INVESTIGATION OF ACRYLATED ALKYDS

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INVESTIGATION OF ACRYLATED ALKYDS

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ABSTRACT

Four model alkyds were prepared to study the grafting mechanism of acrylic monomers, methyl methacrylate and butyl acrylate, onto alkyds. These model alkyds were prepared via a fatty acid process with stearic acid, oleic acid, linoleic acid or linolenic acid with phthalic anhydride and glycerol. Acrylated alkyds were synthesized by copolymerizing these model alkyds and acrylic monomers in the presence of benzoyl peroxide initiator.

To elucidate the grafting sites, 2D gradient heteronuclear multiple quantum coherence Nuclear Magnetic Resonance (2D gHMQC NMR), $^1$H NMR, selective extraction, and gas chromatography were conducted to study each system. For the stearic alkyd model systems, evidence of grafting by hydrogen abstraction from glyceride unit was found. It was surmised that the acrylic macroradical combines with the glyceride radical to form the alkyd-acrylic copolymer. For the oleic alkyd model systems, the grafting site was primarily located at the double bond on the fatty acid chain. For the linoleic alkyd and linolenic alkyd model systems, the grafting reaction mainly occurs at the activated methylene groups on the fatty acid chain via hydrogen abstraction by primary radical attack. In this study, it was found that as long as there are non-conjugated double bonds available, the hydrogen abstraction from the diallylic...
group is the most favorable reaction. When diallylic hydrogens are not present, a
preferred reaction pathway for a benzoyl peroxide radical is to add to a double bond. In
a saturated alkyd model, the grafting will only occur at the glyceride unit via hydrogen
abstraction.
DEDICATION

To my beloved parents, Haitao Wang and Qing Miao, for their unconditional love and endless support.
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CHAPTER I
INTRODUCTION

Alkyd resins are a special category of polyester resin. Traditionally, polyesters are derived from dibasic acids and dibasic polyols. However, alkyds are usually composed of tri-functional polyols, dibasic acid/anhydride, fatty acid. By adding unsaturated fatty acid, often derived from plant and vegetable oils, into the polyester formulation enable the resin to cure in air by autoxidation process. Alkyd coatings are widely used in wood coating, architectural coating, and industrial coatings for its good color retention, high gloss, good thermal stability, and low cost. However, its relatively long drying time, poor hydrolytic and alkaline stability, and poor exterior durability have limited its application.

Modified alkyds especially acrylated alkyds have been in commercial production for over half a century. Vinyl modified alkyd such as styrenated alkyd was first introduced in coating industry as a special kind of modified alkyd characterizing low cost, antioxidative crosslinking, and fast drying properties. Since then acrylated alkyd has drawn a lot of attentions as acrylics can impart similar properties to alkyd like
styrene. However, those authors failed to sufficient spectral information to elucidate the copolymer structure and grafting mechanism. From previous studies, steric hindrance of acrylic monomer is claimed to be crucial to the grafting mechanism. Nevertheless, they neglected the effect of different structures of fatty acids or oils in the alkyd mixture from mono-glyceride process, such as oleic acid containing one double bond and linoleic acid containing two double bonds may have different grafting mechanism resulting from different reactivity of prospective grafting site. The presence of different fatty acids in the matrix complicated the study. In this case, one is not able to tell each grafting mechanism clearly.

In this study, four different alkyds were synthesized with stearic acid, oleic acid, linoleic acid or linolenic acid, phthalic anhydride, and glycerol through fatty acid process to get four model alkyds. Acrylated alkyds were achieved by continuously introducing acrylic monomer and benzoic peroxide initiator into model alkyds. Products were characterized with $^1$H and 2D gHMQC NMR, solvent extraction, and gas chromatography. From those experimental data, a thermodynamic driven grafting mechanism is proposed.
CHAPTER II

BACKGROUND

2.1 Drying Oil

Drying oil is one of the oldest binders for paints since ancient times by artist and the majority of them are derived from liquid vegetable oils that are cured with oxygen to form solid films. Nowadays, drying oils are the most common raw materials for other binders like alkyd, epoxy ester, and uralkyd resin.

CH$_3$(CH$_2$)$_{16}$COOH  Stearic acid
CH$_3$(CH$_2$)$_{14}$COOH  Palmitic acid
CH$_3$(CH$_2$)$_7$CH=CH(CH$_2$)$_7$COOH  Oleic acid
CH$_3$(CH$_2$)$_6$CH=CHCH$_2$CH=CH(CH$_2$)$_7$COOH  Linoleic acid
CH$_3$CH$_2$CH=CHCH$_2$CH=CHCH$_2$CH=CH(CH$_2$)$_7$COOH  Linolenic acid
CH$_3$(CH$_2$)$_3$CH=CHCH=CHCH=CH(CH$_2$)$_7$COOH  Eleostearic acid
CH$_3$(CH$_2$)$_6$CH(OH)CH$_2$CH=CH(CH$_2$)$_7$COOH  Ricinoleic acid

![Figure 2.1 Structure of triglyceride](image_url)

R$_1$, R$_2$, R$_3$ = Fatty acid

Figure 2.1 Structure of triglyceride
Most oils are derived from glycerol and fatty acid through esterification also known as triglycerides and a typical structure of triglyceride is shown in Figure 2.1. The presence of diallylic group (-CH=CHCH$_2$CH=CH-) in unsaturated fatty acid moiety enables the drying oil to go through autoxidation with oxygen in air.

Table 2.1 Typical Fatty Acid Compositions (%) of Vegetable Oils

<table>
<thead>
<tr>
<th>Oil</th>
<th>Saturated</th>
<th>Oleic</th>
<th>Linoleic</th>
<th>Linolenic</th>
<th>Eleostearic</th>
<th>Ricinoleic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Caster</td>
<td>3</td>
<td>7</td>
<td>3</td>
<td></td>
<td></td>
<td>87</td>
</tr>
<tr>
<td>Coconut</td>
<td>91</td>
<td>7</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Linseed</td>
<td>10</td>
<td>22</td>
<td>16</td>
<td>52</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Olive</td>
<td>18</td>
<td>64</td>
<td>16</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Palm</td>
<td>53</td>
<td>38</td>
<td>9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peanut</td>
<td>11</td>
<td>61</td>
<td>22</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Safflower</td>
<td>11</td>
<td>13</td>
<td>75</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soybean</td>
<td>15</td>
<td>25</td>
<td>51</td>
<td>9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sunflower, MN</td>
<td>13</td>
<td>26</td>
<td>61</td>
<td>trace</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sunflower, TX</td>
<td>11</td>
<td>51</td>
<td>38</td>
<td>trace</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tall oil</td>
<td>8</td>
<td>46</td>
<td>41</td>
<td>3</td>
<td></td>
<td>80</td>
</tr>
<tr>
<td>Tung</td>
<td>5</td>
<td>8</td>
<td>4</td>
<td>3</td>
<td></td>
<td>80</td>
</tr>
</tbody>
</table>

Natural oils are mixtures of mixed triglycerides which have various fatty acids located along the triglyceride. Oils could be characterized by high performance liquid chromatography (HPLC) or gas chromatography (GC) of the methyl esters acquired from trans-esterification reaction. A typical fatty acid composition of vegetable oils is
listed in Table 2.1. The compositions are subjected to the origin and production place of those plants, because of humidity, climate, soil conditions. Generally speaking, in order to survive the chilly weather oils from colder places have lower freezing points as result of a higher content of unsaturated fatty acid. This tendency could be easily spotted from the difference in the composition of sunflower oil originated from Minnesota and Texas.\(^7\)

Animal oils are generally composed of saturated fatty acids. The only animal oils used in coating industry are refined fish oils containing triglycerides of unsaturated fatty acids ranging from C\(_{18}\) to C\(_{26}\). Theses oils have up to five non-conjugated double bonds which is highly efficient for autoxidation curing.\(^7\)

2.1.1 Autoxidation of Drying Oil

Drying oils can be simply classified as drying, semi-drying, and non-drying oils by their *iodine value*, which are the grams of iodine required to saturate all the double bonds in 100g oil. If the iodine value is over 140, then it is a drying oil; for semi-drying oil, the iodine value is between 125 to 140; for non-drying oil, the iodine value is below 125.

Another way to differentiate oils is to calculate their *drying index* by an empirical equation as follows:

\[
\text{Drying index} = (\%\text{linoleic acid}) + 2 \times (\%\text{linolenic acid})
\]
Drying oil has a drying index above 70; Semi-drying oil has a drying index between 65 and 70; Non-drying oil has a drying index below 65. In linolenic acids, there are two diallylic methylene groups. Those diallylic sites are the active position for initiating drying process. Therefore, we can associate the average number of diallylic site per molecule also referred to as the number average functionality \( f_n \) to the classification of drying oils. For drying oil, the number is greater than 2.2; for semi-drying oil, the number is slightly below 2.2; there is no distinct border between semi-drying and non-drying oil.\(^7\)

Autoxidation process is composed of four steps, oxygen uptake, peroxide decomposition, propagation, and termination. In general, it is driven by free-radical mechanism.\(^8\)

All unsaturated fatty acids undergo certain peroxidation formation as time goes which is also known as oxygen uptake.

\[
RH + O_2 \rightarrow ROOH
\]

Those free radicals that initiate the autoxidation process is produced from the decomposition of naturally occurring hydroperoxides.

\[
ROOH \rightarrow RO \cdot +HO \cdot
\]

Those free radicals generated from the decomposition are reactive enough to abstract hydrogen from the fatty acid chain especially the hydrogen atoms on the diallylic sites.
However, the existence of naturally present anti-oxidant will consume some free radicals, and then hydrogen atoms from diallylic site will be abstracted, yielding the resonance-stabilized free radical

\[ \text{RO} \cdot \text{(or HO} \cdot \text{)} + -\text{CH} = \text{CH} - \text{CH}_2 - \text{CH} = \text{CH} - \rightarrow \]
\[ -\text{CH} = \text{CH} - \cdot \text{CH} = \text{CH} - +\text{ROH} \text{ (or H}_2\text{O)} \]

(1)

In free radical 1, free electron is delocalized with high electron density on the terminal carbons. There are three different resonance forms and the most predominant conjugated form can react with oxygen to yield a conjugated peroxy free radical like 2, since conjugation is known to be able to stabilize radicals, the autoxidation process is expected to be expedited by conjugation.

