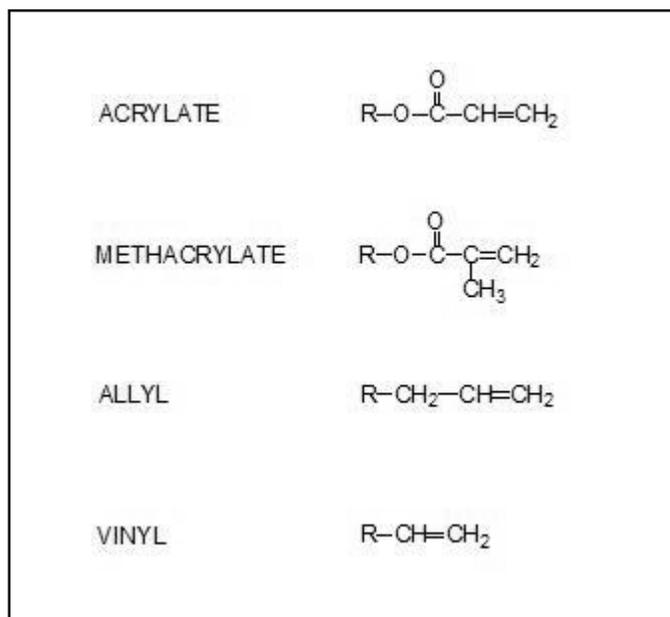


## UV&EB Chemistry and Technology

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The dominant chemistry for both UV and EB curing is the radical polymerization of unsaturated monomers and oligomers. Monomers and oligomers containing acrylate unsaturation are the most commonly utilized in UV&EB initiated radical polymerization due to their higher reactivity compared to methacrylate, allyl or vinyl unsaturation.<sup>1</sup> (See Figure 1.)

**Figure 1. Types of Unsaturation**



While specific formulations will vary greatly depending on end-use requirements, the majority will contain one or more of the following components:

1. **Multifunctional Acrylate Oligomers**, which impart the basic properties of the cured ink or coating.
2. **Multifunctional Acrylate Monomers**, which have the major function of providing lower ink or coating viscosity, but can also be used to modify film properties such as hardness, adhesion and chemical resistance.
3. **Monofunctional Acrylate Monomers**, which lower ink or coating viscosity, and reduce crosslinking in the cured film. Volumetric shrinkage is reduced for improved adhesion; flexibility and impact resistance are increased.

**The acrylate oligomers provide film properties superior to what can be achieved with monomers alone.**

### Acrylate Oligomers

The acrylate oligomers used in UV&EB radical polymerization are typically viscous liquids ranging from a few thousand to greater than 1 million centipoises in viscosity at 25°C. They also typically possess 2 to 6 acrylate groups per molecule, and range in molecular weight from approximately 500 to 20,000.

