization, R_p, and this effect is known as degradative chain transfer.[177,178]

For clarification, inhibitors stop every radical, and the polymerization completely stops until the inhibitor is consumed. Retarders are less effective, and only stop a portion of the radicals. The difference between inhibitors and retarders is a matter of degree.[179] Oxygen, for example, is a well known and powerful inhibitor. Oxygen reacts with radicals to from relatively unreactive peroxy radicals, which reacts with itself or other propagating radicals to from inactive products.[180,181,182] In addition, oxygen has one of the largest ratios of k_{tr}/k_p, which for methyl methacrylate at 50°C is 33,000, making oxygen an extremely effective inhibitor.[183,184] For this reason, acrylates and

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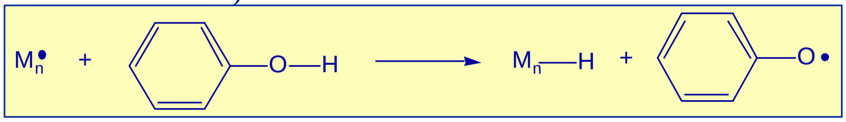
[174] Odian, G., *Principles of Polymerization*, 2nd ed., Wiley: New York, **1981**, 226.
[175] Odian, G., *ibid*., 226, 242-251.
[176] Flory, P., *Principles of Polymer Chemistry*, Cornell University Press: Ithaca, **1953**, 161-174.
[177] Odian, G., *Op. Cit.*.
[178] Flory, P., *Op. Cit.*
[179] Odian, G., *Op. Cit.*, 242.
[180] Odian, G., *ibid*., 249.
[181] Maybod, H.; George, M.H.; *J. Polym. Sci. Polym.Chem. Ed.*, **1977**, *15*, 693.
[182] George, M.H.; Ghosh, A., *J. Polym. Sci. Polym.Chem. Ed.*, **1978**, *16*, 981.
[183] Odian, G., *Op. Cit.*, 246.
[184] Eastmond, G.C., “Kinetic Data for Homogeneous Free Radical Polymerizations of Various Monomers,” in *Comprehensive Chemical Kinetics*, Bamford, C.H.; Tipper, C. Eds., Elsevier: New York, **1976**, *14A*, 132.

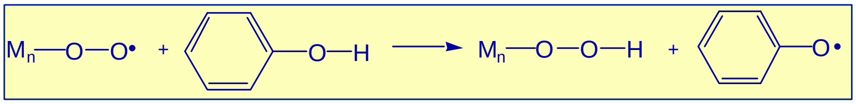
methacrylates are typically stored under oxygen, rather than nitrogen or argon. Prior to polymerization, oxygen can be removed by mild vacuum, followed by a nitrogen gas purge (repeated several times), or by careful distillation over a nitrogen atmosphere. Other inhibitors that may be present to ensure safe storage, such as monomethyl ester hydroquinone (MEHQ), can be removed prior to polymerization by careful distillation over a nitrogen atmosphere, or by passing through a inhibitor removal column containing basic silica or inhibitor removal beads, which are commercially available through Aldrich and other chemical suppliers.[185] Figure 2.13 depicts several types of inhibitors.

Phenols: (Inhibitor/Retarder)



•Electron donating groups at the ortho positions can make this a better inhibitor.

•Phenol can be synergistic with oxygen as an inhibitor.



•Oxidants such as $FeCl_3$ and $CuCl_2$ are strong inhibitors.

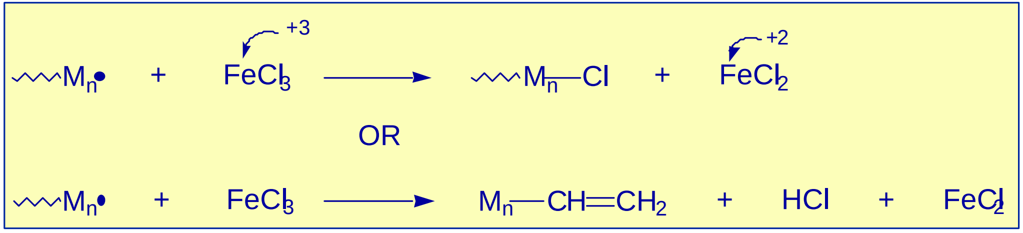


Figure 2.13 Types of Inhibitors[186]

The degree of polymerization, and thus the number average molecular weight, $<X_n>$, is dependent upon the effects of all possible chain transfer reactions within the polymerization, such as monomer, chain transfer agents, which could be solvent, and initiator. This relationship can be expressed by the Mayo Equation (Equation 2.8). The chain transfer constant, C, is the constant for that particular substance, k_{tr}, to the

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[185] Shobha, H.; Sankarapandian., M.; Uhrich, K.; Rasmussen, L., conversations/experience, **1999**.
[186] McGrath, J. E.; Wilkes, G.L.; Ward, T., *ACS Polymer Short Course Notes*, **2001**.