(2)

The peroxy free radicals can abstract hydrogens from double allylic sites, forming additional hydroperoxides and generating free radicals such as 1. Then crosslinking is achieved by termination reaction such as recombination of radicals.
Crosslinking by recombination

R · + R · → R – R

RO · + R · → R – O – R

RO · + RO · → RO – OR

2.2 Alkyd

Alkyd resins are developed in 1920s based on polymeric resins, and first produced commercially by General Electric. Alkyd resins have been used in surface coating and binder for their versatility and profitability ever since, and by the early 1950s alkyd resins had become the preeminent binder in coating industry. The word “alkyd” was created by Kienle and Ferguson in 1927 and “al” stands for alcohol and “cid” from acid which was later changed to “kyd”.

Alkyd resins are a special kind of polyester resins or oil-modified polyester synthesized from three basic components: dibasic acids, polyols, and monobasic fatty acids. The property and formulation of those components affect the performance of the alkyd resins. A typical structure of alkyd resin is shown in Figure 2. 2.
Oil length (OL) is a core concept in the area of alkyd. It normally refers to the oil portion of an alkyd expressed as a percentage of the final alkyd weight. For purpose of convenience the oil length is usually based on a charged weight instead of a final weight. Alkyd resins with less than 40wt% oil length are called short oil. Those that has 40wt%-60wt% OL are referred to as medium oil, and those with OL over 60wt% oil content are referred to as long oil.

\[
\text{Oil Length(Monoglyceride)} = \frac{\text{Weight of Oil}}{\text{Weight of Alkyd} - \text{Weight of Water Evolved}}
\]

\[
\text{Oil Length(Fatty Acid)} = \frac{1.04 \times \text{Weight of Fatty acid}}{\text{Weight of Alkyd} - \text{Weight of Water Evolved}}
\]

The first equation is suitable for oil length calculation in monoglyceride process, as the raw material in that process is oil. The second equation has an extra factor 1.04 which is for the missing glycerol moiety in fatty acid: (weight of glycerol+3*weight of fatty acid)/3*weight of fatty acid≈1.04
*Short oil-length alkyds* are compatible in aromatic but not aliphatic solvents. They are usually used as baking primers and enamels. Short oil alkyd can generally offer high quality color and gloss retention, but slow drying and limited compatibility with low toxicity aliphatic solvent is the main drawbacks of this type of alkyds.

*Medium oil-length alkyds* are compatible in both aliphatic and aromatic solvent. The air-drying medium oil alkyd is commonly used as standard vehicle for industrial coating, like primers and undercoatings, anti-corrosion coatings.

*Long oil-length alkyds* are compatible in aliphatic solvent. They have better pigment dispersion, rheological properties, and storage stability than the other types, therefore they could be applied by brush and be used as exterior trim paints, wall paints, and metal maintenance paints.

*Oil-free alkyds* are mostly used with melamine-formaldehyde (MF) and urea-formaldehyde (UF) resins as high performance stoving coatings like all the other non-drying alkyd resins.
Table 2. Alkyd properties with regard to oil length

<table>
<thead>
<tr>
<th>Property</th>
<th>Long Oil</th>
<th>Medium Oil</th>
<th>Short Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil Length</td>
<td>Highest</td>
<td>Mediocre</td>
<td>Lowest</td>
</tr>
<tr>
<td>Drying Time</td>
<td>Longest</td>
<td>Mediocre</td>
<td>Shortest</td>
</tr>
<tr>
<td>Brushing Application</td>
<td>Best</td>
<td>Mediocre</td>
<td>Worst</td>
</tr>
<tr>
<td>Film flexibility</td>
<td>Highest</td>
<td>Mediocre</td>
<td>Lowest</td>
</tr>
<tr>
<td>Chemical resistance</td>
<td>Worst</td>
<td>Mediocre</td>
<td>Best</td>
</tr>
<tr>
<td>Gloss Retention</td>
<td>Worst</td>
<td>Mediocre</td>
<td>Best</td>
</tr>
</tbody>
</table>

Alkyds also can be classified into oxidizing and non-oxidizing. Oxidizing alkyds can go through autoxidation in air in a certain period. An oxidizing alkyd should have resin-like properties, which means the maximum oil length for oxidizing alkyd is around 50. In the formulation of oxidizing drying oils and semi-drying oils are used to provide adequate unsaturated sites for autoxidation. After crosslinking, the film hardness is inversely proportional to oil-length, namely, fatty acid content in formulation. Non-oxidizing alkyds are often used as polymeric plasticizers or hydroxyl functional resins. They are utilized combining with MF and UF resins.

2.2.1 Raw Materials

Alkyd resins are comprised of polyols, dibasic acids, and oils or fatty acids. The addition of oils or fatty acids make alkyd different from conventional polyester, therefore oils or fatty acids play an important role in the property and performance of alkyds. The degree of unsaturation in oils or fatty acids governs the drying property of
alkyds. The higher iodine number the oils or fatty acids have per mass unit the faster they can drying with equal exterior factors such as temperature.

When it comes to polybasic acids selection, phthalic anhydride is the most common choice due to its ease of handling, balanced properties, and economy. It is usually utilized in its anhydride form, which can be esterified by ring opening reaction with reduced reaction time and water evolved. In addition, its relatively low melting point (131°C) is ideal for melting production. The meta-isomer of phthalic acid isophthalic acid is the second widely used dibasic acid. It will impart tougher, fast drying, more chemical resistance properties to the coating. However, the high melting point of IPA (330°C) leads to a higher temperature and longer reaction time. Along with the high temperature, dimerization of IPA will result in high viscosity and greater extents of polyol side reactions. Therefore, in order to make alkyd with similar viscosity as PA, one must formulate a lower mole ratio of IPA to polyol. Terephthalic acid is not a good choice for making alkyds due to its high process temperature and slow dissolution.

Isomers of phthalic anhydrides are shown in Figure 2.4.

---

Figure 2.3 Structures of isomers of phthalic acid
In general, polyols that have functionalities from 2 to 4 are mostly used in alkyd formulation. Ethylene glycol, diethylene glycol, propylene glycol, and neopentyl glycol are most common diols; glycerol and trimethylol propane are most used triols; and pentaerythritol is the best tetraol choice for branching. Polyols with different functionality will give alkyds various degree of branching. Also, the flexibility of alkyds will be determined by the distance between two hydroxyl groups. For example, diethylene glycol is more flexible than ethylene glycol; and neopenytl glycol is more heat- and hydrolysis- resistant due to its branched structure. Among all those polyol choices, glycerol is the mostly popular choice due to its natural presence in oils. The second most popular choice is penterythritol. Common polyol structures are shown in Figure 2.5.

![Figure 2.5 Structures of typical polyols](image-url)
2.2.2 Synthesis of Alkyd

Preparation of alkyd resins can be carried out in solvent free atmosphere which is often referred to as Fusion method, and it can also proceed with solvent. For fusion method reaction is set at a temperature from 220°C to 250°C with nitrogen purging for removal of water. However it might take away some volatile contents. Besides, it is worth noticing that this procedure is usually for alkyd which has an OL of 60% or even more. For solvent method, reaction is carried out with continuous azeotropic distillation of solvent which is conventionally 5wt% xylene of the total reactant. Xylene is immiscible with water, as the mixture evaporates and collected in the Dean-Stark trap. Water is separated, while the upper layer, namely, xylene returns to the reactor system. In conclusion, solvent method offers better temperature and viscosity control. As the there is no loss of raw material caused by volatilization and sublimation, it also shows better control of the resin composition.

Another difference in designing the reaction is the raw material choices of oils and fatty acid, which are usually called mono-glyceride process and fatty acid process, respectively. The mono-glyceride process is suitable for making alkyd with vegetable oils and glycerol. Heating those two components that has a mole ratio of 1:2 with a catalyst like LiOH to 240°C until the monoglyceride stage is achieved. After monoglyceride is formed, the dibasic acids and more polyols are charged into the flask. Then reduce the reaction temperature to 220°C. After approximately 5 hours, which
may vary according to the actual reaction temperature the mixture became very viscous.

And the condensation reaction is done when the acid value is below 10mg (KOH)/g (sample). Typical triglyceride structure and fatty acid structure are shown in Figure 2.6 and Figure 2.7. Preparation of alkyd resin by monoglyceride process is presented in Figure 2.8.

where R comprises 51wt% linoleic acid, 15wt% stearic acid, 25wt% oleic acid for soybean oil

Figure 2.5 Typical structure of vegetable oil

Stearic fatty acid
Oleic fatty acid
Linoleic fatty acid
Linolenic fatty acid
The fatty acid process employs fatty acids instead of oils as depicted in Figure 2.9. It is obvious that this process is easier due to the removal of the alcoholysis step. This process also makes it very flexible for polyol choices and offers a much better control over molecular weight and molecular distribution. It is also reported that this process enables the condensation reaction to be continued until very low acid value, which gives the product better drying properties. However, utilizing fatty acid will increase the cost a lot, which is just a minor issue.
2.3 Modification of Alkyds

The fact that hybrid polymer of alkyd resin and acrylic monomers combine advantageous properties of both alkyd resins (e.g. high gloss, auto-oxidation, and penetration into porous substrates) and acrylic monomers (e.g. fast curing, color retention, and chemical resistance) has drawn many researchers’ attention.\textsuperscript{3-6, 10-17} Different acrylic monomers can offer diverse properties depending on their own nature. Methyl methacrylate, a common commercial acrylic monomer, could improve more exterior durability, water resistance, and hardness. Butyl acrylate gives better flexibility as well as exterior durability. It also has been also reported that alkyd/ acrylic hybrid offers fast drying, good acid/alkali resistance. Structure of methyl methacrylate and butyl acrylate are depicted in Figure2.10 and different properties imparted from acrylic monomers are listed in Table2.4.
However, alkyd resin and acrylics are not mutually compatible. It is quite easy for them to get phase separated resulting in haziness and lower gloss, therefore compatibilization is need for a homogenous stable phase.\textsuperscript{18,19} Compatibilization could be achieved by forming acrylated alkyd acting as compatibilizer between alkyd phase and acrylic phase as Figure 2.9 shows.