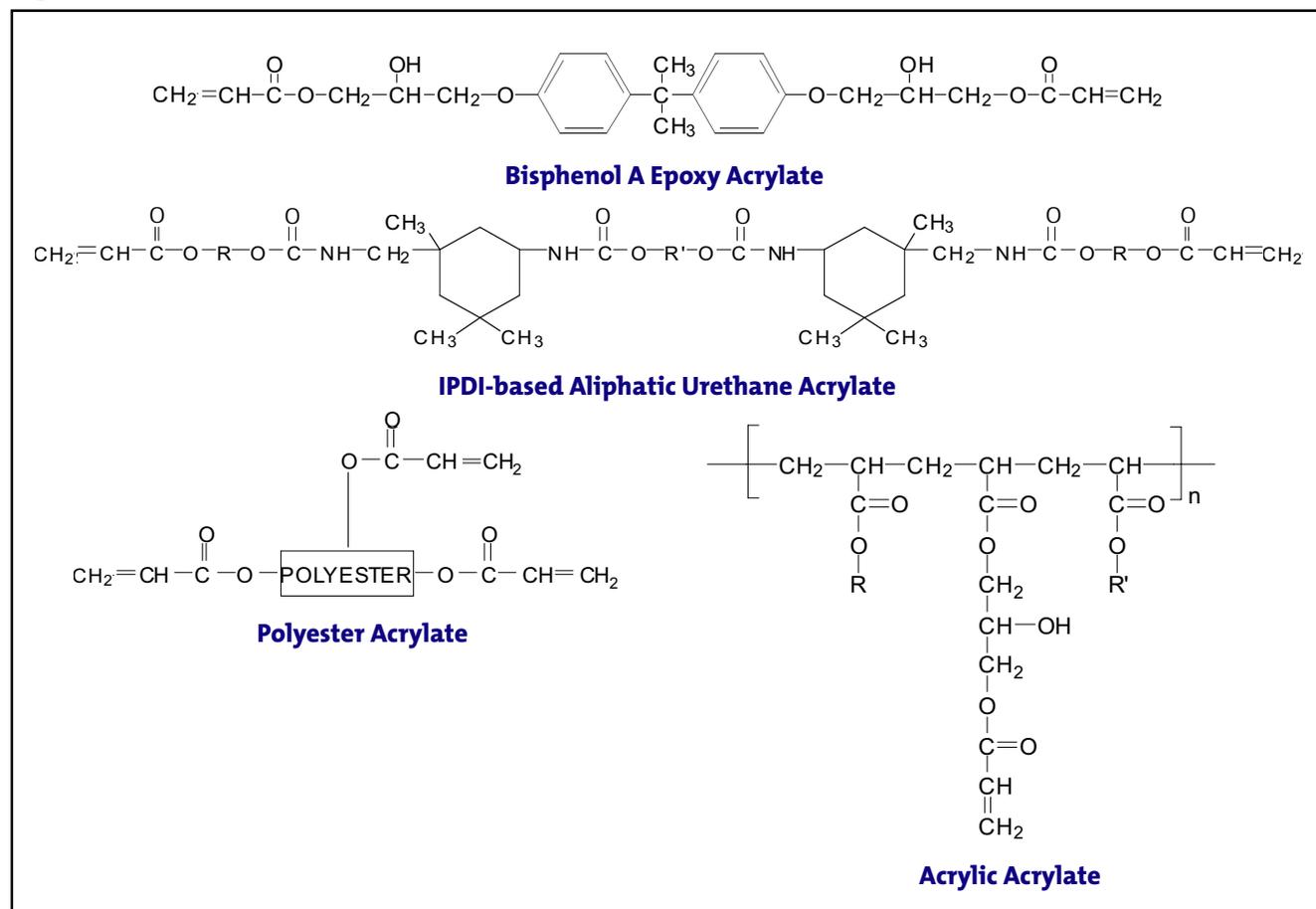
The acrylate oligomers provide film properties superior to what can be achieved with monomers alone. Table 1 lists several types of acrylate oligomers commonly used in UV&EB-curable inks and coatings along with their typical effect and use on ink/coating performance. Figure 2 provides some typical structures of acrylate oligomers.

## Quick summary

- Free radical polymerization of acrylate monomers and oligomers is the most popular chemistry used in the UV&EB curing of inks and coatings.
- The chemical structure of the monomers and oligomers determines the physical properties of a formulation before and after curing.
- By understanding the chemical structures of the materials used in UV&EB curing, one can predict viscosity, reactivity, chemical resistance, flexibility, weathering, adhesion and cost.
- Although the curing mechanism is the same for UV as it is for EB, nitrogen inerting has to be used in EB curing to prevent ozone formation.

