Photo Polymerization

Photo polymerization is a very versatile polymerization mechanism that can be applied to a wide variety of vinyl monomers. The resulting polymeric materials can be used in applications ranging from packaging materials to coatings as well as automotive parts. These different applications require different material properties, which are determined amongst others by the microstructure of the polymer chain, the interactions between the chains and the types of additives.

When one focuses on the microstructure, one can distinguish polymers that differ in the structure of the backbone, in molecular weight, in composition, and in end groups. When a polymer consists of more than one monomer, it is called a copolymer. In this class of polymers several variations are known as well.

Two linear copolymers with the same overall composition can have a different distribution of the monomers over the polymer chain resulting in random, gradient or even block copolymers. Thus, it is clear that in principle several different microstructures can be obtained. However, in free-radical polymerization it is impossible to obtain a polymer in which all chains have exactly the same structure. They will differ in length, composition, end groups and backbone structure, even when all chains are initiated at exactly the same moment and in the same way. During the polymerization these structural differences will usually become larger as the ratios of the different components in the reaction mixture change, so it is not easy to control the polymerization and thus to obtain polymers with a predefined structure. In the past two decades, several techniques were developed to control one or more aspects of the chain structure.

Many of these are aimed at producing homopolymers with narrow molecular weight distributions and eventually block copolymers. Otsu and Yoshida first used to work disulfides that were capable of both initiating and, after dissociation, reversibly terminating the free-radical polymerization. Since then many other techniques were developed that were based on reversibly terminating the growing polymeric radicals, like nitroxide mediated polymerization′ atom transfer radical polymerization and reversible addition fragmentation chain transfer polymerization. Together, these form the field of controlled radical polymerization.

Free radical Polymerization of Methyl Methacrylate

PMMA can be produced using a variety of polymerization techniques. The most common technique is the free radical chain polymerization of MMA. The free radical polymerization of acrylates and methacrylate’s is a chain polymerization across the double bond of the monomer (Figure 1). 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. In order for polymerization to proceed successfully, however, oxygen must be removed from the polymerization. Oxygen is a radical scavenger, and terminates the free radical polymerizations process.(20)

Radicals can be generated with radiation, heat, or chemical agents (usually in conjunction with radiation or heat).

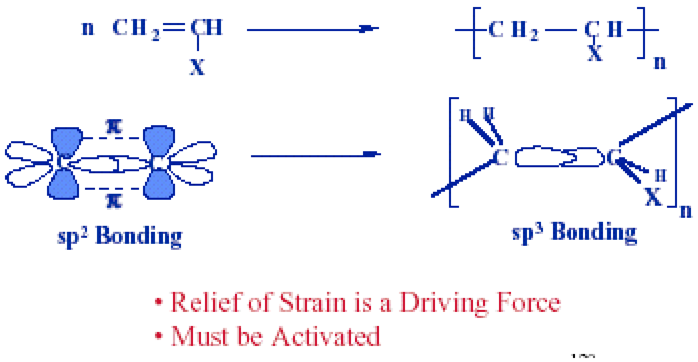
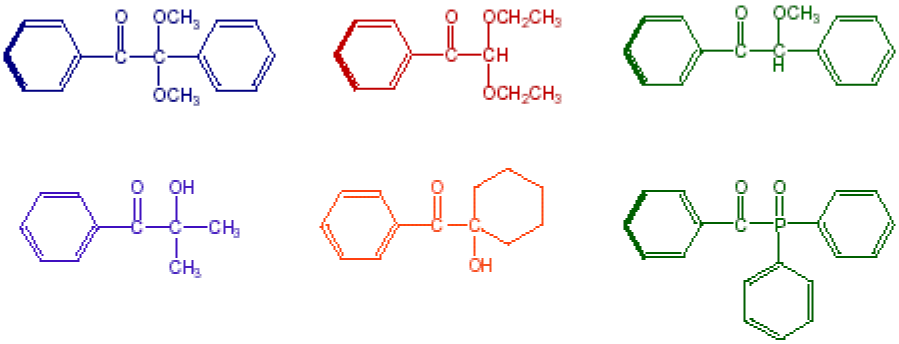


Figure 1-1 Chain polymerization for an acrylate system

Photo initiation Polymerization of MMA

The polymerization of MMA can be initiated with light or γ-radiation. The photoinitiation of MMA, using ultraviolet or visible light, can be performed without sensitizers. It is still not entirely clear whether the photo induced polymerization is by a free radical mechanism or by an excited state mechanism. Typically, photo chemically labile compounds called sensitizers are added. Some examples of photo initiators are anthracene, t-butylperoxide, benzoylperoxide, 1-hydroxycyclohexyl phenyl ketone, and azoisopropane. Figure(1-2)shows examples of various photoinitiators. The mechanism for the photoinitiation from benzophenone is shown in Figure (1-3) The formation of radicals from 1-hydroxycyclohexyl phenyl ketone is shown in Figure (1-4) 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(e.g amine).