![Figure 2.9 Scheme of alkyd/acrylic hybrid](image)

Figure 2. 9 Scheme of alkyd/acrylic hybrid

(a) MMA

(b) BA

![Figure 2.10 Structure of acrylic monomers](image)

Figure 2. 10 Structure of acrylic monomers: (a) Methyl methacrylate, (b) Butyl acrylate
Table 2. 3 Film properties from different monomers

<table>
<thead>
<tr>
<th>Film Property</th>
<th>Acrylic Monomer Sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness</td>
<td>Methyl methacrylate</td>
</tr>
<tr>
<td>Flexibility</td>
<td>Butyl acrylate, methacrylic acid, acrylic acid, and ethyl acrylate</td>
</tr>
<tr>
<td>Water Resistance</td>
<td>Methyl methacrylate</td>
</tr>
<tr>
<td>Exterior Durability</td>
<td>Methacrylate</td>
</tr>
</tbody>
</table>

Nabuurs et al. synthesized alkyd resin/acrylate hybrid by emulsion polymerization. Results showed that as the polymerization proceeded alkyd resin and homoacrylic tends to separate in different particles.\(^4\)

Over the past decade many studies have been accomplished about the grafting mechanisms of alkyd/acyrlic hybrid in mini-emulsion system.\(^3,5\) The graft site, monomer conversion as well as crosslink status have been investigated from experimental data. Authors have predicted that graft site of the copolymerization is driven by steric hindrance with the combination of experimental data and theoretical postulation. However, there is not sufficient direct spectrum is shown to give strong evidence of proposed mechanism.

Shahla Ataei et al. performed copolymerization of alkyd resin and acrylics (MMA and BA) in toluene with free radical initiator such as BPO. The alkyd was derived from oleic acid and a decrease in double bond content is detected by \(^1\)HNMR.\(^14\) The
author also observed a higher conversion level when copolymerizing butyl acrylate with palm alkyd than methyl methacrylate due to less steric hindrance.

Majumdar et al.\textsuperscript{20} studied acrylate grafted dehydrated castor oil (DCO) alkyd as the majority portion of DCO alkyd is linoleic alkyd. The author proposed that the grafting is achieved by hydrogen abstraction via primary radical attack and monomer propagated onto the generated radical site on fatty acid chain. Significant improvements were observed after modification including drying time and mechanical properties, weather resistance, and exterior durability.

Recently, Monika Goikoetxea et al. came up with a novel strategy to enhance compatibility between alkyd resin and acrylic polymer in high solid aqueous hybrid dispersion without affecting alkyd double bonds during copolymerization by introducing glycidyl methacrylate (GMA) into alkyd resin before copolymerization.\textsuperscript{18} In this way, the unsaturation groups from alkyd backbone are not substantially reduced during functionalizing the alkyd resin with acrylic monomers. However, the grafting mechanism is not studied in this research.

Grafting mechanism of alkyd/acrylic hybrid system derived from monoglyceride process has been studied by means of combination of 1D/2D NMR method. But conclusions seem to be conflicting with the experimental result. Moreover, some research has been done in the condition of solution free radical polymerization by fatty
acid process. However, the author only use one acrylic monomer, his results is inconvincible due to lack of comparison with various monomer and fatty acid choices.

2.4 Unsaturated polyester

Unsaturated polyester resins (UPRs) along with polyurethane are the most extensively used thermoset polymer. UPRs are widely used in glass-reinforced composites, gel-coats, and wood finishing coating as fillers, topcoats, and sealer. UPRs are usually synthesized by polyesterification with multifunctional carboxylic acid and polyol as shown in Figure 2.12. A reactive diluent, unsaturated monomer, is usually added into the unsaturated polyester formulation to decrease the viscosity and cost, and at the same time increase the crosslink density of UPRs by free radical polymerization initiated by peroxide, azo compounds or photochemical.  

\[
\text{maleic anhydride} + \text{phthalic anhydride} + \text{propylene glycol} \rightarrow 
\]

Figure 2.11 Scheme of typical unsaturated polyester
Styrene is widely used as crosslinking monomer in UPRs. Vinlytoluene, 2-hydroxyethyl methacrylate and glycerol monoallyl ether were also good substitutes for styrene. Lower volatility and toxicity are preferred when choosing the monomer. On the basis of the DSC tests on kinetics of the free radical copolymerization, the reactivity of those monomers occurs in the sequence: glycerol monoallyl ether > vinyltolene > styrene > 2-hydroxyethyl methacrylate.\textsuperscript{21}

In the curing of UPRs, free radicals can open the double bonds in the polyester backbone or the double bond from unsaturated monomer forming oligoradical. Either of those previous two radicals can propagate with unsaturated monomers and finally uniting the UPRs into a three-dimensional network by crosslinking. Usually, an optimum cure is considered when the conversion of unsaturated monomer is between 92 to 95%\textsuperscript{22}.

2.5 Free radical polymerization

Free radical polymerization is a type of chain growth polymerization (or addition polymerization), along with anionic, cationic and coordination polymerization. Free radical polymerization is a method of polymerization by which a polymer forms by the successive addition of free radical. A typical free radical polymerization consists of four steps: \textit{initiation}, \textit{propagation}, \textit{termination}, and \textit{chain transfer}.\textsuperscript{23} Free radical polymerization is usually initiated by the dissociation of initiator. Initiators can be divided into several types including: Thermal initiator, photolysis initiator, redox
initiator, persulfates initiator etc. Among these initiators thermal initiator is most commonly used such as organic peroxides and azo compounds. When thermal initiator is heated up to a certain temperature, its bond is cleaved homolytically, resulting two radicals. As presented below, where I represents initiator, R· represents reactive species, M stands for monomer, and f is initiator efficiency:

$$I \rightarrow 2fR\cdot$$

$$f = \frac{\text{Radicals incorporated into polymer}}{\text{Radicals formed by initiators}}$$

$$R\cdot + M \rightarrow RM\cdot$$

The initiator efficiency depends on not only the initiator nature property but also the conditions of polymerization reaction, such as temperature and solvent. According to experimental data, it usually ranges from 0.3 to 0.8.

Azo compounds such as 2,2’-azobisisobutyronitrile (AIBN) and peroxides such as benzoyl peroxide (BPO) are very common members in this family.

![Figure 2](image)

AIBN dissociates into free radicals and nitrogen

AIBN is pretty stable at 0°C or lower, however when heated up to 70°C or higher it becomes very susceptible to decomposition. If the temperature comes to 100°C, the half-life of AIBN is only 7.2 min. Thus AIBN is commonly used at 50-70°C. The
The dissociation scheme of AIBN is shown in Figure 2.11 and relationship between initiator half-life and temperature is listed in Table 2.5.

Table 2.4 Half-life of some common initiators

<table>
<thead>
<tr>
<th>Initiator</th>
<th>Temperature (°C) for Half-life ($t_{1/2}=0.693/K_d$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10h</td>
</tr>
<tr>
<td>AIBN</td>
<td>64</td>
</tr>
<tr>
<td>BPO</td>
<td>71</td>
</tr>
<tr>
<td>t-butyl peroxide</td>
<td>121</td>
</tr>
</tbody>
</table>

*Half-life values are measured from toluene or benzene solution of those initiators

Figure 2.13 Benzoyl peroxide dissociation into free radicals

Benzoyl peroxide is usually used at 80-95°C. When it reaches very high temperature such as 130°C, BPO will first decompose into reactive benzoyloxy free radical, and then it will further dissociate to yield a highly reactive phenyl free radical and CO$_2$. The whole dissociation scheme is shown in Figure 2.12. The highly reactive phenyl free radical is very efficient when abstracting hydrogen from almost any aliphatic hydrogen leading to branching of polymer product.

Initiators are usually an indispensable part in a free radical polymerization.

Nevertheless, they are often added in a small amount, approximately 0.5wt%-4wt% the
weight of monomer. The concentration of monomer would also effects molecular
weight control of the product. The higher concentration of the initiator is, the lower the
molecular weight is. With higher initiator concentration, more free radicals will be
generated to react with monomers, therefore more chains are initiated, propagated, and
terminated leading to lower molecular weight.

The polymer chain grows mainly by means of propagation, in which the monomer
free radical adds to another one until a macromolecule is formed. Propagation reaction
is usually very fast compared to initiation, because initiation is limited by the speed of
initiator decomposition. In a single second, hundreds of monomers can be added onto a
growing reactive species:

\[ \text{RM} \cdot + \text{M} \rightarrow \text{RMM} \cdot \]

\[ \text{RMM} \cdot + \text{M} \rightarrow \text{RMMM} \cdot \]

\[ \text{RMMM} \cdot + \text{nM} \rightarrow \text{RM}_{n+3} \cdot \]

Termination is the end of growing. There are two kinds of termination reactions,
combination and disproportion:

\[ \text{RM}_{n+3} \cdot + \text{RM}_{n+3} \cdot \rightarrow \text{RM}_{n+3} - \text{M}_{n+3} \text{R} \]

\[ \text{RM}_{n+3} \cdot + \text{RM}_{n+3} \cdot \rightarrow \text{RM}_{n+2} = \text{M} + \text{RM}_{n+3} \]
Free radical polymerization has been a useful method for organic coating for decades because its features like irreversible, no side product, and better control. Alkyd/acrylic hybrid can be achieved using this method by grafting acrylic monomers onto alkyd resin in the presence of initiator.

2.6 Nuclear Magnetic Resonance

NMR has been a reliable characterization tool for determining polymer structure characterization since it was first invented in late 1945. Later with the introduction of Fourier transform and noise decoupling carbon NMR became also available for chemists to investigate more information. The main data from a NMR spectrum is the chemical shift in a unit of part per million (ppm). The first two-dimensional NMR (2D NMR), COSY (Correlation Spectroscopy), was proposed and implemented in the 1970s. Homo-nuclear experiments mainly contain correlation spectroscopy (COSY) and nuclear overhauser effect spectroscopy (NOESY). The two-dimensional spectrum from COSY experiment gives the frequencies for a single isotope, most commonly hydrogen along both axes. COSY spectra have two types of peaks. Diagonal peaks have the same frequency coordinate on each axis, while cross peaks have different values for each frequency coordinate and appear off diagonal. Diagonal peaks correspond to the peaks in the same 1D experiment, while the cross peaks indicate coupling between pairs of nuclei from which one can determine the connection of two atoms. The spectrum obtained from NOESY is similar to COSY, nevertheless the cross peaks show
resonances from protons that are spatially close rather than structurally close. Also, NOESY is a phase sensitive experiment that needs to be phase correctly for a good result. Heteronuclear correlation spectroscopy gives signals from the coupling between two different types of nuclei, mostly protons and carbons.