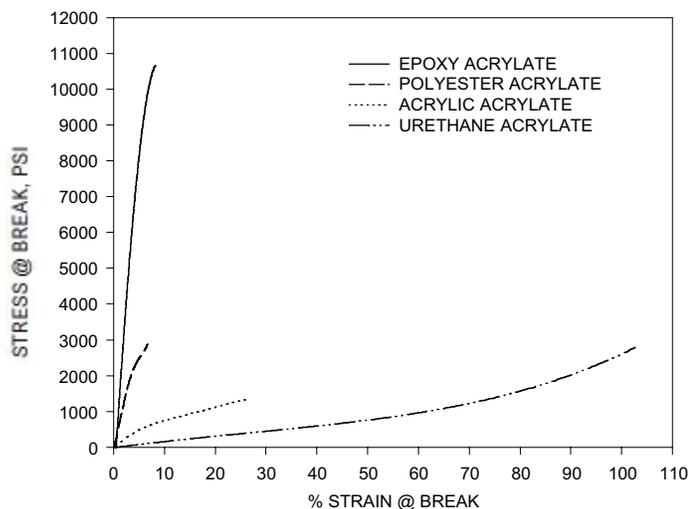
**Table 1. Acrylate Oligomer Types, Performance Effects & Use in Inks and Coatings**

Oligomer Type	Performance Effects	Use in Inks and Coatings
Epoxy Acrylate	Increase reactivity, hardness, chemical resistance; Decrease cost	Oligomer of choice for coatings; Used to lower cost in inks
Aliphatic Urethane Acrylate	Increase flexibility, toughness, weathering; Multi-functionals increase reactivity, hardness, chemical resistance; Decrease yellowing	Increase flexibility or hardness; For tough, weatherable screen inks
Aromatic Urethane Acrylate	Increase flexibility, toughness; Multi-functionals increase reactivity, hardness, chemical resistance; Decrease cost (vs. aliphatic)	Increase flexibility or hardness; Not weatherable
Polyester Acrylate	Increase wetting; Decrease viscosity	For pigment wetting, adhesion; Oligomer of choice for litho inks due to water balance and printability
Acrylic Acrylate	Increase adhesion, weathering	Increase adhesion

**Figure 2. Typical Structures of Acrylate Oligomers**


This variety of oligomer types yields UV&EB-cured polymers with a wide range of physical properties. There are oligomers that form hard, rigid polymers with high tensile strength and modulus, and others that form soft, extensible polymers with high elongation. Graph 1 displays stress/strain curves of UV cured polymers typical of each oligomer type.

**Graph 1. Typical Tensile Properties of Acrylate Oligomer Types\***



\* It should be noted that within each oligomer type there exist a variety of structure variations to modify physical properties. These variations can result in epoxy acrylates with high elongation, and urethane acrylates with high tensile strength and modulus.

### Acrylate Monomers

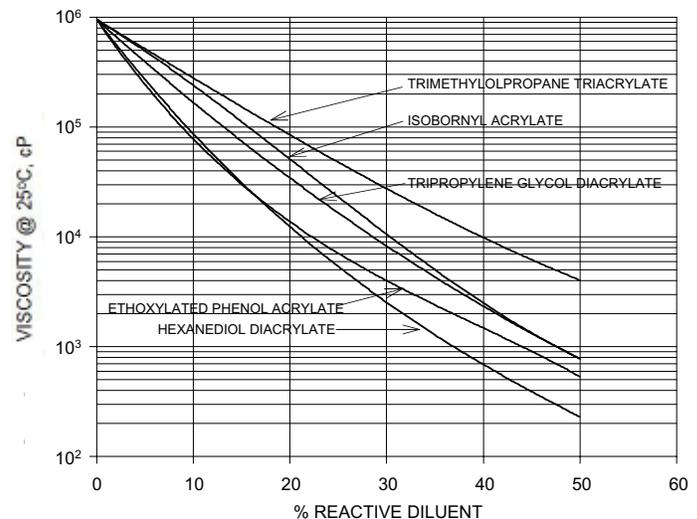
The acrylate monomers used in UV&EB curing typically have from 1 to 4 acrylate groups and range in molecular weight from approximately 150 to 500. They are commonly light colored liquids with viscosities from 5 to 200 centipoises at 25°C. Volatility ranges from low to moderate.

