

**PRODUCTION AND CHARACTERIZATION OF
ULTRAVIOLET CURED PALM OIL BASED
RESIN**

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**PRODUCTION AND CHARACTERIZATION OF
ULTRAVIOLET CURED PALM OIL BASED
RESIN**

by

TAI NYOK LING

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requirements for the Degree of
Master of Science**

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LIST OF SYMBOLS

$\frac{d\alpha}{dt}$	Rate of reaction
α	Degree of conversion or the fraction of the sample that reacted
β	Heating rate
t	Time
n	Reaction order
k	Arrhenius rate constant
Z	Preexponential constant
E_a	Activation energy
R	Universal gas constant
T	Absolute temperature
W	Weight

LIST OF ABBREVIATIONS

%	Percentage
UV	Ultraviolet
VOC	Volatile organic compound
GMA	Glycidyl methacrylate
ASTM	American Society for Testing and Material
EFB	Empty fruit branches
Eq	Equivalent
M	Monomer
PI	Photoinitiator
R_1, R_2	Radical fragments of the photoinitiator
UV	Ultraviolet
FTIR	Fourier transform infrared spectroscopy
DSC	Differential Scanning Calorimeter
TGA	Thermogravimetry analysis
GC	Capillary gas chromatography

**PENGHASILAN DAN PENCIRIAN RESIN BERDASARKAN MINYAK
KELAPA SAWIT YANG DIMATANGKAN MELALUI SINARAN
ULTRAUNGU**

ABSTRAK

Dalam kajian ini, resin berasaskan minyak kelapa sawit yang dimatangkan melalui sinaran ultraungu telah disediakan melalui pengubahsuaian minyak kelapa sawit dengan gliserol dan glisidil metakrilat (GMA). Dalam kajian awal, parameter-parameter seperti jumlah pemangkin yang diperlukan, suhu tindakbalas, masa tindakbalas dalam pengubahsuaian kimia telah dikaji. Daripada analisis *Fourier Transform Infrared* (FTIR), didapati GMA telah berinteraksi secara kimia dengan monogliserida (MG), kenaikan puncak 1630 cm^{-1} dalam spectrum FTIR telah diperhatikan apabila lebih GMA telah digunakan dalam pengubahsuaian kimia tersebut. Dalam kajian seterusnya, kesan nisbah gliserol/ minyak kelapa sawit (MG) kepada GMA/MG dalam penyediaan resin MG-GMA telah dikaji. Didapati bahawa, nombor hidroksil MG meningkat apabila lebih banyak gliserol digunakan dalam campuran gliserol/minyak kelapa sawit dalam proses alkoholisis. Ini menunjukkan bahawa kebanyakan kumpulan hidroksil adalah disumbangkan oleh MG seperti yang ditunjukkan dalam keputusan kromatografi gas kapilari (GC). Berat purata berat molekul (M_w) resin meningkat apabila nisbah GMA/MG meningkat sehingga mencapai ke titik ambang yang mana selepas itu M_w menurun. Fenomena ini disebabkan oleh berlakunya homopempolimeran monomer GMA semasa rawatan MG dengan GMA. Corak yang sama telah ditunjukkan dalam keputusan kelikatan. Kandungan gel filem MG-GMA termatang melebihi 98%. Selain itu, didapati kekerasan, perekatan lorekan silang dan kestabilan terma filem MG-GMA boleh dipengaruhi oleh jumlah GMA serta gliserol yang digunakan dalam penyediaan MG. Kedua-dua kalorimetri pembezaan (DSC) and analisis termogravimetri (TGA) menunjukkan bahawa penambahan GMA dalam resin MG-GMA telah meningkatkan kestabilan terma pada filem termatang UV. Kinetik penguraian terma filem MG-GMA termatang menunjukkan kaedah *Friedman* adalah serupa dengan kaedah *Ozawa-Flynn-Wall* (O-F-W). Kinetik FTIR pematangan (RT FTIR) resin MG-GMA menunjukkan penukaran ikatan berganda dan kadar pempolimeran resin adalah dipengaruhi oleh kepekatan kumpulan ikatan berganda.

PRODUCTION AND CHARACTERIZATION OF ULTRAVIOLET CURED PALM OIL BASED RESIN

ABSTRACT

In this study, a Ultraviolet-radiated curable resin from palm oil was prepared by modifying palm oil with glycerol and glycidyl methacrylate (GMA). In the preliminary study, different parameters such as the amount of catalyst needed, reaction temperature and time for this chemical modification had been studied. From the Fourier Transform Infrared (FTIR) analysis, GMA was proved to be chemically attached to the monoglyceride (MG), an increment at peak 1630 cm^{-1} in FTIR spectrum was observed when more GMA was used in the chemical modification. In the subsequent study, the effect of different glycerol/palm oil (MG) to GMA/MG ratio in the preparation of MG-GMA resin was studied. It was noticed that hydroxyl number of MG increased as more glycerol was used in the glycerol/palm oil mixture in alcoholysis process. This indicated that most of the hydroxyl groups were contributed by MG as shown by capillary gas chromatography (GC) results. The weight average molecular weight (M_w) of the resin increased as the ratio of GMA/MG was increased to a threshold point after which it decreased. This phenomenon was due to homopolymerization of GMA monomer during the treatment of MG with GMA. A similar trend was also observed in the result of viscosity. The gel content of the cured MG-GMA film was more than 98%. The hardness, cross hatch adhesion and thermal stability of the MG-GMA film was influenced by the amount of GMA used as well as the glycerol used in MG preparation. Both differential scanning calorimetry (DSC) and thermogravimetry analysis (TGA) showed that the increment of GMA amount in MG-GMA resin had improved the thermal stability of the UV-cured films. Thermal decomposition kinetics of MG-GMA film discovered that Friedman method showed a good agreement with that of Ozawa-Flynn-Wall (O-F-W) method. Real time FTIR (RT FTIR) curing kinetics of MG-GMA resin showed that double bonds conversion and polymerization rate of the resin were affected by the concentration of unsaturation groups.

CHAPTER 1 INTRODUCTION

1.1 Background

Polymer resins prepared from renewable natural resources have become increasingly important due to the low cost, ready availability as starting materials, and biodegradability (Li et al., 2003, Mosiewicki et al., 2005). The continuously decreasing petroleum based resources coupled with the ever increasing environmental concerns and legislation constrains, imposing numerous restrictions on the use of chemicals that may generate volatile organic compound (VOC). Synthesized resins as well as other chemicals utilized in various industrial applications are oppressed day by day due to the mentioned causes. Therefore, there is a need to evaluate, identify and use products and processes, that employ rapid, energy efficient and non-polluting polymerization techniques.