2.7 Gas Chromatography

Gas chromatography (GC) is a useful chromatography in analytical chemistry for characterizing small molecule compounds by vaporizing them with decomposing. In a GC experiment, a known volume, mostly 1μL, of analyte is injected into the head of a column. A carrier gas, usually helium, which is also called mobile phase is utilized to carry the sample being injected going through a column to a detector. Most of the columns are capillary tubes with a stationary phase on its inner wall. A molecule that spends less time in the stationary phase will have a shorter retention time than the other components. After eluting from the column, components are taken into detectors such as flame ionization (FID) by carrier gas, and chemicals are identified electronically.

GC is especially effective in quantitative analysis for a small amount of sample as the peak area of each analyte is proportional to the concentration of itself in the chromatogram. Therefore, the analyte concentration from the sample can be
calculated from its peak area in the chromatogram. By externally establishing a
calibration standard curve of a series of concentrations of pure analyte, a linear
relation is established. Analyte concentration in the sample can be achieved by
simply substituting peak area into the linear function.
3.1 Materials

Stearic acid (99%), oleic acid (99%), linoleic acid (99%), linolenic acid (99.9%),
glycerol (99.9%), phthalic anhydride (PA, 99%), p-xylene, benzoyl peroxide (BPO,
99.9%), potassium hydroxide (99%), methyl methacrylate (MMA, 99%), and butyl
acrylate (BA, 99%) were all purchased from Sigma-Aldrich, and are all used as
received except acrylic monomers which are purified by aluminum oxide column
(Sigma-Aldrich) to remove inhibitors and recrystallization are performed with BPO.
Chloroform-d (CDCl₃, 100%) was supplied by Cambridge Isotope Laboratories, Inc.

3.2 Synthesis of alkyd

Fatty acid process was utilized to synthesize alkyd resin in the presence of reflux
agent. Weight composition of alkyd is calculated from the following equation²:

\[
R = \frac{|x(1-L)2L|E_1}{\left[|\left(\frac{L}{x}\right)-1\right]E_1 + E_2 + \left(\frac{2}{x}\right)E_x}\]  

Equation 1

\[
A_1(\text{Fatty acid}) = \frac{1 - \left(\frac{E_r}{E_1}\right)}{1 + R}\]  

Equation 2
\[ A_2(Phthalic\ anhydride) = \frac{(2R/x)}{(2 + R)} \]  \hspace{1cm} \text{Equation 3}

\[ B_x(Glycerol) = \frac{R}{1+R} \]  \hspace{1cm} \text{Equation 4}

Where R is defined as alkyd constant for formulating alkyd composition, L is oil length of desired alkyd, x is the functionality of polyol, \( E_1 \) is the equivalent molecular weight of fatty acid, \( E_2 \) is the equivalent molecular weight of phthalic anhydride, \( A_1 \) is the molar equivalent of fatty acid, \( A_2 \) is the molar equivalent of phthalic anhydride, \( B_x \) is the molar equivalent of glycerol.

So, for a medium oil alkyd from fatty acid, glycerol, and phthalic anhydride, \( R = 1.053, A_1 = 0.146 \text{mol}, A_2 = 0.34 \text{mol}, B_x = 0.51 \text{mol} \) (\( A_1, A_2, \) and \( B_x \) are all molar equivalent). With this formulation four kinds of alkyds are made with each corresponding fatty acid.

**Stearic alkyd preparation**: Stearic acid (41g, 0.144mol), PA (25g, 0.17mol), glycerol (15.3g, 0.17mol), xylene (4g, 5wt% of total weight) were formulated according to Eq.1-4. Reactants were charged into a 250mL four-neck round bottom flask equipped with a mechanical stirrer, reflux condenser, thermometer, Dean-Stark trap, inert gas inlet. The temperature of this setup was slowly heated to 220°C. The reaction progress was monitored by acid number (AN) according to ASTM D1639-90 until acid number was under 10mg (KOH)/g (sample) was achieved. A creamy solid was obtained after rotary evaporation and cooling down: \(^1\text{H NMR (500 MHz, CHLOROFORM-d)} \delta \text{ (ppm)} = 0.75 – 0.95 \text{ (m, 3H,} \)
-CH₃), 1.05 - 1.33 (m, 22H, -CH₂-), 1.33 - 1.78 (m, 2H, -OCOCH₂CH₂-), 2.22 - 2.41 (m, 2H, -OCOCH₂CH₂-), 4.06 - 4.94 (m, 6H, -OCH₂CHCH₂O-), 7.27 (s, 1H, CDCl₃), 7.38 - 7.98 (m, 4H, -OOCPhCOO-);

Oleic alkyd preparation: Oleic acid (41g, 0.145mol), PA (25g, 0.17mol), glycerol (15.3g, 0.17mol), xylene (4g, 5wt% of total weight) were formulated according to Eq.1-4². Reactants were charged into a 250mL four-neck round bottom flask equipped with a mechanical stirrer, reflux condenser, thermometer, Dean-Stark trap, inert gas inlet. The temperature of this setup was slowly heated to 220°C. The reaction progress was monitored by acid number (AN) according to ASTM D1639-90² until AN was under 10mg (KOH)/g (sample) was achieved. A slightly yellow viscous liquid was obtained after rotary evaporation: ¹H NMR (500 MHz, CHLOROFORM-d) δ (ppm) = 0.85 - 1.05 (m, 3H, -CH₃), 1.05 - 1.53 (m, 20H, -CH₂-), 1.53 - 1.78 (m, 2H, -OCOCH₂CH₂-), 1.78 - 2.22 (m, 4H, cis -CH₂CH=CHCH₂-), 2.22 - 2.41 (m, 2H, -OCOCH₂CH₂-), 4.06 - 4.94 (m, 6H, -OCH₂CHCH₂O-), 5.23 - 5.45 (m, 2H, cis -H=C=CH₂), 7.27 (s, 1H, CDCl₃), 7.38 - 7.98 (m, 4H, -OOCPhCOO-);

Linoleic alkyd preparation: Linoleic acid (41g, 0.146mol), PA (25g, 0.17mol), glycerol (15.3g, 0.17mol), xylene (4g, 5wt% of total weight) were formulated according to Eq.1-4². Reactants were charged into a 250mL four-neck round bottom flask equipped with a mechanical stirrer, reflux condenser, thermometer, Dean-Stark trap, inert gas inlet. The temperature of this setup was slowly heated to 220°C. The reaction progress was monitored
by acid number (AN) according to ASTM D1639-90\textsuperscript{25} until AN was under 10mg (KOH)/g (sample) was achieved. A yellow viscous liquid was obtained after rotary evaporation: \textsuperscript{1}H NMR (500 MHz, CHLOROFORM-d) δ (ppm) = 0.83 - 1.12 (m, 3H, -CH\textsubscript{3}), 1.12 - 1.50 (m, 14H, -CH\textsubscript{2}-), 1.50 - 1.78 (m, 2H, -OCOCH\textsubscript{2}CH\textsubscript{3}-), 1.78 - 2.22 (m, 4H, cis -CH\textsubscript{2}CH=CHCH\textsubscript{2}CH=CHCH\textsubscript{2}CH=CHCH\textsubscript{2}CH=CHCH\textsubscript{2}CH=CHCH\textsubscript{2}CH=CH-), 2.22 - 2.41 (m, 2H, -OCOCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}-), 2.60 – 2.85 (m, 2H, cis -CH=CHCH\textsubscript{2}CH=CH-), 4.06 - 4.94 (m, 6H, -OCH\textsubscript{3}CHCH\textsubscript{2}O-), 5.23 - 5.45 (m, 4H, cis -HC=CH-), 7.27 (s, 1H, CDCl\textsubscript{3}), 7.38 - 7.98 (m, 4H, -OOCPhCOO-);

Linolenic alkyd preparation: Linolenic acid (41g, 0.147mol), PA (25g, 0.17mol), glycerol (15.3g, 0.17mol), xylene (4g, 5wt\% of total weight) were formulated according to Eq.1-4\textsuperscript{2}. Reactants were charged into a 250mL four-neck round bottom flask equipped with a mechanical stirrer, reflux condenser, thermometer, Dean-Stark trap, inert gas inlet. The temperature of this setup was slowly heated to 220\textdegree C. The reaction progress was monitored by acid number (AN) according to ASTM D1639-90\textsuperscript{25} until AN was under 10mg (KOH)/g (sample) was achieved. A brownish viscous liquid was obtained after rotary evaporation: \textsuperscript{1}H NMR (500 MHz, CHLOROFORM-d) δ (ppm) = 0.83 - 1.12 (m, 3H, -CH\textsubscript{3}), 1.12 - 1.50 (m, 10H, -CH\textsubscript{2}-), 1.50 - 1.78 (m, 2H, -OCOCH\textsubscript{2}CH\textsubscript{3}-), 1.87 - 2.24 (m, 4H, cis -CH\textsubscript{2}CH=CHCH\textsubscript{2}CH=CHCH\textsubscript{2}CH=CHCH\textsubscript{2}CH=CHCH\textsubscript{2}CH=CHCH\textsubscript{2}CH=CH-), 2.22 - 2.41 (m, 2H, -OCOCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}-), 2.60 – 2.85 (m, 4H, cis -CH=CHCH\textsubscript{2}CH=CH-), 4.06 - 4.94 (m, 5H, -OCH\textsubscript{3}CHCH\textsubscript{2}O-), 5.23 - 5.45 (m, 6H, cis -HC=CH-), 7.27 (s, 1H, CDCl\textsubscript{3}), 7.38 - 7.98 (m, 4H, -OOCPhCOO-);
Another neck is used to taking product out to test acid value

Figure 3.1 Reaction setup of alkyd synthesis

3.3 Synthesis of acrylic/alkyd copolymer

Alkyd resin (7.5g), n-butanol (2.2g, 0.03mol) were charged into a 250mL four-neck round bottom flask equipped with a reflux condenser, mechanical stirrer and pump/syringe system. A mixture of n-butanol (2.2g, 0.03g), acrylic monomer (2.5g) and BPO (0.025g,
1 wt% monomer) is introduced into the flask continuously in 1 h via the pump/syringe. After complete addition of mixture the system was keep at the same condition for another one hour to ensure completion of the reaction.