Acrylate monomers act as diluents for the acrylate oligomers in order to achieve ink and coating viscosities suitable for typical application equipment. Graph 2 demonstrates the viscosity reduction of several common monomers on a high viscosity acrylated oligomer.

Unlike solvents, the acrylate monomers co-polymerize with the acrylate oligomers to form an integral part of the cured ink or coating, and can have significant effects on the coating performance.

The functionality of the monomer has a very significant effect on properties of the cured coating. Table 2 lists the typical performance effects of each monomer type. Figure 3 shows the structures of typical monomers.

**Graph 2. Viscosity Reduction of Selected Monomers**



Like the acrylate oligomers, the acrylate monomers within each type exhibit a considerable range of performance. Some monofunctional acrylate monomers will impart greater hardness to a coating than others, while some trifunctional acrylate monomers provide more flexibility relative to other triacrylate monomers.

### Comparison of UV and EB Curing

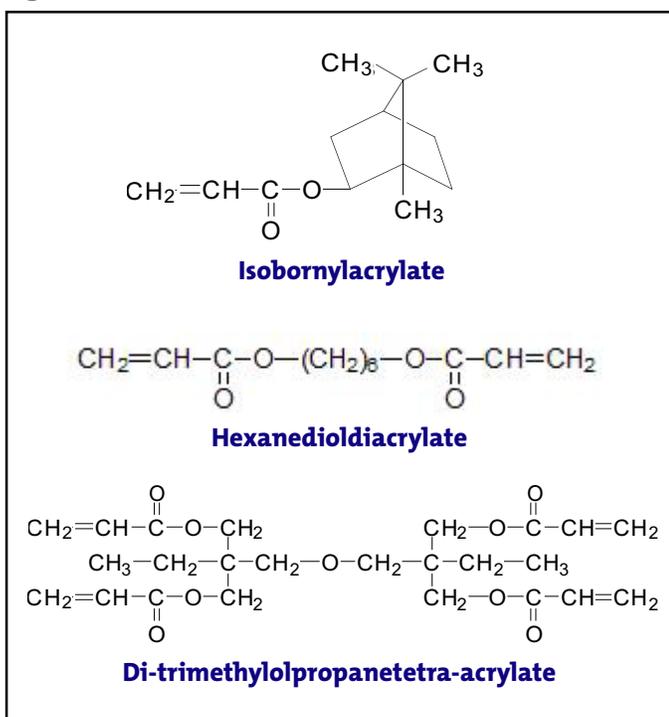
The UV and EB processes share some key performance characteristics. Both are efficient compared to thermal curing methods, consuming many times less energy. Neither process exposes substrates to high temperature, allowing a high degree of crosslinking of inks and coatings on temperature sensitive materials. Both UV- and EB-curing equipment require only a few square meters of installation space. Of greatest significance, both processes can convert low-viscosity liquids to durable polymer inks or coatings nearly instantaneously.

There are also very significant distinctions between the UV&EB curing processes. The radical polymerization common to both processes is inhibited by oxygen in the atmosphere. Advances in the chemistry of UV systems, as well as improvements in UV-curing equipment, have largely overcome the effects of this inhibition, and most UV curing is conducted in air. With EB systems, a nitrogen atmosphere is typically used to avoid ozone formation that results from the interaction of electrons with oxygen. Because of this inert atmosphere, oxygen inhibition is minimal in EB cure.