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

Figure (1-2) Chemical structure of organic photo initiators

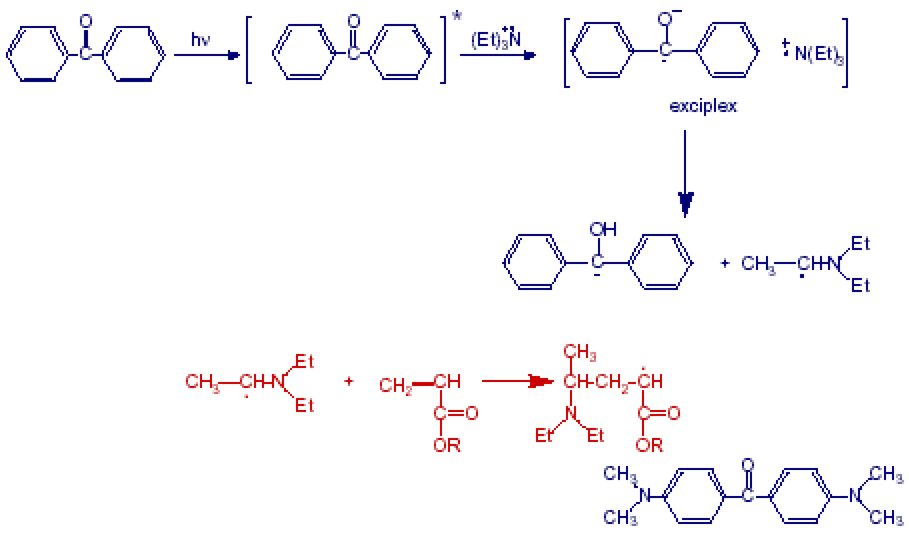
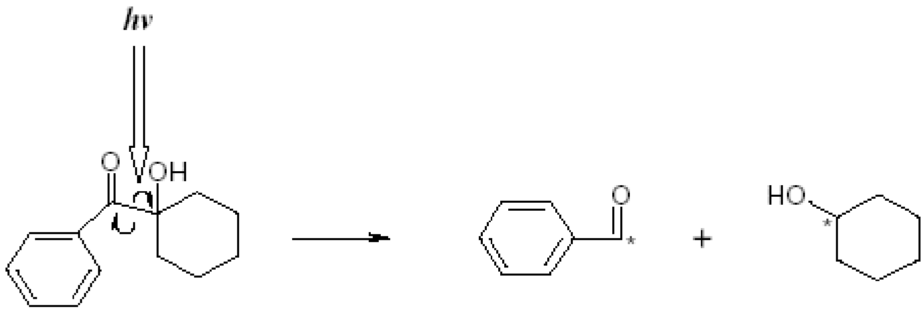


Figure (1-3) Photoinitiation mechanism by Benzophenone(27)



Figure(1-4) Radical formation of 1–Hydroxycylohexyl Phenyl Ketone by UV radiation(27)

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.(29) PMMA can also be produced by initiation with γ-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. 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.

INITIATION BY TRANSITION METAL COMPLEXES

Photoinition of Free radical Polymerzation by Transition Metal Derivatives

Two types of photoinitiator are considered: (1) transition metal complexes (mainly carbonyls), (2) chelates of transition metals. In systems of type (1) the metal is in a low oxidation state and an organic halide is generally, but not always, presents; on the other hand, in (2) the metal is initially in a high oxidation state.

Transition metal complex/halide systems

Photo initiation

Carbonyls of Group VIA—Ultra-violet irradiation ($\lambda < 350$ nm) of simple metal carbonyls results in scission of carbon monoxide and formation of a coordinately unsaturated species:

$$\mathbf{M(CO)}_n + h\nu \rightarrow \underset{\text{excited}}{[\mathbf{M(CO)}_n]^{\star}} \rightarrow \mathbf{M(CO)}_{n-1} + \mathbf{CO} \text{ -------------- } (1\text{-}4)$$

Where M = metal atom

In equation (1-4) M represents the metal atom. A summary of the experimental evidence with the relevant theoretical background for this type of primary photochemical process has been given in a review by Koerner von Gustorf and Grevels . The product $M(CO)_{n-1}$ may combine with carbon monoxide to regenerate the original carbonyl, or it may react by addition of an n- or Π-donor S (e.g. the monomer) according to equation (1-5).