3.4 Characterization

$^1$H and $^{13}$C as well as gHMQC 2D NMR was used to study the products. Deuterated-chloroform was used as solvent, for its relatively low polarity and tetramethylsilane (TMS) was added to reference the chemical shift in NMR spectra. Proton spectrum was processed with a sample of 10 mg per 5 cm of solvent in NMR tube, and for carbon and 2D spectrum samples of 100 mg per 5 cm of solvent in NMR tube were used. All spectra were recorded on Varian NMRS 500MHz spectrometer. All NMR spectra were referenced relative to the reference resonance of TMS ($\delta$ 0.0 ppm) and all the chemical shifts were assigned by chemical software.

According to $^1$H NMR, reacted double bond (RDB) of each fatty acid chain can be calculated based on the following equation:

$$
\text{RDB} = \left[ 1 - \frac{C_{5.3}}{C_{7.6}} \right] \times 100\% 
$$

where $C_{5.3}$ stands for the integration of resonance around $\delta$ 5.25-5.45 ppm in copolymer spectrum. And $A_{7.6}$ correlates to the integration of resonance signal around $\delta$ 7.40-7.85 ppm in the spectrum of alkyd.
The degree of grafting of each alkyd/acrylic system was determined by solvent extraction in Soxhlet extractor using diethyl ether as solvent. 1g of dried sample was wrapped with filter paper and inserted into extraction thimble. After 24h of extraction with diethyl ether in the extractor, the residual in the thimble was dried and weighted. The degree of grafting is calculated based on the residual weight and the total acrylic monomer weight in each system as follow:

\[
\text{Degree of grafting} = \frac{\text{Mole of acrylics grafted to alkyd}}{\text{Mole of total acrylic monomer}} \times 100%
\]

\[
= \frac{\text{total mole of acrylic} - \text{mole of acrylic residue}}{\text{total mole of acrylic}} \times 100%
\]

Quantitative analysis of degree of hydrogen abstraction was carried out by gas chromatography. In order to make a standard solution, a known amount of purified benzoic acid was dissolved into HPLC grade acetonitrile to get 25, 50, 100, 150ppm (μg/ml) standard solution with a 10mL volumetric flask and store the solution in a cool and dark place. Samples were made by measuring a known amount of alkyd/acrylic mixture in a weighing balance with a least count of 0.0001g and dissolve in acetonitrile with a 10mL volumetric flask to obtain the solution for testing the sample. The injector temperature is set at 250°C, FID detector temperature is 300°C, the carrier gas is Helium, and flow rate is 0.9mL/min. Column oven temperature is 50°C initially for 2min and is increased to 280°C held for 2 min with a rate of 15°C/min. The sample injection volume is 1μL. Monomer concentration is calculated from the calibration standard curve.
CHAPTER IV

RESULTS

This study aims to locate the graft site of acrylic monomer onto alkyds by free radical polymerization in solution via $^1$H and two-dimensional (2D) NMR techniques. 2D NMR has been extensive utilized in identifying polymer structure since it was invented in the 1980s, its advantage lie in its ability to resolve ambiguous signals, namely, overlapping resonance signals resulting from one nucleus-$^1$H along the indirect dimension of another nucleus-$^{13}$C. Then combining with proton NMR solving quantitative issues in this system the graft mechanism and location can be understood. It has been reported that monomer steric hindrance is the driving force of graft copolymerization in mini-emulsion polymerization systems, for example methyl methacrylate contain an extra steric factor resulting from its methyl group which butyl acrylate does not have could lead to different grafting mechanism and location.\textsuperscript{6,16,17} However, with the variation of reactant, solvent, and reaction conditions the graft mechanism and location may vary.\textsuperscript{11,12,15} The main goal of this research was to utilize $^1$H and 2D gHMOC NMR method to investigate whether the mechanism proposed by
previous authors in mini-emulsion and conventional solvent-borne systems is applicable in this current system. Fatty acid process utilized fatty acid, phthalic anhydride, and glycerol as raw materials to prepare alkyd resin in this work. This process enables a broader polyol choice and gives much better control over molecular weight and its distribution. Stearic acid, oleic acid, linoleic acid, and linolenic acid are chosen purposely to compare the effect of diallylic system with vinyl and saturated system. MMA and BA are chose because MMA have an extra steric hindrance contributed from methyl group while BA does not. BPO is the most common oil-soluble initiator and is described as highly efficient hydrogen abstractors. Benzoyl peroxide is documented to be able of attack the allylic site of polybutadiene as primary radical and abstract hydrogen from it.

Characterizations used in this research are mainly proton NMR, gHMQC 2D NMR, solvent extraction, and gas chromatography. Proton spectra are severely overlapped in this complex system and 2D spectra are incapable of quantitative analysis because the integration of resonance signal depends on the relaxation time of nucleus its scalar and dipolar decoupling constant. By solvent extraction, the degree of grafting can be obtained to get a sense of how many acrylic monomers are grafted onto alkyd resin. With gas chromatography, a quantitative analysis can be carried out with regard to the amount of hydrogen abstraction of benzoic peroxide initiator.
Generally, there are three different mechanisms for an acrylic monomer to graft onto alkyd backbone. First, the acrylic monomer could directly attack the double bond on the pendant fatty acid, which will simply result in an addition across double bond. Second, hydrogen abstraction from the activated methylene group on the fatty acid diallylic site is also a possible approach. Especially, it is more reasonable for linoleic fatty acid to be grafted in this way with the existence of double allylic site. As the hydrogen is activated by the diallylic relation, it is more reactive than the hydrogen allylic only to one allylic group. In addition, a hydrogen abstraction through polyol backbone is also proposed in the previous literature.\textsuperscript{11,12}

![Figure 4.1 Grafting mechanism of acrylics direct addition onto double bonds\textsuperscript{16}](image-url)
4.1 Alkyd and alkyd/acrylic hybrid 1D NMR spectra

The proton NMR spectrum of alkyd is presented in Appendix, the low field region (δ 6.0-8.0) ppm involves the protons on phthalic anhydride segment and protons on benzene or benzoic acid, if applicable. Also, very few protons are spotted from xylene which is used as reflux agent in alkyd synthesis. The medium field region (δ 3.0-6.0) ppm includes the vinyl protons on fatty acid side chains and protons neighboring hydroxyl and ester groups on polymer backbone. The high field region (δ 0-3.0 ppm)
includes methylene and methyl peaks from fatty acid protons with different resonance depending on their relative position from adjacent double bonds.

4.2 Alkyd/acrylic 2D gHMQC NMR spectra

2D gHMQC NMR were achieved from Varian 500 spectrometer. For each spectrum, a whole view of entire spectrum is shown and three individual windows are presented for different proton and carbon ranges. The first window ranges from δ 0.5-3.5 ppm on proton scale and δ 10-45 on carbon scale; The second window ranges from δ 3.0-6.0 ppm on proton scale and δ 45-90 ppm; The third window ranges from δ 5.0-8.5 ppm on proton scale and δ 120-145 ppm on carbon scale. All the 2D gHMQC spectra are obtained by overlaying each corresponding alkyd resin spectrum onto each alkyd resin/acrylic hybrid to get a clearer view of the structure after grafting.
CHAPTER V

DISCUSSION

Modified alkyds especially acrylated alkyds have been in commercial production for over half a century. Vinyl modified alkyd such as styrenated alkyd was first introduced in coating industry as a kind of modified alkyd characterizing low cost, autoxidative crosslinking, and fast drying properties. Since then acrylated alkyd has drawn a lot of attentions as acrylics can impart similar properties to alkyd like styrene. However, those authors haven’t provided sufficient spectral information to prove the structure and grafting mechanism. From previous studies, steric hindrance of acrylic monomer is claimed to be crucial to the grafting mechanism. Nevertheless, they neglected the effect of different structures of fatty acids or oils in the alkyd mixture from mono-glyceride process, such as oleic acid containing one double bond and linoleic acid containing two double bonds may have different grafting mechanism resulting from different reactivity of prospective grafting site. In this case, one is not able to tell each grafting mechanism clearly.

In this research, four alkyds are synthesized with each corresponding fatty acids to get pure alkyd products instead of a mixture, and then copolymerize alkyds with acrylic
monomers in the presence of free radical initiators, and then the influence of different fatty acid and steric hindrance of different acrylic monomer in each different individual alkyd system are studied by proton NMR and 2D gHMQC NMR experiments. With the aid of 2D gHMQC NMR technique, one would be able to locate the grafting sites and get to a better understanding of the grafting mechanism.

Table 5. 1 \(^1\)H and \(^{13}\)C chemical shift prediction for potential sites

<table>
<thead>
<tr>
<th>Structure</th>
<th>Proton shift (ppm)</th>
<th>Carbon shift (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Structure 1" /></td>
<td>4.54-5.14</td>
<td>77</td>
</tr>
<tr>
<td><img src="image2" alt="Structure 2" /></td>
<td>3.5</td>
<td>62</td>
</tr>
<tr>
<td><img src="image3" alt="Structure 3" /></td>
<td>2.1</td>
<td>35</td>
</tr>
</tbody>
</table>
Typically, alkyds will offer several grafting sites for acrylic monomers. For instance, in the case of linoleic alkyd, acrylic monomers can graft through direct addition onto double bonds; acrylic monomers can graft onto the double allylic site through hydrogen abstraction; acrylic monomers can graft onto the single allylic site through hydrogen abstraction; acrylic monomers can also grafting onto the polyol backbone by hydrogen abstraction. However, due to the extra steric hindrance introduced by the methyl group, methyl methacrylate is expected to graft through hydrogen rather than direct addition onto double bonds.  