UV curing is dependent upon sufficient light energy penetrating throughout the ink or coating to insure adequate polymerization at the bottom layer of the film. Materials such as pigments, which absorb the UV light energy required for polymerization, reduce penetration

**Table 2. Acrylate Monomer Types & Performance Effects**

Monomer Type	General Performance Effects	Comments
Monofunctional	Reduce crosslinking, lower shrinkage, increase adhesion, best viscosity reduction, can increase residual uncured material; Decrease chemical resistance and reactivity	May cause swelling of photopolymer printing plates and rollers (not used in litho); Used extensively in screen for adhesion and flexibility
Difunctional	Good compromise between flexibility, hardness, viscosity reduction, chemical resistance and reactivity	Aggressive monomers may cause swelling of photopolymer printing plates and rollers; (Hexanediol diacrylate not used in litho.)
Trifunctional & greater	Increase crosslinking, reactivity, hardness, chemical resistance, scratch resistance, shrinkage; Decrease flexibility and adhesion; Not as effective in reducing viscosity	Some are good pigment wetters (propoxylated glycerol triacrylate); Ethoxylated monomers can improve flow

**Figure 3. Structures of Typical Monomers**

of the light energy, and subsequently limit the thickness at which the ink or coating can be cured. While the UV cure of a clear coating several hundred microns thick is feasible, UV cure of a highly pigmented ink or coating is limited to relatively low-film thickness.

In EB curing, the opacity of the coating is irrelevant. The energy potential (accelerating voltage) of the electrons and the density of the coating govern the depth to which a coating can be adequately polymerized. Most EB-curing units are capable of generating accelerating voltages of 150 KeV or more. In most cases, 150 kilovolt electrons can easily penetrate films opaque to UV.

EB curing equipment is a source of ionizing radiation. When accelerated electrons strike metal, X-rays are generated. Suitable shielding is required to prevent exposure to these X-rays. EB equipment used to cure inks and coatings contains thin lead shielding that lines the accelerating and curing chambers. This shielding allows personnel to work in close proximity to the operating EB equipment.

It must be noted that with UV equipment, direct exposure to the UV lights must be avoided. This is relatively easily accomplished with engineering controls. Also, in UV curing, residual photoinitiator fragments can impart odor to the cured ink or coating and increase yellowing with exposure to sunlight, though specialty photoinitiators are available that address these potential shortcomings. EB curing avoids these issues since photoinitiators are not required.

High EB doses can negatively affect some plastic and paper substrates, reducing strength or causing embrittlement. UV curing does not generally pose this problem.

Finally, the relative complexity of EB-curing units results in significantly higher equipment cost, roughly three times that for a typical UV installation.<sup>3</sup>

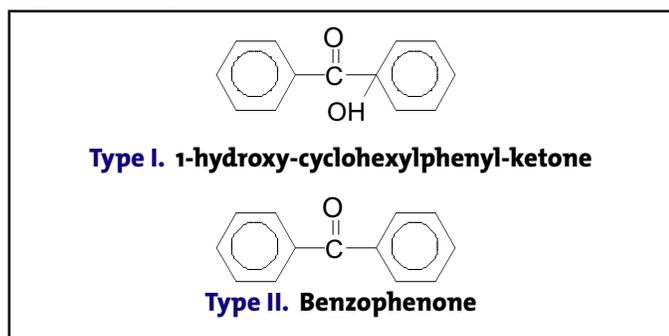
### Photoinitiators

Photoinitiators are chemicals that form energetic radical species when exposed to UV light. They are essential ingredients in UV-curable inks and coatings, necessary in order to obtain polymerization. Depending on factors such as film thickness, UV-light source, and particular ink or coating performance requirements, the amount of photoinitiator in a UV ink or coating formulation can range from approximately 0.5-15%. Photoinitiator systems vary widely in composition depending on the particular requirements needed: very

thin ( $\leq 6\mu$ ) clear coatings vs. thin ( $\leq 25\mu$ ) pigmented inks or coatings vs. very thick ( $\geq 100\mu$ ) clear coatings.

There are two main types of free radical photoinitiators, Type I and Type II.<sup>4</sup> Figure 4 shows the structures of typically used Type I and Type II photoinitiators. Type I photoinitiators are those compounds that undergo cleavage upon irradiation to generate two free radicals. Generally, only one of these free radicals is reactive and goes on to initiate polymerization. Benzoin and benzoin ethers were some of the earliest used Type I photoinitiators. Today, 1-hydroxy-cyclohexylphenyl-ketone is widely used.