Research efforts are already directed towards reducing VOC which have proven to have an adverse effect on the environment and human health depending on the chemicals used. If we look around us today, there is a world of ultraviolet (UV) or electron beam (EB) products. These products, in some way, have utilized or could utilize UV or EB radiation techniques for their curing of coatings in various sectors of applications such as graphic arts, microelectronics inks and adhesives. The industry has made the shift since 1990; they have embraced sustainable concepts (Weiss, 1997, Koleske, 2001, Chen et al., 2011). UV radiation curing now represents one of the new techniques that are replacing the use of conventional thermally curable or low solids, solvent borne coatings. Besides the ecological aspect of minimizing the VOC and ensuring that the resins are environmentally friendly, ultra

fast cure speed, room temperature operation, consequent low energy consumption, and high-quality end products are additional aesthetic and economic factors of noteworthy significance (Paul, 1996, Crivello et al., 1997, Kumar et al., 2006, Rozman et al., 2010). Thus UV/EB curable resins are popular and it should play a key role in producing materials by non-polluting polymerization process.

While the petroleum based resources are diminishing due to the depleting of their natural resources, the use of vegetable oils to replace the petroleum based resources in polymer resins in the world market is ever increasing. World market for vegetable oils witnessed a significant rise in terms of value and volume over the last decade, the total production of vegetable oil in the world at 1997 is 73 million metric tons, reaching 146 million metric tons at 2010 and is estimated to reach 169 million tons by the year 2015 (United Soybean Board, 2005, Jose, 2010, American Soybean Association, 2011). Hence, it is high time to find alternative sources from which these prepolymers (oligomers) or monomers that can be conveniently, easily and cheaply prepared. For these reasons, vegetable oils have attracted considerable amount of attention as a raw material for polymeric material preparation. Vegetable oils such as linseed oil and tung oil have long found various uses in paint and varnishes industries. Soybean oil, safflower oil, castor oil, sunflower oil and canola oil have also been used in preparation of resin (Rheineck and Cummings, 1966, Li and Larock, 2000, Li et al., 2001, Güner et al., 2002, Kolot and Grinberg, 2004, Mosiewicki et al., 2005, Kong and Narine, 2007).

Vegetable oils are considered to be one of the most important classes of renewable sources. Vegetable oil or plant oils' constituents made up of complex

multi component mixtures of fatty acids and glycerol ester, those triglycerides with numerous active sites amenable to chemical reactions to be converted into useful polymeric materials (Khot et al., 2001, Tan and Chow, 2010). The usages of vegetable oils are well known in the manufacturing of alkyl resin, however, relatively little work has been reported on the conversion of fats and oils to high molecular weight polymers. Since the unsaturated group in the fatty acid are unable to be polymerized, an interesting alternative is to modify the triglyceride structure by attaching reactive groups to the molecule.

In Malaysia, our main agriculture product palm oil which constitutes 41.37% of the total world production is a type of vegetable oil. With nearly 4.85 million hectares of planted land and 416 mills operating across the country, Malaysian palm oil industry is expected to generate over 19.8 million tonnes of Empty Fruit Bunches (EFB) and 60 million tonnes of palm oil mill effluent (MPOB, 2009, Lim, 2010, Ng et al., 2011). In the year 2000, Yusof reported that Malaysia monopolized half of the world's palm oil production (Yusof, 2002). About 80 to 85% of the total world production of palm oil was dominated by Malaysia and Indonesia in 2008, in which, they held a world market share of approximately 31% (Tan and Chow, 2010). Palm oil is a non drying oil which cannot be polymerized when exposed to air. It can only be polymerized when an effective and suitable modification is conducted to introduce the appropriate reactive groups. Thus, it is believed that by attaching a functional group to palm oil molecule, the behaviour of palm oil change from non-curable palm oil to a curable product. The technology of palm oil in the coatings industry area is relatively new and in a steady course of development, hence, more research and developments need to be carried out. Furthermore, palm oil is

considered to be a more suitable raw material for the production of coatings as compared to soya bean oil, tung oil, castor oil and linseed oil because it contains lower levels of unsaturation.

Driven by stricter environment and legislation constraints, coatings industry is moving through a major revolution to a “greener” industry. It is of our interest to find out to what extent palm oil or its products could be applied in coatings industry. In this study, UV curable resin was prepared from monoglyceride (MG). MG produced from palm oil was treated with glycidyl methacrylate (GMA) in order to introduce unsaturated groups to MG (MG-GMA) through etherification reaction. Etherification reaction is believed as one of the novelty in this research. Then, MG-GMA was mixed with different percentages of photoinitiator to study the extent of reaction of the former. Other parameters studied relative to GMA modification of MG were reaction temperature, reaction time and the amount of catalyst. It is believed that the findings from this research could be a worthy contribution to the advancement of green technology which will become increasingly important in the future because of the ultimate goal of supporting a sustainable world by producing a green product.

1.2 Objectives

- To determine the reaction condition in the preparation of MG-GMA resin.
- To study the effect of glycerol/ palm oil ratio (MG) on the properties of cured MG-GMA.
- To study the effect of GMA/MG ratio on the properties of cured MG-GMA.
- To investigate the reactivity of the prepared palm oil based UV curable resin with photoinitiator in UV curing systems.

CHAPTER 2 LITERATURE REVIEWS

2.1 Surface Coatings

Today, many objects that we come across in our daily lives, including the house in which we live and the materials we use, such as, toothbrushes, pots and pans, refrigerators, televisions, computers, cars, furniture etc, all come under the “umbrella” of coated materials. Likewise, fields such as military applications, vehicles, artilleries and invisible radars and aerospace products all involve the widespread use of coated materials. Clearly, the importance of coatings has increased hugely during the modern era of technology. In general, paints, varnishes and lacquers (opaque or colored varnishes) are termed as coatings (Gradzielski, 2008).

Coatings may be described by their appearance (e.g., clear, pigmented, metallic, or glossy) and by their function (e.g., corrosion protective, abrasion protective, skid resistant, decorative, or photosensitive). Coatings are mainly applied on surfaces for decorative, protective, or functional purposes, but in most cases it is a combination among them (Goldschmidt and Streitberger, 2003, Schwalm, 2007a).