5.1 Oleic alkyd/acrylic hybrid

Proton and 2D gHMQC NMR spectra of oleic alkyd, oleic alkyd/MMA hybrid and oleic alkyd/BA hybrid are shown in Appendix. Chemical shift assignments are listed in Table 5.1. The integration of resonance signal from vinyl group of MMA and BA decreased to zero indicating all acrylic monomers are consumed during polymerization forming either homo-acrylic polymer or alkyd/acrylic copolymer. At the same time, both alkyd/MMA and alkyd/BA systems show a noticeable decrease in the integration of resonance signals of double bond from fatty acid chain in proton spectrum suggesting double bonds are involved in the copolymerization. While compared to a previous work of synthesis of acrylated alkyd by free radical polymerization, which reported new chemical shifts at δ 4.2 ppm proton shift due to hydrogen abstraction from polyol backbone and δ 3.5 ppm proton shift due to hydrogen abstraction from allylic
site, the new chemical shift are not identified in this study. In the 2D gHMOC spectra of oleic alkyd/MMA hybrid and oleic alkyd/BA hybrid resonance signals at δ 2.1 ppm proton shift and δ 35 ppm carbon shift are observed in accordance with decrease of double bond content from direct addition across vinyl groups on fatty acid chain. Combining $^1$H NMR and 2D gHMOC NMR experimental data, it is concluded that copolymerization are proceeding via direct addition onto double bonds onto fatty acid chain rather than hydrogen abstraction from either allylic sites or polyol backbone in both oleic alkyd/MMA hybrid and oleic alkyd/BA hybrid systems.

5.1.1 Reaction of double bonds

In light of the NMR analysis of oleic alkyd/acrylic system above, for oleic alkyd and acrylic hybrid the change of double bond could be observed through a quantitative analysis of proton NMR. The resonance signal $\delta$ 5.3ppm corresponds to the chemical shift of hydrogen on double bond carbon. And the two resonances at $\delta$ 7.6ppm are the resonance signal of aromatic hydrogen. Resonance at $\delta$ 7.6ppm remains unchanged during the copolymerization due to its stability. Thus it can be used as a reference.

For both oleic alkyd/MMA hybrid and oleic alkyd/BA hybrid the RDB are around 20%, which approximately means 80% of those double bonds on pendent fatty are not involved in the graft polymerization. This result agree with previous work by X.Q. Wu et al. in mini-emulsion system.$^3$ A reasonable explanation for the low addition reaction
across the double bond on the fatty acid is that interaction between functional group and
the reactivity of double bond may vary for diverse locations.

Table 5. 2 List of reaction of double bond (RDB) of different alkyls and acrylated alkyls

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>$\frac{C_{5.3}}{C_{7.6}}$</th>
<th>RDB</th>
<th>Direct Addition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oleic alkyd</td>
<td>0.6</td>
<td>-</td>
<td>——</td>
</tr>
<tr>
<td>Oleic alkyd+MMA</td>
<td>0.51</td>
<td>15.0%</td>
<td>✓</td>
</tr>
<tr>
<td>Oleic alkyd+BA</td>
<td>0.48</td>
<td>20.0%</td>
<td>✓</td>
</tr>
<tr>
<td>Linoleic alkyd</td>
<td>0.73</td>
<td>-</td>
<td>——</td>
</tr>
<tr>
<td>Linoleic alkyd+MMA</td>
<td>0.70</td>
<td>4.1%</td>
<td>✗</td>
</tr>
<tr>
<td>Linoleic alkyd+BA</td>
<td>0.72</td>
<td>1.4%</td>
<td>✗</td>
</tr>
<tr>
<td>Linolenic alkyd</td>
<td>0.93</td>
<td>-</td>
<td>✗</td>
</tr>
<tr>
<td>Linoleinic alkyd+MMA</td>
<td>0.91</td>
<td>2.2%</td>
<td>✗</td>
</tr>
<tr>
<td>Linoleinic alkyd+BA</td>
<td>0.91</td>
<td>2.2%</td>
<td>✗</td>
</tr>
</tbody>
</table>

Direct addition grafting mechanisms have been documented in several oleic
alkyd-acrylic hybrid systems.\textsuperscript{13, 14} Authors explained the phenomenon by stating
direct addition onto a π-bond is energetically favored over abstracting an allylic
hydrogen with σ-bond. This also applies in this current oleic alkyd model system, as
NMR results showed that 20% double bond in oleic acid were consumed during
copolymerization.

Previous works concerning grafting acrylic monomer onto alkyd via mini-emulsion
polymerization reported that the graft sites are predominated by steric hindrance.
Methyl methacrylate with a methyl group providing a steric hindrance prefers to graft by means of hydrogen abstraction, however BA mainly graft onto the double bonds on the pendant fatty acid by addition reaction.\textsuperscript{16} In this sense, the result of oleic alkyd/butyl acrylate system in current research is in harmony with the previous prediction by Tsvalas et al.\textsuperscript{16}, but oleic alkyd/methyl methacrylate does not. Instead of abstracting hydrogen from either allylic sites or polyol back bone as direct addition is inhibited by steric hindrance, methyl methacrylate directly cleaves the double bond as butyl acrylate does. This discrepancy between water-borne and solvent-borne systems could be explained as differences in reaction media and reaction conditions.\textsuperscript{12} To be more specific, in the waterborne system, surfactant and co-surfactant are utilized to stabilize the mini-emulsion system, thus particle formation occurs predominately by monomer droplet nucleation. Each surfactant micelle containing monomers is significantly small resulting in a large monomer surface area in the waterborne system, and reaction between alkyd resin and acrylic monomers is faster. Due to the large amount of free radicals in the monomer droplet and the reactivity of alkyd as the massive existence of free radical the reaction between alkyd resin and acrylic monomers in mini-emulsion system would exhibit a sterically driven mechanism. On the other hand, monomers are not ideally dispersed as mini-emulsions and less monomer concentration is localized, therefore the reaction between alkyd resin and acrylic monomers in solvent-borne system is more driven by thermodynamics rather than steric hindrance. Moreover, the previous author synthesized alkyd resin by mono-glyceride process which makes the
system inevitably complicated with a mixture of alkyds (e.g. oleic alkyd, linoleic alkyd, and linolenic alkyd) which needlessly made the consideration of the situation in the copolymerization very tricky.

Unsaturated polyester resin prepared with maleic anhydride or fumaric acid also has a similar vinyl structure on its backbone. Waigaonkar et al.\textsuperscript{28} prepared unsaturated polyester with orthophthalic anhydride, maleic anhydride, and propylene glycol. The resin was cured with styrene forming crosslinking structure. A free radical polymerization mechanism was proposed to elucidate the crosslinking reaction. The styrene monomer propagates onto polyester backbone by direct addition and combination of propagating species terminated the polymer into a crosslinking network.

In this current oleic alkyd model system, oleic acid only has one double bond on the pendant fatty acid, which is comparatively less reactive than di-allylic structure that can activate the adjacent methylene group which does not exist in oleic alkyd, but the double bond is the more reactive than the allylic hydrogen in this system.\textsuperscript{29} Thus, addition across the double bond is the only possible pathway.
Table 5.3 Bond dissociation energy of different sites

<table>
<thead>
<tr>
<th>Graft site</th>
<th>Chemical Structure</th>
<th>Bond dissociation energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen abstraction from diallylic</td>
<td><img src="image1" alt="Image" /></td>
<td>272kJ/mol</td>
</tr>
<tr>
<td>Addition onto double bond (π-bond)</td>
<td><img src="image2" alt="Image" /></td>
<td>284kJ/mol</td>
</tr>
<tr>
<td>Hydrogen abstraction from monoallylic</td>
<td><img src="image3" alt="Image" /></td>
<td>322kJ/mol</td>
</tr>
<tr>
<td>Hydrogen abstraction from polyol</td>
<td><img src="image4" alt="Image" /></td>
<td>381kJ/mol</td>
</tr>
</tbody>
</table>

Bond dissociation energy (BDE, also called bond dissociation enthalpy) is characterized as the amount of energy or enthalpy needed to homolytically break a bond into free radicals. As is shown in Table 5.3, the bond dissociation energy for cleaving the π-bond of the bond is less than that of abstracting the hydrogen from the allylic group on the pendent fatty acid. So, direct addition onto the double bond is preferred than hydrogen abstraction from the allylic group. The mechanism of acrylic monomer grafting onto alkyd is shown in Figure 5.1. Besides, similar results are found in literature, which proposed and proved that grafting mechanism in oleic alkyd/MMA system is mainly direct addition across double bond on the pendent acid.\textsuperscript{13, 14}
Figure 5. Expected grafting pattern for acrylic monomers onto double bonds in oleic fatty acid chains.

5.2 Linoleic alkyd/acrylic hybrid

Proton and 2D gHMQC NMR spectra of linoleic alkyd, linoleic alkyd/MMA hybrid, linoleic alkyd/BA are shown in Appendix. Chemical shifts are predicted by chemical software. The integration of resonance signal from vinyl group of MMA and BA decreased to zero indicating all acrylic monomers are consumed during polymerization forming either homo-acrylic polymer or alkyd/acrylic copolymer. Compared to the previous oleic alkyd/acrylic hybrids, those spectra do not show significant decrease of
double bond on the pendant fatty acid, instead a new broad resonance signal shows up at \( \delta 3.5 \) ppm proton shift, \( \delta 62 \) ppm carbon shift which accordingly is the relevant resonance signal of the predicted mechanism of hydrogen abstraction from the diallylic group by either primary radical and/or macroradical. After the hydrogen is abstracted, macroradical or oligoradical may terminate with the generated site by recombination.\textsuperscript{16}

Table 5.4 Comparison of predicted chemical shift of acrylated linoleic and linolenic alkyd in 2D \textit{gHMQC}\textsuperscript{12}

<table>
<thead>
<tr>
<th>Graft Location</th>
<th>Predicted Chemical shift</th>
<th>Actual chemical shift</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Proton</td>
<td>Carbon</td>
</tr>
<tr>
<td>Direct Addition on Double Bonds</td>
<td>2.08</td>
<td>34.5-38.3</td>
</tr>
<tr>
<td>Hydrogen abstraction from diallylic</td>
<td>3.5</td>
<td>60</td>
</tr>
<tr>
<td>Hydrogen abstraction from allylic</td>
<td>2.78</td>
<td>38.2</td>
</tr>
<tr>
<td>Hydrogen abstraction from polyol</td>
<td>4.54</td>
<td>77</td>
</tr>
</tbody>
</table>

NMR results can be explained by bond dissociation energy (BDE), which describes the energy required to cleave a bond to form a free radical. Table 5.3 lists the BDE related to the schemes proposed earlier in this paper. Following the sequence of the BDE, it can be easily found out that grafting occur predominately at the methylene group on the fatty acid chain in linoleic alkyd system. From all those spectra of linoleic alkyd and linoleic alkyd/ acrylic hybrid, there is no double bond on fatty acid chain loss is spotted from the pendant fatty acid side chain according to \textsuperscript{1}H NMR integration.
Therefore, direct addition onto the double bond of the pendant fatty acid is not feasible for linoleic alkyd/acrylic system. In addition, the predicted resonance signal of hydrogen abstraction from the polyol backbone could not be found on the spectrum either. To sum up, the reaction pathway for linoleic alkyd/acrylic system is presumed to be mainly via hydrogen abstraction from the activated methylene position in diallylic sites and acrylic macroradical or oligoradical terminate with those generated sites by recombination as is shown in Figure 5.2.  