**Figure 4. Types of Photoinitiators**



Type II photoinitiator systems are those compounds that form an excited state upon irradiation, and then abstract an atom or electron from a donor molecule (synergist). The donor molecule then acts as the initiating species for polymerization. A widely used Type II photoinitiator system uses benzophenone. Tertiary amines are typically used as synergists because they react with benzophenone very efficiently, and also serve to retard the inhibition of polymerization by oxygen. Acrylated tertiary amine compounds are used when odor and extractables are of concern.

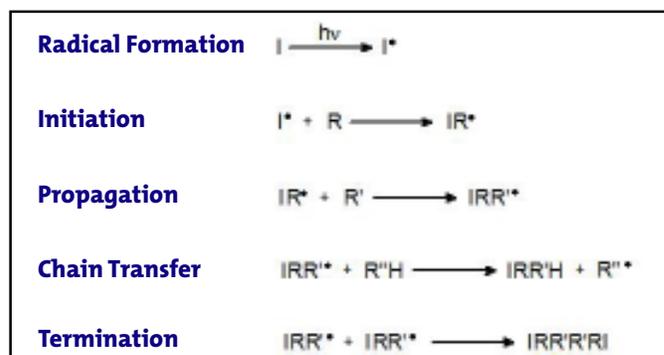
In EB curing, the core ingredients of the coating formulations are the same as in UV curing. However, the addition of the photoinitiator is not necessary. The electrons generated by the EB-curing equipment carry sufficient energy to lead to initiation of the polymerization process.

### Free Radical Polymerization

The free radical UV-polymerization process is shown in Figure 5.<sup>5</sup> In this figure, the photoinitiator (I) absorbs light and forms a radical species. This radical species then reacts with an acrylate functional material (R) in the initiation step. Propagation occurs as the reactive species or growing polymer ( $IR^*$ ) reacts with additional acrylate functional materials. The propagation step is the process that builds the molecular weight and the crosslinking of the polymer. Propagation continues for as long as the

reactive species can locate an acrylate functional material, or until chain transfer or termination occurs. At some point in the process, the mobility of the growing polymer ( $IRR^*$ ) will be limited by the viscosity build of the system (caused by the increase in molecular weight and crosslinking of the polymer). This lack of mobility will limit its ability to find acrylate functional materials, and the propagation reaction will stop. Chain transfer occurs when the growing polymer abstracts a hydrogen atom from a donor molecule. This chain transfer stops the polymerization of the growing polymer, and begins the formation of a new polymer. Thus, chain transfer can be used to limit the molecular weight of a polymer. Termination occurs when two growing polymer chains react with each other to stop polymerization.

**Figure 5. UV Free Radical Polymerization Process**



In EB-free radical polymerization, there is no specific radical formation step as there is with UV, since photoinitiators are not used. The formation of initiating radicals usually involves the interaction of the electrons onto the acrylate functional materials themselves thus forming the reactive species ( $R^*$ ). The reactive species then reacts via the same propagation, chain transfer, and termination steps as with UV.

### Oxygen Inhibition

Oxygen, which is present in ambient air as molecular oxygen, is an effective inhibitor of free radical polymerization.<sup>6</sup> It can also be present as dissolved oxygen in the raw materials used in UV&EB formulations. Molecular oxygen is a diradical and can react with the free radicals that are generated during the radical formation, initiation, and propagation steps of polymerization, effectively removing those free radicals from the polymerization process. Hence, chain growth is stopped and there is "poor cure." Oxygen inhibition most often manifests itself as a thin, unpolymerized layer of material at the surface of a film (where the air is located).