Based on applications, coatings may also be classified as:-

- (i) architectural (decorative) coatings
- (ii) product coatings used by original equipment manufacturers (OEM coatings)
- (iii) special purpose coatings, and specialty (maintenance) coatings
- (iv) miscellaneous coatings

Architectural coatings include all paints, varnishes, and lacquers sold for direct application to either interior or exterior surfaces of residential, commercial, institutional, and industrial buildings. Typical types of paint sold as architectural coatings include house paint, stains, and undercoats (i.e. primers and sealers). They are often called trade sales paints. They are sold directly to painting contractors and do-it-yourself users through paint stores and other retail outlets (Weiss, 1997, Wicks, 2007).

Product coatings, also called industrial coatings, are applied in factories on products such as automobiles, appliances, magnet wire, aircraft, furniture, metal cans, chewing gum wrappers—the list is almost endless. This market is often called the OEM market, that is, the original equipment manufacturer market. The volume of product coatings depends directly on the level of manufacturing activity. This category of the business is cyclical, varying with OEM cycles. In most cases, product coatings are custom designed for a particular customer's manufacturing conditions and performance requirements. The number of different types of products in this category is much larger than in the others; research and development requirements are also higher (Weiss, 1997, Wicks, 2007).

Special purpose coatings include industrial coatings applied outside a factory, along with a few miscellaneous coatings, such as coatings packed in aerosol containers. It includes refinish coatings for cars and trucks that are applied outside the OEM factory (usually in body repair shops), marine coatings for ships (they are too big to fit into a factory), and striping on highways and parking lots. It also

includes maintenance paints for steel bridges, storage tanks, chemical factories, etc (Wicks, 2007).

According to Wicks (2007), the Census Bureau defines miscellaneous paint and coating products as paint removers, thinners, pigment dispersions, glazing compounds, etc. The terms 'paint' and 'surface coating' are often used interchangeably. In the strictest sense, the term "surface coating" is the more general description of any material that may be applied as a thin continuous layer to a surface, whereas, the term "paint" refers to any pigmented materials used in a film layer as distinct from clear films which are more properly called lacquers or varnishes (Lambourne and Strivens, 1999, Zarras et al., 2007).

A paint coating is basically a polymer resin, dispersed in a solvent, modified by additives to achieve specific properties and pigments for providing colour, corrosion protection and other important properties. The nature of the coating revolves round the type of resin that is used, whether alkyd, epoxy, urethane, vinyl or polyester (Khanna et al., 2008, Gradzielski, 2008). Depending on their compositions, paints can be divided into three groups: solvent-borne, water-borne and solvent-free (100% solid). Solvent-borne paints consist of resin, additives and pigments that are dissolved or dispersed in organic solvents. Similarly, in water-borne paints the ingredients are dispersed in water. In solvent-free compositions, the paints do not contain any solvent or water and the ingredients are dispersed directly in the resin (Gradzielski, 2008).

Coatings dry by several mechanisms. The simplest is by evaporation of the solvent. The second most common mechanism is reaction with oxygen. Oil based coatings such as alkyd coatings dry by the reaction of oils with oxygen. But this process is rather slow; it needs several days to completely cure an alkyd coating. The third main mechanism of curing is the chemical reaction between resin and hardener in two-component systems. As the resin and the hardener or catalyst are mixed, crosslinking starts and with time the hardness of the mixture increases till it becomes the complete solid. The fourth mechanism is radiation curing, where the paint is dried by exposing it to microwave radiation or UV radiation. In the fifth case, the paints are dried by heating. This process is called stoving. In coil coatings, where the strips are coated online, the immediate coated strip is passed through a long furnace, maintained at a fixed temperature (Khanna et al., 2008).

Over the past 25 years, coatings technologies have been influenced by the need to lower VOC emissions because of their detrimental effect on air quality as well as to reduce the use of costly petroleum based solvents (Weiss, 1997, Baghdachi, 2009, Chen et al., 2011). Concern about toxic hazards has led to the need to change many raw materials that were traditionally used in coatings (Wicks, 2007). Owing to the raw material cost rising and the stricter environmental regulations, the coatings industry is transforming to a “greener” industry by incorporating more alternative renewable raw materials and “greener” technologies such as radiation cure, high solids, and waterborne coating technologies (Joshi et al., 2008, Chen et al., 2011). The industry has made the shift since 1990s. It has embraced sustainable concepts. The future of green technology is bright because its ultimate goal is to support a sustainable world by producing environment friendly products. Waterborne, powder,

UV-curable and high solids coatings have shown a significant growth (Weiss, 1997, Baghdachi, 2009).

Although waterborne, powder and high solids coatings have emerged recently in which solvent emission is minimized, they still do not meet the stringent VOC regulations. The key features of radiation curing are that the reactive monomeric liquids used eliminate the need for volatile solvents, thereby meeting existing and forthcoming VOC regulations (Rao et al., 1995, Groshart, 1997). Radiation cure coating technology including UV (ultraviolet) and EB (electron beam) cure has the capability to produce high performance coatings with high productivity, low energy consumption and extremely low VOC emissions. It has been enjoying fast market growth since its introduction to the coatings industry. Utilization of biorenewable raw materials in the radiation cure coatings is a promising “green + green” solution to the challenges that the coatings industry is facing (Rao et al., 1995, Groshart, 1997, Chen et al., 2011).

2.2 Resin (Binder)

Resins are the generally solid, sticky materials that hold the system together. They are also called binders (Lambourne and Strivens, 1999, Tracton, 2005, Talbert, 2007). The resin or binder is the film forming element of a coating or adhesive. In simple terms, a coating’s resin is the “glue” which holds together, and which is principally responsible for providing adhesion to a substrate, binds pigments and extenders together, and determines important properties of the coating film such as durability, flexibility and gloss. The character of the resins has the greatest impact on

the performance of the coatings, and defines its properties (Marrion, 2004, Talbert, 2007, Wicks, 2007). With a few exceptions, the resin is nearly always organic, consisting of natural resins or man-made polymers or prepolymers (Weldon, 2009). The formulation of a paint material and the particular chemicals used are influenced by the particular resin or resin combination used. When in a solvent, resins are the vehicles for the system (Tracton, 2005, Talbert, 2007).