Comparing linoleic alkyd model systems with oleic alkyd model systems, the distinguishing difference is an extra double bond in linoleic acid and the two unconjugated double bond forming a double allylic system. The hydrogen is activated by the double allylic site. Therefore, direct addition is no longer preferred as Ateai et al.  

predicted instead abstracting the activated hydrogen is thermodynamically favored. Similar results can be found in the literature, Majumdar et al. studied acrylate grafted dehydrated castor oil (DCO) alkyd as the majority portion of DCO alkyd is linoleic alkyd. The author proposed that the grafting is achieved by hydrogen abstraction via primary radical attack and monomer propagated onto the generated radical site on fatty acid chain.

5.3 Linolenic alkyd/acrylic hybrid

Proton and 2D gHMQC NMR spectra of linolenic alkyd, linolenic alkyd/MMA hybrid, linolenic alkyd/BA are shown in Appendix. Chemical shifts are predicted by
chemical software. The integration of resonance signal from vinyl group of monomer MMA and BA decreased to zero indicating all acrylic monomers are consumed during polymerization forming either homo-acrylic polymer or alkyd/acrylic copolymer. Linolenic acid has three cis-form double bonds in one fatty acid chain, therefore it has two double allylic sites for grafting by hydrogen abstraction. It is clearly shown in 2D gHMQC NMR spectra that linolenic alkyd/acrylic hybrid has a new resonance signal at δ 3.5 ppm proton shift and δ 62 ppm carbon shift resulting from grafting between alkyd resin and acrylic monomers. This resonance signal is pretty reasonable according the previous proposed bond energy explanation that abstracting diallylic hydrogen is the most probable reaction pathway. Also, there is not distinct decrease of the double bond extent from fatty acid chain before and after reaction which indicates that there is no direct addition involved in this reaction system. At the intermediate region of those spectra, resonance signal of grafting onto polyol back bone (δ 4.54 ppm, δ 77 ppm) are not found. The grafting preference is summarized as following sequence: Hydrogen abstraction from diallylic site> Direct addition > Hydrogen abstraction from allylic site > Hydrogen abstraction from polyol backbone, which is also indicated by the sequence of bond dissociation energy.
5.4 Stearic alkyd/acrylic hybrid

Proton and 2D gHMQC NMR spectra of stearic alkyd, stearic alkyd/MMA hybrid, stearic alkyd/BA are shown in Appendix. Chemical shifts are predicted by chemical software. Stearic alkyd is the only saturated alkyd resin used in this research. It is primarily used to study whether grafting reaction without unsaturation sites on fatty acid chain will occur or not. The integration of resonance signal from vinyl group of...
monomer MMA and BA decreased to zero indicating all acrylic monomers are reacted
during polymerization forming either homo-acrylic polymer or alkyd/acrylic
copolymer. The resonance at δ 3.7 ppm on proton scale is the corresponding signal for
methyl methacrylate homopolymer and/or copolymer. Compared to the previous oleic
alkyd/acrylic hybrids, linoleic alkyd/acrylic hybrids, and linoleinic alkyd/acrylic
hybrids, those spectra of stearic alkyd do not shown either significant decrease of
double bond on the pendant fatty acid or new broad resonance signal at δ 3.5 ppm
proton shift and δ 62 ppm carbon shift which accordingly is the relevant resonance
signal of the predicted mechanism of hydrogen abstraction from the diallylic group.
However, the resonance signal of proposed mechanism of hydrogen abstraction from
polyol backbone at δ 4.54-5.14 ppm proton shift and δ 77 ppm carbon shift is observed
on the 2D gHMQC. This signal indicates that new grafting site is generated via
abstracting hydrogens from glycol unit on alkyd backbone without the presence of
other reactive groups like fatty acid double bonds. The newly generated radical could
combine with acrylic macroradical or oligoradical to form alkyd/acrylic copolymer as
is shown in Figure 5.3.⁶
5.5 Selective Extraction

Selective extraction was performed using Soxhlet extractor. Diethyl ether is used as solvent as it was found to be a good solvent for both neat alkyd and hybrid graft copolymer, but a non-solvent for homo-polymer of acrylic, such as PMMA and PBA. Therefore, during the extraction alkyd and alkyd/acrylic copolymer are extracted by diethyl ether into the flask below while homo-polymer remains in the extraction

Figure 5. 3 Expected grafting pattern for acrylic monomers onto glycol unit of steric alkyd.
thimble. Degree of grafting was calculated from the weight of dried acrylic homopolymer and shown in Table 5.5.

Table 5.5 Degree of grafting of each system

<table>
<thead>
<tr>
<th>Sample</th>
<th>Residual Weight (g)</th>
<th>Degree of Grafting (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stearic alkyd/MMA</td>
<td>0.185</td>
<td>26.0%</td>
</tr>
<tr>
<td>Stearic alkyd/BA</td>
<td>0.163</td>
<td>34.8%</td>
</tr>
<tr>
<td>Oleic alkyd/MMA</td>
<td>0.135</td>
<td>46.0%</td>
</tr>
<tr>
<td>Oleic alkyd/BA</td>
<td>0.077</td>
<td>69.2%</td>
</tr>
<tr>
<td>Linoleic alkyd/MMA</td>
<td>0.034</td>
<td>86.4%</td>
</tr>
<tr>
<td>Linoleic alkyd/BA</td>
<td>0.027</td>
<td>89.2%</td>
</tr>
</tbody>
</table>

From Table 5.5, we can see that butyl acrylate generally gives a better grafting efficiency than methyl methacrylate due to its less sterical hindrance. Also, with the increase of double bond content in alkyd resin more acrylic monomers are grafted onto alkyd chains.

Comparing the grafting efficiency of butyl acrylate versus methyl methacrylate in Table 5.5 with previous results reported by Tsavalas and Luo\textsuperscript{16}, it is not surprising to see that butyl acrylate leads to a higher grafting efficiency in both systems. This is explained by the extra methyl group renders MMA sterically more difficult for it to be involved in grafting reaction and the tertiary MMA radical is stabilized by the electron-donating alkyl group.
The residue in the filter paper is characterized by $^1$H NMR and 2D gHMQC NMR. As is shown in Figure 5.4, the only chemical in the residual is homopolymer of methyl methacrylate, which indicates that no alkyd or alkyd/acrylic hybrid is left in the residual. Then, those residual poly methyl methacrylate (PMMA) is extracted again in the diethyl ether to confirm that PMMA does not dissolve in diethyl ether in a noticeable amount. Results confirmed that PMMA is not extracted along with alkyd and alkyd/acrylic hybrid, and the weight of PMMA remains the same before and after the extraction.

![Proton spectrum of extraction residual](image)

After the extraction, polymer dissolved in diethyl ether was obtained by reduced pressure distillation and characterized by NMR experiments. As we can see from Figure 5.5 and 5.6 that the chemical shift at δ 3.5 ppm proton scale and δ 62 ppm carbon
scale which correlates to hydrogen abstraction at the methylene position on the pendant fatty acid still exists as well as the signal of hydrogens from the methanol moiety of methyl methacrylate at δ 3.6 ppm proton scale and δ 52 ppm carbon scale. Being aware of the removal of homo-polymer of MMA in the extraction process, the existence of grafting between alkyd and acrylic monomers by hydrogen abstraction from double allylic site is further proved.

Figure 5. Proton spectrum of extracted sample from linoleic alkyd
Figure 5. 6 2D gHMQC spectrum of extraction from linoleic alkyd/MMA hybrid

Window 1

Window 2
5.6 Gas chromatography

Gas chromatography is employed to quantitatively study hydrogen abstraction product from benzoyl peroxide as shown in Figure 5. 7.
The standard benzoic acid solution in acetonitrile is made with known concentration of 25, 50, 100, and 150 ppm (μg/mL). From the chromatogram, the retention time of benzoic acid is approximately at 8.3 min in this method. The corresponding peak areas are listed in Table 5.6. The peak area versus concentration curve is plotted in Figure 5.8.

Table 5.6 Corresponding peak area of standard solution

<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration</th>
<th>Injection volume</th>
<th>Retention time</th>
<th>Peak area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25 ppm</td>
<td>1 μL</td>
<td>8.221 min</td>
<td>5226</td>
</tr>
<tr>
<td>2</td>
<td>50 ppm</td>
<td>1 μL</td>
<td>8.292 min</td>
<td>8827</td>
</tr>
<tr>
<td>3</td>
<td>100 ppm</td>
<td>1 μL</td>
<td>8.242 min</td>
<td>13928</td>
</tr>
<tr>
<td>4</td>
<td>150 ppm</td>
<td>1 μL</td>
<td>8.218 min</td>
<td>18901</td>
</tr>
</tbody>
</table>

Figure 5.8 Standard calibration curve of benzoic acid
According to the standard curve benzoic acid weight percentage and benzoyl peroxide conversion into benzoic acid is calculated and shown in Table 5.7. In stearic alkyd system, only 1.42wt% of BPO converted into benzoic acid through hydrogen abstraction. The only pathway for hydrogen abstraction in stearic alkyd system is abstracting the hydrogens on the polyol backbone, and the poor conversion is due to the low reactivity of those hydrogens on the glycol unit. In oleic alkyd system, the conversion is also limited, as the relative higher reactivity of the double bonds will lead to direct addition onto double bonds on oleic acid chain instead of abstracting hydrogens from allylic site. A significant increase in hydrogen abstraction by benzoyl peroxide is found in both linoleic alkyd and linolenic alkyd system. This result is in line with the previous conclusions made out of 2D gHMQC spectra that hydrogen abstraction from diallylic site by primary radical attack in linoleic alkyd and linolenic alkyd system.