Several methods of mitigating oxygen inhibition have been developed over the years, and are shown in Table 3. The most common methods are use of Type II photoinitiators or use of inert atmospheres. In Type II systems, the amine radical preferentially reacts with oxygen to form a peroxy radical. The peroxy radical then abstracts a hydrogen atom from another amine molecule, forming hydroperoxide and a new amine radical that can initiate polymerization.

**Table 3. Methods to Mitigate Oxygen Inhibition**

- Use of Type II photoinitiators
- Increasing UV radiation intensity, especially shorter wavelengths
- Curing in an inert atmosphere
- Addition of oxygen scavengers
- Addition of waxes
- Use of shielding films
- Use of dye sensitizers
- Use of surface-active initiators
- Use of high photoinitiator concentration

**Crosslinking of Polymers**

Crosslink density is an indication of how tightly a polymer network is interconnected, and is predictive of many of the properties of the final ink or coating.<sup>7</sup> The weight per acrylate double bond of the formulation can be used to provide an indication of the crosslink density. To obtain the weight per acrylate double bond, divide the average molecular weight of the formulation by the average functionality of the formulation. The most common method of reducing crosslink density is through the addition of mono-functional monomer to the formulation. Table 4 lists some properties that are affected by crosslink density or weight per double bond.

**Table 4. Effect of Weight per Double Bond on Properties of Inks and Coatings**

Low	Weight per Double Bond	High
	<b>Property</b>	
Faster	Cure Speed	Slower
Lower	Flexibility	Higher
Higher	Tensile Strength	Lower
Higher	Shrinkage	Lower
Higher	Chemical Resistance	Lower
Worse	Adhesion	Better

**UV&EB Cationic Curing**

While radical curing chemistry accounts for a large majority of UV&EB-curable formulations, another significantly utilized chemistry is the UV&EB-initiated cationic polymerization of epoxide functional materials.

In UV&EB-cationic curing, a reactive chemical species is generated by the disassociation of a salt molecule (typically an arylsulfonium or aryl iodonium salt molecule) on exposure to UV or EB energy.<sup>8</sup> This reactive species opens the epoxy ring structure causing polymerization. Figure 6 shows the polymerization process for UV-cationic systems. The steps of this process are analogous to those of the free radical process, acid formation (instead of radical formation), initiation, chain reaction (or propagation), chain transfer, and termination. For EB-cationic polymerization, an initiator is necessary, and acid is formed by interaction of the initiator with the electrons.<sup>9</sup>