$$M(CO)_{n-1} + S \rightarrow S\cdots M(CO)_{n-1} \qquad \text{------------------------------(1-5)}$$

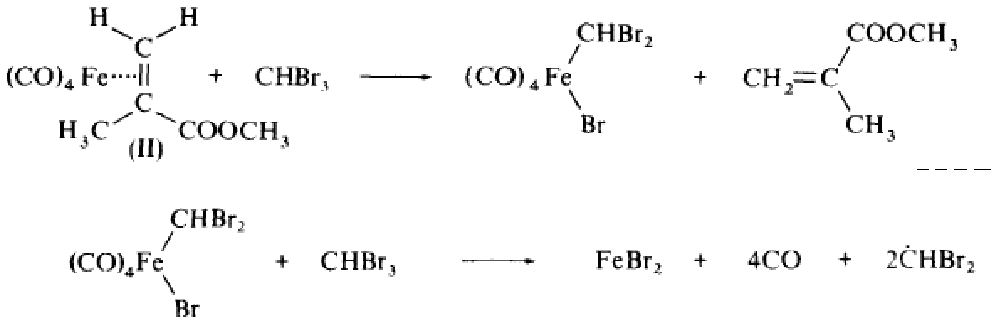
Where M= monomer molecule

More complex reactions are also possible, for example, with other metal carbonyls in the system, or with certain molecules of type X—Y which may add with splitting of the X—Y bond.

Reactions in equations (1-4) and (1-5) clearly constitute an SN_1 mechanism for ligand replacement. Their occurrence with Group VIA carbonyls and several types of n-donor has been demonstrated by Strohmeier and Dobson and their colleagues . Many examples are known of photochemical substitution in transition metal carbonyls by n and Π-donors, occurring by processes essentially similar to equations (1-4) and (1-5). Ligand exchange by an SN2 route is also possible with more complex carbonyls; here the photoexcited carbonyl reacts directly with the ligand before dissociation .

The species $S\ldots M(CO)_{n-1}$ arising from equations (1-4), (1-5) are the same as the complexes, previously designated as (I), which are formed by the thermal reactions discussed earlier. They would therefore be expected to react with suitable halides in a manner represented by equation (1-3), with generation of free radicals.

Thus, mixtures of simple carbonyls and halides should behave as photoinitiators of free-radical polymerization. Many such systems have been found to function in this way. Complexes formed by irradiation of $Fe(CO)_5$ in the presence of several olefinic monomers (M), including methyl methacrylate, vinyl chloride, styrene, propylene vinyl ethyl ether, and vinyl acetate have been studied by Koerner von Gustorf and colleagues and shown to have the structure MFe(CO)4, in which the iron atom is coordinated to the double bond [e.g. (II), equation (1-6)]. Similar adducts also arise from thermal reactions . Further, it has been demonstrated that irradiation of the carbonyl in the presence of an organic halide leads to photoinitiated polymerization in suitable systems. Initiation, also, occurs when the halide is added to the complex $MFe(CO)_4$ in the dark. It has been suggested that the reactions shown in equation (1-6) for M =methyl methacrylate may be a possible source of free radicals .



----------(1-6)

One can see that reaction in equation (1-6) involves splitting of the halide molecule and addition to the metal atom. Strohmeier and co-workers reported for the polymerization of ethyl acrylate monomer by a number of metal carbonyls and related derivatives in the presence of carbon tetrachloride, also Strohmeier and co-workers made similar observations on vinyl chloride monomer. But they didn't suggest any detailed reaction mechanisms, it seems most probably reactions in equations (1-3)and (1-4) are responsible for photoinitiation. When molybdenum carbonyl dissolved in ethyl acetate is irradiated a yellow solution containing $(EtOAc)Mo(CO)_5$ is formed, according to equations (1-4), (1-5) (M = Mo, S = EtOAc, n = 6) A solution of carbon tetra bromide in methyl methacrylate was added to this liquid and the polymerization happened in the dark at 25°C. The rate of thermal polymerization initiated by $Mo(CO)_6/CBr_4$ (without irradiation) under these conditions is insignificant in comparison.

Obviously a reaction similar to equation (1-3) leads to free-radical generation and initiation under these conditions. However, oxidation of molybdenum proceeds beyond the Mo^{IV} stage, since during reaction the development of a characteristic electron-spin-resonance spectrum, attributable to a Mo^{V} species, may be observed. Oxidation to this level also occurs during the thermal reaction at 80^0C.