Paint binders may be referred to as convertible and nonconvertible types. Convertible paints are materials that are used in an unpolymerized or partially polymerized state and undergo reaction to form a solid film after application to the substrate. Nonconvertible paints are based on polymerized binders dispersed or dissolved in a medium that evaporates after the coating has been applied to leave a coherent film on the substrate surface. Convertible binders include oils, oleoresinous varnishes, alkyds, amino resins, epoxy resins, phenolic resins, polyurethane resins, and thermosetting acrylics. Nonconvertible resins such as cellulose, nitrocellulose, chlorinated rubber, and vinyl resins will not be covered in this study, because they are usually used in low solid, high-solvent content coatings that are not compliant for the majority of modern industrial applications (Talbert, 2007).

2.3 Natural oils based resin

Natural resins and oils have a long history being used in the manufacture of decorative and protective coatings. They are derived from natural sources such as plants, animals and fossilized remains (Sharma and Kundu, 2006, Weldon, 2009, Chen et al., 2011).

There has been a growing trend in utilizing the vegetable oils extensively as raw materials for the preparation of resins and polymeric materials due to their inherent biodegradability, low cost, societal favourably advantages and availability. The main intention of using vegetable oil is to replace the traditional use of petroleum based raw materials due to the environment issue. Various researches have been conducted to make full use of linseed, castor, soya, safflower, sunflower, canola, tung, tall oils etc (Rheineck and Cummings, 1966, Li et al., 2001, Güner et al., 2002, van Haveren et al., 2007, Kong and Narine, 2007).

Vegetable oils are tri-glyceride esters of fatty acids, the general structure of which is shown in Figure 2.1. Triglycerides comprise three fatty acids joined by a glycerol center (Khot et al., 2001). The fatty acids bonded in the oils are relatively long-chain, aliphatic, unbranched monocarboxylic acids; they may be saturated or varying highly unsaturated (containing double bonds) (Brock et al., 2000). Most of the common oil contains fatty acids that vary from 14 to 22 carbons in length, with 1– 3 double bonds (Khot et al., 2001). The fatty acid distribution of several common oils is shown in Table 2.1. In addition, there are some oils comprise fatty acids with other types of functionalities (e.g., epoxies, hydroxyls, cyclic groups and furanoid groups) (Sharma and Kundu, 2006).

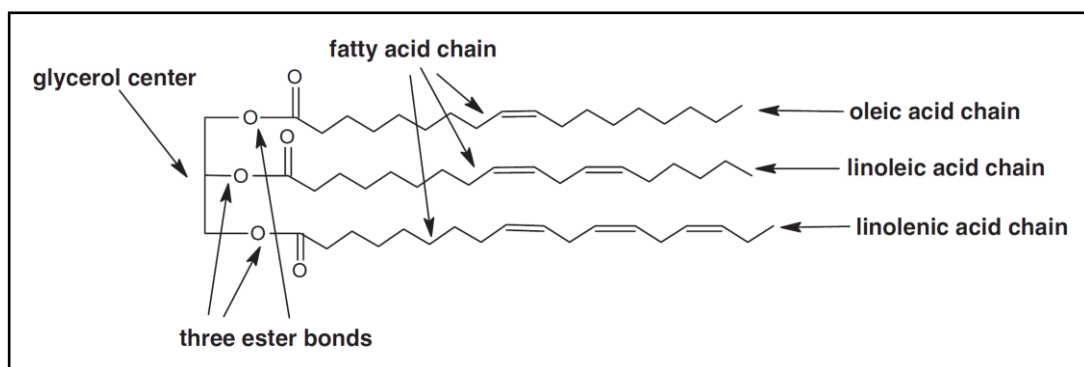


Figure 2.1: The triglyceride chain containing three fatty acid chains joined by a glycerol center (Li et al., 2001)

Table 2.1: The type and percentage present of fatty acid compositions of some commonly used oils (Oldring et al., 2002)

Type of Fatty Acid and % present	Copra	Palm	Castor Oil	Dehydrated Castor Oil	Olive	Groundnut	Rape	Cottonseed	Soy bean	Sunflower	Poppy seed	Safflower	Linseed	Perilla	Ortica	Tung oil	Refined tall oil	Tallow
Saturated																		
Caprylic	8																	
Capric	7																	
Lauric	49																	
Mystiric	17	2									1							4
Palmitic	9	39	1	1	14	7	2	20	7	6	4	5	6	4	6	4	4	31
Stearic	2	5	1	1	1	3	1	2	3	4	3	2	5	3	4	1	3	17
Arachidic						4	2	1	1									
Behenic						2												
Unsaturated																		
Oleic	6	45	2	2	76	64	20	35	30	42	36	20	21	8	8	7	46	43
Ricinoleic			92	11														
Erucic							50											
Linolenic	2	9	4	85	9	20	22	42	54	47	62	72	17	38	8	10	35	5
Linoleic							3		5	1		1	51	47			12	
Oleostearic																78		
Lieanic															74			
Iodine Value	9	54	84	60	88	92	100	107	127	130	145	145	178	190	150	163	130	45

Vegetable oil contains a higher percentage of a desirable fatty acid and crops that contain unique, unusual fatty acids, those triglycerides with numerous active sites amenable to chemical reactions to be converting to useful polymeric materials (Derksen et al., 1995, Khot et al., 2001, Tan and Chow, 2010). For non-food applications, oleochemical as well as fine chemicals industries have expressed their interest in new fatty acids with unusual properties and functionalities, since current

sources contain more than 10 different types of fatty acid as shown in the Table 2.2 (Oldring et al., 2002).