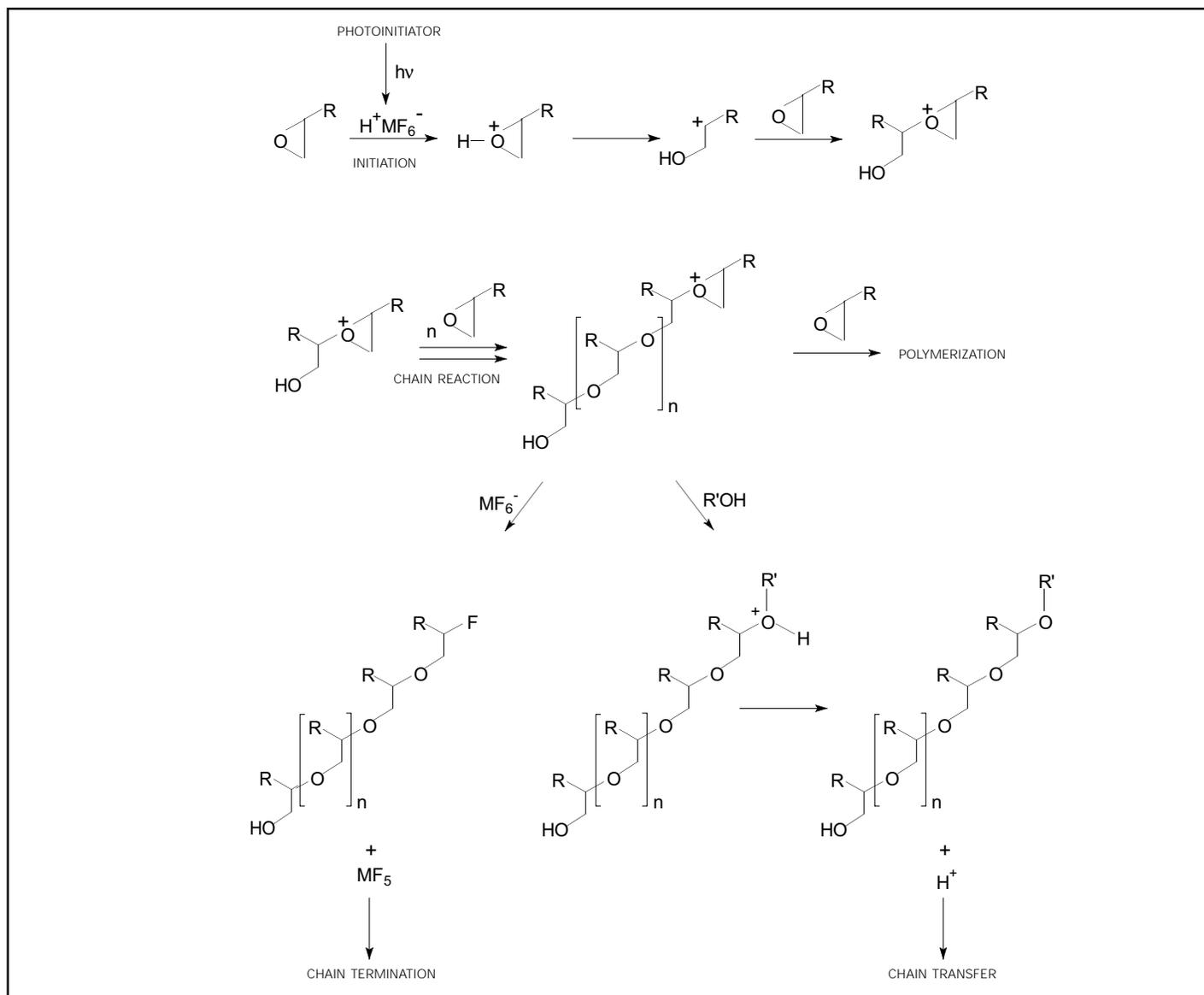
Cycloaliphatic epoxides are the most commonly used formulation component due to their higher reactivity (compared to glycidyl ether epoxies) and their relatively low viscosity. Hydroxy functional materials can co-polymerize with the epoxides, and polyols are commonly used to modify coating properties. Vinyl ether monomers also react cationically. They are sometimes used as reactive diluents. Vinyl ether oligomers are also available.

**In UV&EB-cationic curing, a reactive chemical species is generated by the disassociation of a salt molecule (typically an arylsulfonium or aryliodonium salt molecule) on exposure to UV or EB energy.<sup>8</sup>**

UV&EB cationic curing systems can offer some performance advantages over radical curing systems. The adhesion of cationic systems is generally superior to radical systems, particularly on substrates such as unprimed metal and plastics. UV&EB cationic curing systems (those that involve the ring opening reaction) have significantly lower shrinkage upon polymerization.<sup>10</sup> Table 5 highlights some significant distinctions between UV&EB radical and cationic curing systems.

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**Figure 6. UV Cationic Polymerization Process**

**Table 5. Comparison of Radical & Cationic Curing Systems**

Radical	Cationic
Wide variety of raw materials	More limited raw materials
Inhibited by oxygen	Not inhibited by oxygen
Not inhibited by high humidity	Inhibited by high humidity
Not inhibited by basic materials	Inhibited by basic materials
Full cure in seconds	Full cure in hours unless given thermal "bump"
Adhesion: less	Adhesion: greater
Shrinkage: greater	Shrinkage: less
Depth of cure: greater	Depth of cure: less
Initiator needed for EB cure: no	Initiator needed for EB cure: yes

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