propagation rate constant k_p. The chain transfer constants for monomer, chain transfer agent, and initiator are C_M, C_S, and C_I, respectively.[187,188,189] The C_M at 60°C for methyl methacrylate is 0.07-0.25 x 10^{-4}.[190,191,192] The C_S for chloroform in a methyl methacrylate polymerization at 80°C is 1.7 x 10^{-4}.[193]

$$\frac{1}{\langle X_n \rangle} = \frac{k_t R_p}{k_p^2 [M]^2} + C_M + C_S \frac{[S]}{[M]} + C_I \frac{k_t R_p{}^2}{k_p^2 f k_d [M]^3} \qquad \textbf{Equation 2.8}$$

$$\text{where } C_M = \frac{k_{tr,M}}{k_p} \qquad C_S = \frac{k_{tr,S}}{k_p} \qquad C_I = \frac{k_{tr,I}}{k_p}$$

$\langle X_n \rangle$ = number average molecular weight

[S] = concentration of chain transfer agent

[M] = concentration of monomer

k_t = termination rate constant

f = initiator frequency (fraction of radicals produced in the reaction that initiates polymer chains)

k_d = initiator decomposition rate constant

Another phenomenon that must be considered is chain transfer to another polymer molecule. Chain transfer to polymer forms a free radical propagating site on a polymer chain. The subsequent polymerizations of monomer leads to the production of a branched polymer (Figure 2.14). Termination by combination of branched, propagating polymer chains can lead to a cross-linked polymer. Chain transfer to polymer is more of a consideration at high or complete conversions. Branching and cross-linking greatly

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[187] Odian, G., *Principles of Polymerization*, 2nd ed., Wiley: New York, **1981**, 227.

[188] Flory, P., *Principles of Polymer Chemistry*, Cornell University Press: Ithaca, **1953**, 138.

[189] Heuts, J.; Davis, T.P.; Russell, G.T., *Macromolecules*, **1999**, *32*, 6019.

[190] Brandrup, J.; Immergut, E.H.; Grulke, E.A. Eds., *Polymer Handbook*, 4th ed., Wiley: New York, **1999**, *V*, 88.

[191] Ayrey, G.; Haynes, A.C., *Makromol. Chem.*, **1974**, *175*, 1463.

[192] Stickler, M.; Meyerhoff, G., *Makromol. Chem.*,**1978**, *179*, 2729.

[193] Rudin, A., *The Elements of Polymer Science and Engineering*, Academic Press: New York, **1982**, 219.

effect the physical properties of a polymer. Branching drastically reduces the crystallinity of a polymer; cross-linking causes the polymer to be infusible.[194]

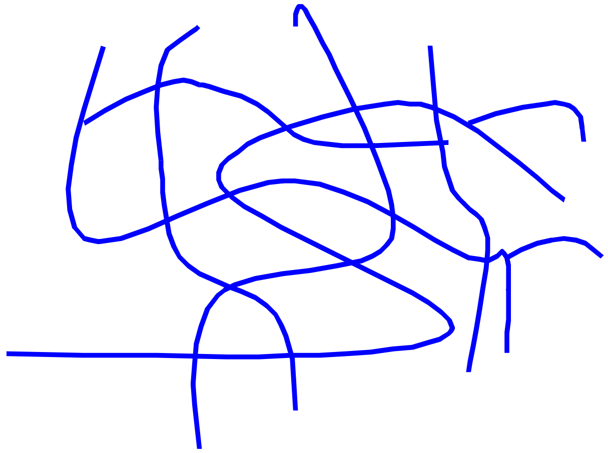

Figure 2.14 Cross-linked Polymer, with Branches

The branching density, ρ, can be expressed as a function of the polymer transfer constant, C_P, and the extent of the polymerization reaction, *p* (Equation 2.9).[195]

$$\rho = -C_P[1 + (1/p)\ln(1-p)] \qquad \textbf{Equation 2.9}$$

The branching density is the number of branches per molecule polymerized. Particularly for poly(ethylene), poly(vinyl acetate), and poly(vinyl chloride) (PVC), the extent of branching can be varied considerably by controlling the polymerization temperature and other reaction considerations.[196,197] Long branches in PVC arise from hydrogen abstraction in the CHCl repeat unit within the polymer chain.[198] The polymer transfer constant C_P is about 10^{-4} or slightly higher for many polymers, such as polystyrene and

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[194] Odian, G., *Principles of Polymerization*, 2nd ed., Wiley: New York, **1981**, 238-242.
[195] Odian, G., *ibid.*, 240.
[196] Odian, G., *ibid.*
[197] Wolf, C.; Burchard, W., *Makrolmol. Chem.*, **1976**, *177*, 2519.
[198] Odian, G., *Op. Cit.*, 242.

PMMA.[199,200,201] Assuming a C_P of 10^{-4}, at 80 % conversion, there should be one branch for every 10,000 monomer units polymerized. At 99 % conversion, one branch would be expected for every 2,000 monomer units polymerized. For many of the polymerizations conducted in this thesis research, chain transfer to polymer may have played a significant role.

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[199] Odian, G., *Principles of Polymerization*, 2nd ed., Wiley: New York, **1981**, 240.

[200] Brandrup, J.; Immergut, E.H.; Grulke, E.A. Eds., *Polymer Handbook*, 4th ed., Wiley: New York, **1999**, *V*, 88.

[201] Corner, T., *Adv. Polm. Sci.*, **1984**, *62*, 97.