Table 2.2: The composition of fatty acids (Oldring et al., 2002)

Common Name	No. of Carbon	Type	Formula
Lauric	12	Saturated	$\text{CH}_3\text{-(CH}_2\text{)}_{10}\text{-COOH}$
Myristic	14	Saturated	$\text{CH}_3\text{-(CH}_2\text{)}_{12}\text{-COOH}$
Palmitic	16	Saturated	$\text{CH}_3\text{-(CH}_2\text{)}_{14}\text{-COOH}$
Stearic	18	Saturated	$\text{CH}_3\text{-(CH}_2\text{)}_{16}\text{-COOH}$
Arachidic	20	Saturated	$\text{CH}_3\text{-(CH}_2\text{)}_{18}\text{-COOH}$
Oleic	18	Unsaturated	$\text{CH}_3\text{-(CH}_2\text{)}_7\text{CH=CH(CH}_2\text{)}_7\text{-COOH}$
Ricinoleic	18	Unsaturated	$\text{CH}_3\text{-(CH}_2\text{)}_4\text{-CHOH-CH}_2\text{-CH=CH(CH}_2\text{)}_7\text{-COOH}$
Linoleic	18	Unsaturated	$\text{CH}_3\text{-(CH}_2\text{)}_4\text{-CH=CH-CH=CH-(CH}_2\text{)}_7\text{-COOH}$
Linolenic	18	Unsaturated	$\text{C}_2\text{H}_5\text{-CH=CH-CH}_2\text{-CH=CH-CH}_2\text{-CH=CH-(CH}_2\text{)}_7\text{-COOH}$
Oleostearic	18	Unsaturated	$\text{(CH}_2\text{)}_3\text{(CH}_2\text{)}_3\text{-CH=CH-CH=CH-CH=CH-(CH}_2\text{)}_7\text{-COOH}$
Liconic	18	Unsaturated	$\text{CH}_3\text{-(CH}_2\text{)}_3\text{-CH=CH-CH=CH-CH=CH-(CH}_2\text{)}_4\text{-CO-(CH}_2\text{)}_2\text{-COOH}$

Vegetable oils could be classified as drying, semi-drying, or non-drying, and this is related to the behaviour of the unmodified oil, depending on whether it is, on its own, able to oxidize and crosslink to a dry film. A good drying oil contains over 60% of the polyunsaturated linoleic and linolenic acids, while semi-drying oil contains just over 50% of linoleic acid. By contrast, a non-drying oil contains 90% saturated lauric acid and less than 10% unsaturated fatty acid (Lambourne and Strivens, 1999).

The vegetable oil or its drying form owe their value as raw materials for surface coating (including decorative) to their ability to polymerize and cross-link, or dry (cure) after they have been applied to surface, to form a tough, adherent, impervious, and abrasion-resistant polymeric film on the surface. Their film-forming properties are closely related to their degree of unsaturated centers or double bonds that polymerization and crosslinking take place. Unsaturation is an important factor

of vegetable, which enhances its use in coating industries. In terms of paint properties, the number of double bonds is the most important feature (Crivello and Narayan, 1992, Mosiewicki et al., 2005, Sharma and Kundu, 2006). Figure 2.2 is selected fatty acid for paint application.

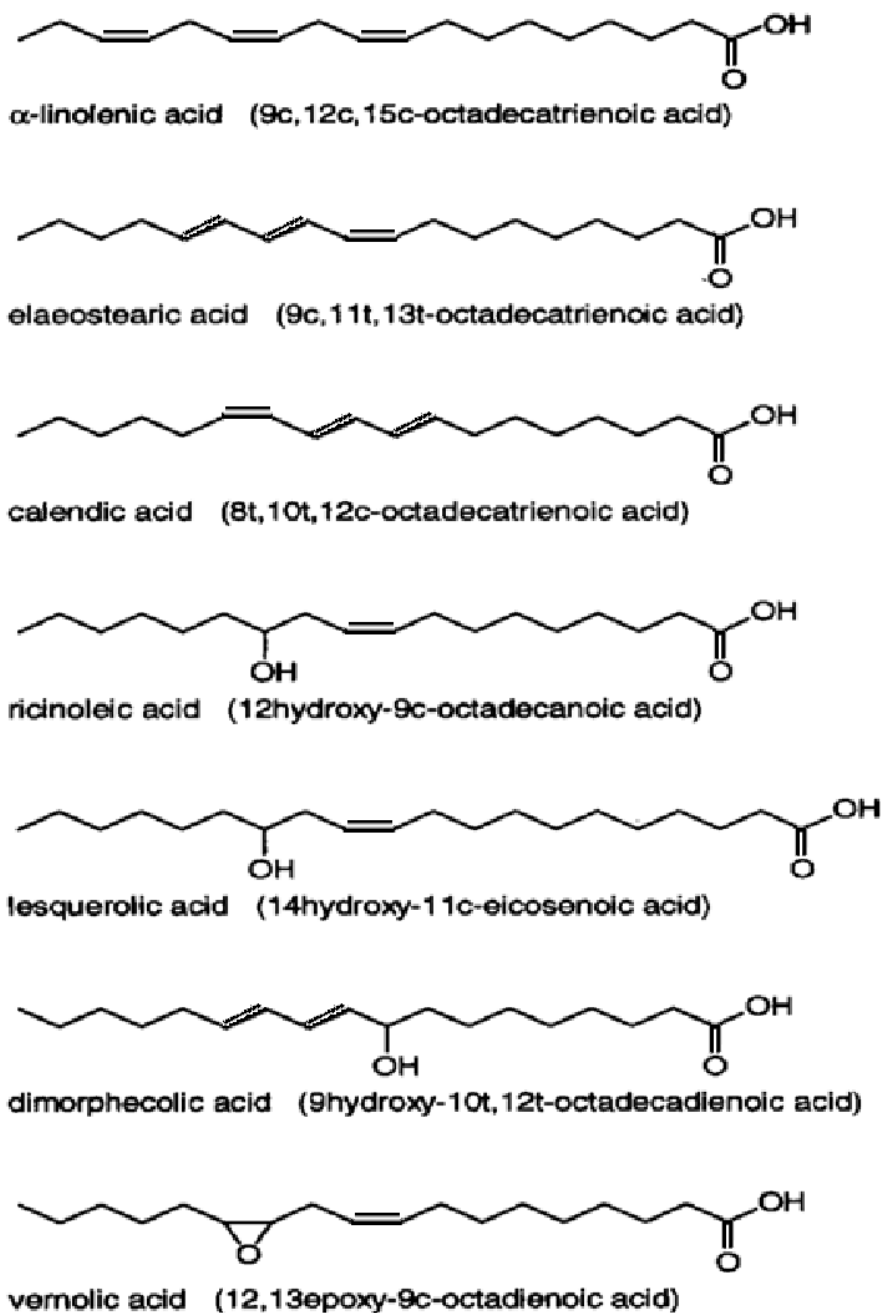


Figure 2.2: Selected fatty acid for paint application (Derksen et al., 1996)

2.4 UV-radiation curing technology

During the sixties, the oil crisis was followed by ever escalating costs of conventional energy sources and petrochemical derived solvents. This trend has been spurred not only by the realization that the supply of fossil resources is inherently finite, but also the threat of environmental concerns on VOC and energy shortages. Simultaneously, this had created a favourable climate for the development of radiation curing technology (Dufour et al., 1991, Derksen et al., 1996, Weiss, 1997). Radiation cure coatings technology represents one of the new techniques that replacing the use of conventional or low solids, solvent-borne coatings (Weiss, 1997, Satas and Tracton, 2001, Koleske, 2001). As radiation curing technology was the one answering the challenge of the future and modern finishing by meeting the 3 “E” rules fixed as a basic for each new development in the much diversified areas of coatings. The 3 “E” are Economy, Energy and Ecology (Dufour et al., 1991). Moreover, the quality demands while taking into consideration environment pollution and energy saving, this has lead to an increasing use of the UV technology in the coatings, paint and ink industries.

The radiation curing technology which has been widely used in the application of coatings, paint and ink industries are ultraviolet (UV) or electron beam (EB) radiation technology. Both UV and EB radiations are classified as electromagnetic radiations along infrared (IR) and microwave (MW). The main difference between UV and EB curing lies in the frequency, wavelength and mechanism by which the polymerisation reactions are induced (Groshart, 1997, Gloeckner, 2008). In UV cure coatings, it has low energy irradiation, thus the initial step requires photoinitiators (or photosensitizer) by absorption of photons of UV–

visible electromagnetic radiation to achieve effective curing. In EB cure coatings, the initial step is ionization and excitation of the coating resins by high energy electrons. EB are so energetic, so that photoinitiators are not required. Cross-linking is initiated by reactive intermediates that are generated from the photoexcited photoinitiator in UV curing and from excited and ionized resins in EB curing. Without any doubt, UV irradiation process is the lowest-cost option because the equipment is simpler, smaller and considerably less expensive to purchase and operate (Braithwaite et al., 1991, Rao et al., 1995, Gloeckner, 2008).

UV radiation is used to transform a reactive liquid monomers and oligomers to solids polymer (crosslinked polymer), at ambient temperature using ultraviolet (UV) radiation. This process involved the essentially physical changes due to either polymerization, crosslinking or grafting (Mehnert, 1998, Davidson, 2001, Christian, 2002).

For a photocuring polymerization of formulations to occur, there are three key requirements. The first is a UV irradiation source that produces high intensity UV radiation, the second are vehicles containing unsaturated polymerisable multifunctional monomers or oligomers (prepolymers), and last is a photoinitiator (Fouassier and Rabek, 1993, Dietliker et al., 2007, Chittavanich, 2009). Most monomers do not produce initiating species with sufficiently high yields when they are exposed to UV light, therefore a photoinitiator must be added to the formulations to generates reactive species (free radicals or ions) to initiate the polymerization reaction process (Decker, 1996, Decker 2001). In addition, formulations may consist of co-initiator, pigments, fillers, thermal stabilizer or additives. The overall

photocurable formulation process can be represented schematically as shown in Figure 2.3.

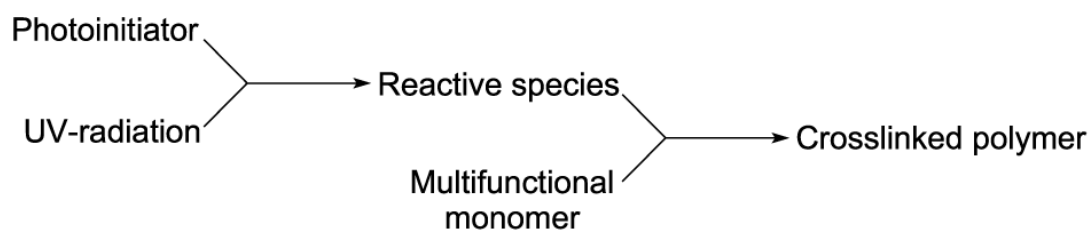


Figure 2.3: Photocurable formulation (Decker, 1996).

There are two classes of polymerization reactions in UV curing, which are free-radical and cation-initiated chain-growth polymerization. The latter is not common in use today and is not covered here. The details of free-radical polymerization will be discussed in details in this chapter. Free radical polymerization currently dominates because of its low cost and the ease of design afforded by a wide selection of usable monomers. Cationic polymerization has poor reactivity, sensitive to moisture and high water uptake of polymer are the adverse effect (Gruber et al., 2011). Cationic polymerization will continue outside the irradiation zone (dark cure), even when the initiating species are no longer being created, providing chain transfer and termination reactions do not occur due to the presence of nucleophilic species (Kennedy, 1982). During ambient UV curing there is the ever present and uncontrolled nucleophile water. The water will be present either dissolved within the liquid coating, chemically bound to substituents within the coating, such as fillers or pigments, or will be present in a gaseous state. Furthermore, the cationic UV catalyst can suffer poisoning effects (Brann, 1990).

2.4.1 Advantages of UV curing technology

UV radiation curing has become a well-accepted technology which has found a large variety of industrial applications because of its peculiar characteristic and distinct advantages compare to thermal and solvent based coatings. Overall, the most important features of this technology can be summarized in Table 2.3 (Rao et al., 1995, Koleske, 2001, Satas and Tracton, 2001, Schwalm, 2007a, Gloeckner, 2008, Drobny, 2010).

Table 2.3: Advantages of UV radiation curing technology (Rao et al., 1995, Koleske, 2001, Satas and Tracton, 2001, Schwalm, 2007a, Gloeckner, 2008, zDorbny, 2010).

<p>Energy</p> <ul style="list-style-type: none">• Saving in energy: energy is used to initiate the radical polymerization which then cures the coatings. Commonly rapid cure at room temperature, no energy require heating the substrate.• Energy saving: green energy <p>Economy advantages</p> <ul style="list-style-type: none">• High productivity: High curing speed.• Saving in investment cost: compact installations.• Saving in materials: often lower film weight coatings, giving better properties are possible with radiation cure formulations.• Saving man power: possibility of achieving different coating in line.• Decrease floor space: Small space requirements <p>Ecology</p> <ul style="list-style-type: none">• No pollution of the atmosphere: solvent free formulations (VOC reduction), 100% solid system possible.• Minimal CO₂ evolution: energy used is electricity and therefore no carbon dioxide is formed by burning gas or oil to thermally cure the coating. However, unless nuclear or hydro-generation of electricity is used then there will be CO₂ evolution associated with the consumption of electricity.• Possibility of easy recycling: waste reduction

2.4.2 UV and Visible Radiation

UV radiation is part of the electromagnetic spectrum which is shown in Figure 2.4 and it spans wavelength in the range from 100 to 400 nm (Dufour et al., 1991, Drobny, 2010). The UV lamp is used to generate UV light which is a non-ionizing or actinic radiation and has short wavelength cover the energy band from 100-400 nm. The particular wavelength of UV radiation is emitted by heating the inert gas within the bulb, thereby vaporizing of mercury and causing emission of UV light.

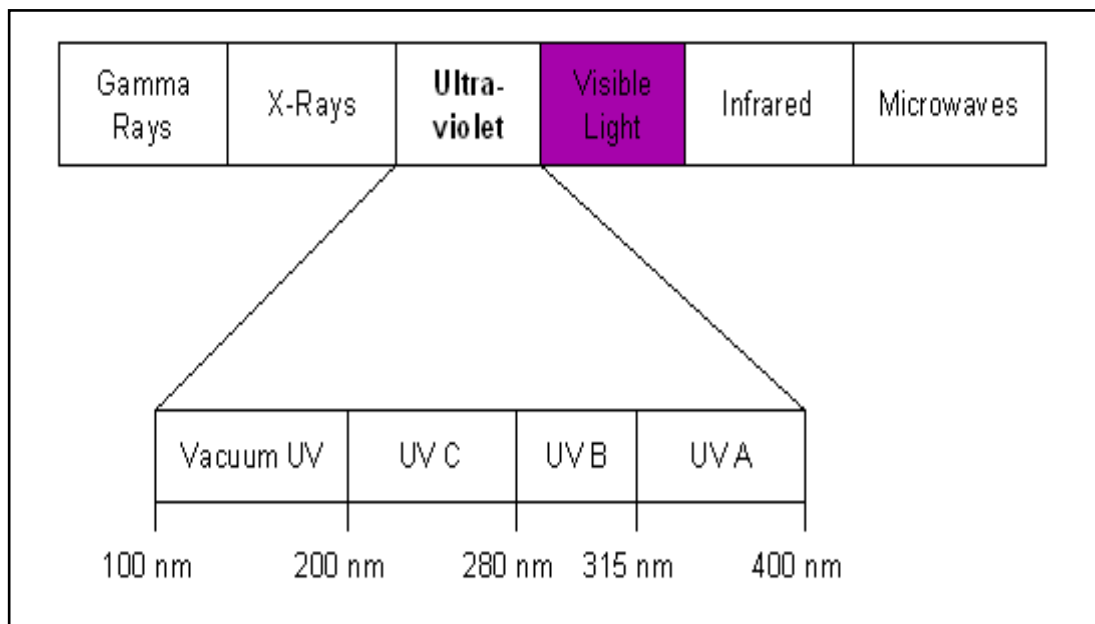


Figure 2.4: Electromagnetic energy spectrum (Dufour et al., 1991).

UV radiation is divided into four regions, namely UVA, UVB, UVC and VUV. While UV light wavelengths are divided into three categories, which are referred as long, medium and short wavelength (Dufour et al., 1991, Arthur Green, 2010, Drobny, 2010). Table 2.4 show the UV radiation regions and its applications.

Table 2.4: UV radiation regions and its applications (Dufour et al., 1991, Arthur Green, 2010, Drobny, 2010)

Name	Wavelength range (nm)	Applications
UVA (longwave, or black wave)	400nm - 315nm	Used for low energy UV polymerization reactions, non-destructive fluorescent inspection methods and tanning salons. Photons in UVA always promote through cure with thicker film layers.
UVB (medium wave)	315nm – 280nm	Used along with UVA for polymerization, is the most energetic region of natural sunlight, for accelerated light aging of materials and medical treatment curing. Photons inUVB contribute to bulk cure.
UVC (short wave, or germicidal)	280nm – 100nm	Used for rapid surface cure of UV inks and lacquers, sterilization and germicidal irradiation and application, the most energetic of the wavelength used in UV curing. Photons in UVC are important for surface cure and promote surface properties such as hardness, stain resistance, and abrasion resistance.
VUV (Vacuum Ultraviolet)	100nm – 200nm	Only can be used in a vacuum, they have very significant commercial importance. Used as envelope material for bulbs.

2.4.3 UV radiation polymerization reaction

UV radiation process is a photochemical process in which an abundant amount of UV energy is produced by a mercury discharge lamp and focused at monomers through cross linking or polymerization. In photochemical process, energy is absorbed from a photon to form an energised or excited state. This excited state must lose its excess energy to become stable and this can be lost in one of two ways. The first involves re-radiation of energy and the second a non-radiative energy transition. In both processes excited states are interconverted with each other or with the ground state. The processes can be called photophysical process. As a generalisation, the net effect of light energy being absorbed is that light can be

converted to light of a different wavelength, heat or to a potentially chemically reactive moiety (Allan et al., 1991, Drobny, 2010).

In photochemical process, a photon is absorbed to initiate the reaction then produce new chemical species which are different from the starting materials. Whereas in photophysical process do not produce new chemical compounds, but it interconvert excited states with each other or excited state with ground state (Dietliker, 1991a, Koleske, 2002).

Basically, at the beginning of the photochemical reaction, a photon is absorbed by a molecule called as photoinitiator, it causes the generation of species which is capable of initiating polymerization of polymerisable constituents within the coating directly or indirectly (Dietliker, 1991a, Satas and Tracton, 2001). Photoinitiator plays a key role in converting the absorbed energy from the incident light into chemical energy in the form of reactive intermediates (Dietliker, 1991b). These intermediates are either free radicals which are able to initiate radical polymerization or reactive cationic species which are able to initiate cationic polymerization.

2.4.4 Mechanism of free radical polymerization

In the UV radiation polymerization reaction mechanism, the production of an initiating species by photochemical reaction occurs in the first step from photo-polymerizable formulations and then the chain process amplifies the first photochemical reaction (Mehnert et al., 1998).

To produce free radicals, the photoinitiator has first to absorb energy from the UV light, the energy absorbed is sufficient to form an excited species. The photoinitiator fragments into free radicals that are the reactive species for the polymerisation of unsaturated moieties of monomers or oligomers, this process is the ignition of the polymerization reaction. Generally, no polymerisation would occur in UV curable system in the absence of photoinitiator (Dietliker, 1991a)

Free radical photopolymerization involves four processes: initiation, propagation, chain transfer, and termination. Only the initiation step is photosensitive; all the other steps are thermally driven (Dietliker, 1991b, Davidson, 2001, Arthur Green, 2010):

- (i) Initiation - comprises the process of absorption of UV energy by a photoinitiator, the generation of radical species from the reaction is known as the photoinitiation process (initiation step) follow by photo polymerization process.
- (ii) Propagation – repeating addition of monomeric units in a chain reaction to produce the polymer backbone.
- (iii) Chain transfer- involves the reaction of the growing polymer chain by hydrogen donor to terminate the growing chain with concomitant production of a new donor radical that can generate a new polymer chain by reacting with more monomer. If the newly formed radical can start another chain reaction, this is called a chain transfer process.
- (iv) Termination- the continuance of the free radical chain can be terminated by various processes such as recombination and disproportionation reactions to

give a neutral species, so that the polymer chain stops growing and subsequently form a solid polymer matrix.

Several steps involved in the photoinitiated polymerization can be summarized in the following Figure 2.5.

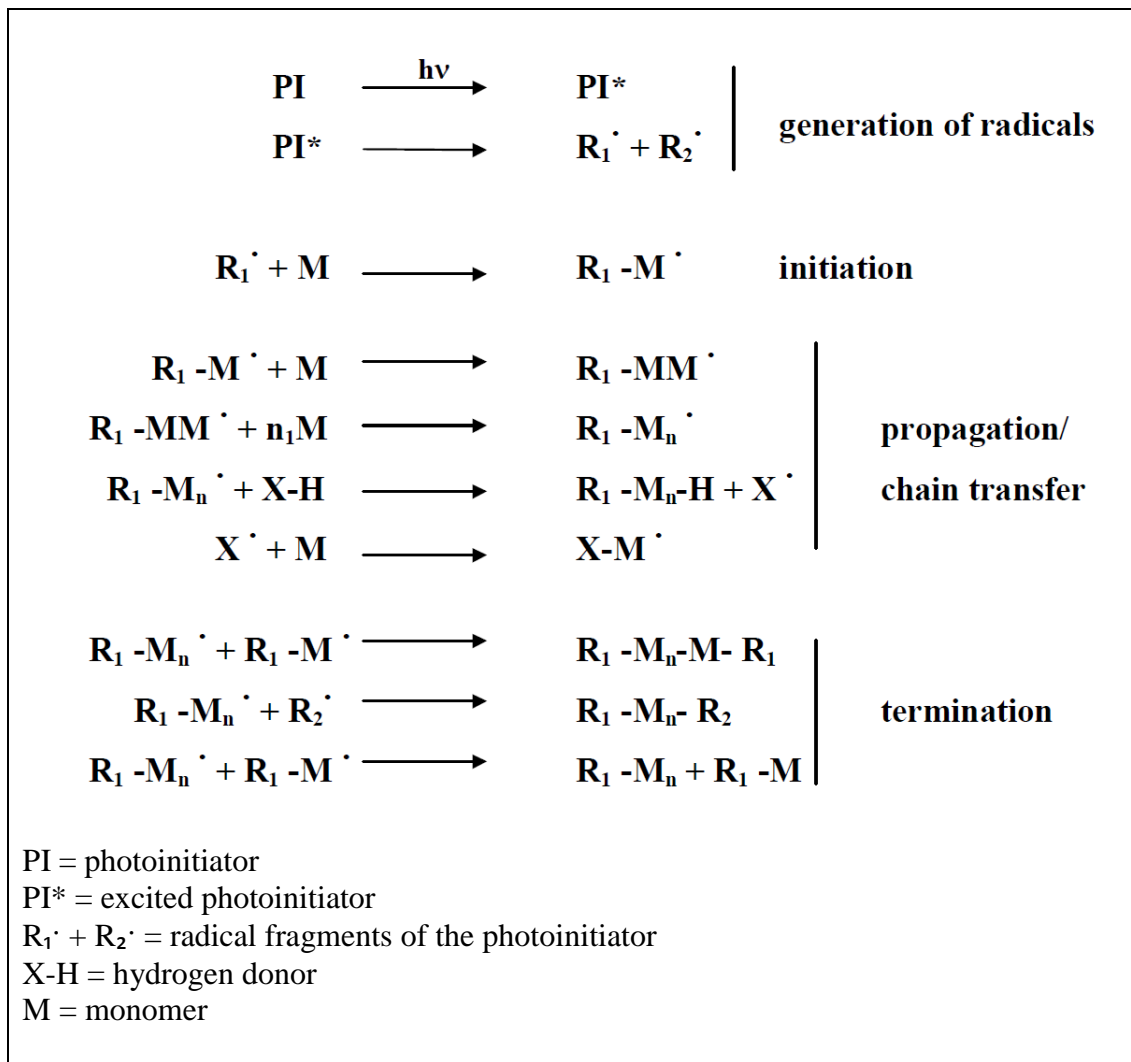


Figure 2.5: Various steps in a photoinitiated polymerization (Dietliker, 1991a)

In coatings cured by free radical initiated by UV radiation, free radicals are photogenerated and initiate polymerization by adding to vinyl double bonds, primarily acrylates. In all practical cases, the initiating radicals are generated from electronically excited photoinitiator molecules. There are three basic stages involve in this photoreaction (Allan et al., 1991):

- i) Absorption of a photon resulting in an electronically excited state.
- ii) A primary photochemical process which may involve rearrangements in the electronically excited molecules.
- iii) A secondary or dark process which results from the intermediates produced from the primary photochemical process.

From schematic mechanism (as shown schematically in the Figure 2.6), a photoinitiator molecule AB is excited into the singlet state (S_1) by photon absorption. Radical formation occurs via a triplet state (T_1). Fast transformation of the singlet into a triplet by inter system crossing (ISC) is a necessary condition for obtaining a high radical yield. Although, sometimes side reaction such singlet decay by fluorescence or triplet quenching by oxygen have to be avoided. Radical formation occurs via two possible reaction sequences. They are designated as Norrish type I (α -cleavage) and Norrish type II (intermolecular hydrogen transfer) reactions. In the first case, the photoinitiator triplet state decays into a radical pair by homolytic decomposition. In the second case, the photoinitiator triplet state decays into a radical pair by hydrogen abstraction or electron transfer from a co-initiator. A geminate radical pair is formed surrounded by solvent cage. Diffusional motion prevents the immediate recombination of the radical in the pair and is the driving