Results from gas chromatography quantitative analysis generally support previous NMR and solvent extraction experimental outcomes which is the proposed thermodynamic driving reaction mechanism. It gives a new outlook of utilizing quantitative method to study this complex system.

Table 5.7 Benzoic acid product weight percentage in four samples

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Weight of sample</th>
<th>Peak area</th>
<th>Benzoic acid concentration</th>
<th>Benzoic acid weight percentage</th>
<th>BPO conversion</th>
<th>Moles of benzoic acid</th>
</tr>
</thead>
</table>

62
<table>
<thead>
<tr>
<th></th>
<th>(g)</th>
<th>on (μg/mL)</th>
<th>(wt%)</th>
<th>(wt%)</th>
<th>(mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stearic/aacrylic</td>
<td>0.4208</td>
<td>3789</td>
<td>7.2</td>
<td>0.02%</td>
<td>1.42%</td>
</tr>
<tr>
<td>Oleic/aacrylic</td>
<td>0.2080</td>
<td>4124</td>
<td>10.3</td>
<td>0.05%</td>
<td>3.55%</td>
</tr>
<tr>
<td>Linoleic/aacrylic</td>
<td>0.0471</td>
<td>6156</td>
<td>29.3</td>
<td>0.62%</td>
<td>44.02%</td>
</tr>
<tr>
<td>Linolenic/aacrylic</td>
<td>0.1961</td>
<td>15397</td>
<td>115.7</td>
<td>0.59%</td>
<td>41.89%</td>
</tr>
</tbody>
</table>
CHAPTER VI

CONCLUSIONS

In this work, four model alkyds were prepared to study the grafting mechanism of acrylic monomers, methyl methacrylate and butyl acrylate, onto alkyds. These model alkyds were prepared via a fatty acid process with stearic acid, oleic acid, linoleic acid or linolenic acid with phthalic anhydride and glycerol. Acrylated alkyds were synthesized by copolymerizing these model alkyds and acrylic monomers in the presence of benzoyl peroxide initiator. The $^1$H spectra and 2D gHMQC spectra give valid proves of different grafting reaction mechanisms:

1. For the stearic alkyd model systems, evidence of grafting by hydrogen abstraction from glyceride unit was found. It was surmised that the acrylic macroradical combines with the glyceride radical to form the alkyd-acrylic copolymer.

2. For the oleic alkyd model systems, the grafting site was primarily located at the double bond on the fatty acid chain as a noticeable decrease of double bond is discovered from the integration of resonance signal of vinyl double bond.
3. For the linoleic alkyd and linolenic alkyd model systems, the grafting reaction mainly occurs at the activated methylene group on the fatty acid group via hydrogen abstraction by primary radical attack.

It is concluded that the grafting reaction tends to follow the sequence of bond dissociation energy, in other words, grafting will occur at the position that require the lowest energy. As long as there are non-conjugated double bonds available, the hydrogen abstraction from the diallylic group is the most favorable reaction. When diallylic hydrogens are not present, a preferred reaction pathway for a benzoyl peroxide radical is to add to a double bond. In a saturated alkyd model, the grafting will only occur at the glyceride unit via hydrogen abstraction. NMR results are supported by solvent extraction and gas chromatography quantitative analysis. In solvent extraction experiments, degree of grafting shows that the more double bond content there is in a certain amount of alkyd, the higher degree of grafting could be achieved. Butyl acrylate tends to give a higher degree of grafting than methyl methacrylate as butyl acrylate has less steric hindrance. Gas chromatogram indicates that there are major hydrogen abstraction by benzoyl peroxide radical forming benzoic acid after abstracting hydrogens from diallylic site in linoleic and linolenic acid chain. In general, grafting mechanism in this system is driven by thermodynamics rather than monomer choice.
REFERENCES


Figure 1 Proton NMR spectrum of stearic alkyd

Figure 2 Proton NMR spectrum of stearic alkyd acrylated with MMA
Figure 3 Proton NMR spectrum of stearic alkyd acrylated with BA

Figure 4 Proton NMR spectrum of oleic alkyd
Figure 5 Proton NMR spectrum of oleic alkyd acrylated with MMA

Figure 6 Proton NMR spectrum of oleic alkyd acrylated with BA
Figure 7 Proton NMR spectrum of linoleic alkyd

Figure 8 Proton NMR spectrum of linoleic alkyd acrylated with MMA
Figure 9 Proton NMR spectrum of linoleic alkyd acylated with BA

Figure 10 Proton NMR spectrum of linolenic alkyd
Figure 11 Proton NMR spectrum of linolenic alkyd acrylated with MMA

Figure 12 Proton NMR spectrum of linolenic alkyd acrylated with BA
Figure 13 2D gHMQC overlay of MMA grafted stearic alkyd over stearic resin

Window 1 ($^1$H: 0.5-3.5 ppm, $^{13}$C: 10-45 ppm)

Window 2 ($^1$H: 3.0-6.0 ppm, $^{13}$C: 45-90 ppm)

Window 3 ($^1$H: 5.0-8.5 ppm, $^{13}$C: 120-145 ppm)
Figure 14 2D gHMQC overlay of BA grafted stearic alkyd over stearic resin

Window 1 ($^1$H: 0.5-3.5 ppm, $^{13}$C: 10-45 ppm)

Window 2 ($^1$H: 2.5-6.0 ppm, $^{13}$C: 45-90 ppm)
Figure 15 2D gHMOC overlay of MMA grafted oleic alkyd over oleic alkyd resin

Window 3 (\(^1\)H: 5.0-8.5 ppm, \(^{13}\)C: 120-145 ppm)

Window 1 (\(^1\)H: 0.5-3.5 ppm, \(^{13}\)C: 10-45 ppm)
Window 2 ($^1$H: 3.0-6.0 ppm, $^{13}$C: 45-90 ppm)

Window 3 ($^1$H: 5.0-8.5 ppm, $^{13}$C: 120-145 ppm)
Figure 16 2D gHMQC overlay of BA grafted oleic alkyd over oleic alkyd resin

**Window 1** ($^1$H: 0.5-3.5 ppm, $^{13}$C: 10-45 ppm)

**Window 2** ($^1$H: 3.0-6.0 ppm, $^{13}$C: 45-90 ppm)

**Window 3** ($^1$H: 5.0-8.5 ppm, $^{13}$C: 120-145 ppm)
Figure 17 2D gHMQC overlay of MMA grafted linoleic alkyd over linoleic alkyd resin

Window 1 ($^1$H: 0.5-3.5 ppm, $^{13}$C: 10-45 ppm)

Window 2 ($^1$H: 3.0 -6.0 ppm, $^{13}$C: 45-90 ppm)
*red circle indicates the newly generated by hydrogen abstraction

Window 3 ($^1$H: 5.0-8.5 ppm, $^{13}$C: 120-145 ppm)

Figure 18 2D gHMOC overlay of BA grafted linoleic alkyd over linoleic alkyd resin
Window 1 ($^1$H: 0.5-3.5 ppm, $^{13}$C: 10-45 ppm)

Window 2 ($^1$H: 3.0-6.0 ppm, $^{13}$C: 45-90 ppm)

*red circle indicates the newly generated by hydrogen abstraction

Window 3 ($^1$H: 5.0-8.5 ppm, $^{13}$C: 120-145 ppm)
Figure 19 2D gHMQC overlay of MMA grafted linolenic alkyd over linolenic alkyd resin

Window 1 ($^1$H: 0.5-3.5 ppm, $^{13}$C: 10-45 ppm)

Window 2 ($^1$H: 3.0-6.0 ppm, $^{13}$C: 45-90 ppm)

*red circle indicates the newly generated by hydrogen abstraction
Window 3 ($^1$H: 5.0-8.5 ppm, $^{13}$C: 120-145 ppm)

Figure 20 2D gHMQC overlay of BA grafted linolenic alkyd over linolenic alkyd resin

Window 1 ($^1$H: 0.5-3.5 ppm, $^{13}$C: 10-45 ppm)

Window 2 ($^1$H: 3.0-6.0 ppm, $^{13}$C: 45-90 ppm)

84
*red circle indicates the newly generated by hydrogen abstraction

Window 3 ($^1$H: 5.0-8.5 ppm, $^{13}$C: 120-145 ppm)
Figure 21 Gas chromatography of benzoic acid standard solution (concentration of 25ppm)

Peak Info for 25ppm standard sample:

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Figure 22 Gas chromatography of benzoic acid standard solution (concentration of 50ppm)

Peak Info for 50ppm standard sample:

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Figure 23 Gas chromatography of benzoic acid standard solution (concentration of 100ppm)

Peak Info for 100ppm standard sample:

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Figure 24 Gas chromatography of benzoic acid standard solution (concentration of 150ppm)

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Figure 25 Gas chromatography of stearic/acrylic system before reaction

Peak Info for Stearic before reaction

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2.464 0.000 0.0000 VV 13.80 12796424 82.783394
3.089 0.000 0.0000 TF 0.00 2309 0.014938
3.142 0.000 0.0000 TF 0.00 461759 2.987238
3.619 0.000 0.0000 VP 1.85 2172040 14.051490
9.542 0.000 0.0000 TF 0.00 1185 0.007664
9.762 0.000 0.0000 TF 0.00 3587 0.023205
15.083 0.000 0.0000 VV 0.00 1757 0.011369
15.196 0.000 0.0000 VV 0.00 1662 0.010754
17.887 0.000 0.0000 VV 0.00 1632 0.010558
Figure 26 Gas chromatography of stearic alkyd/acrylic system after reaction

Peak Info for Stearic after reaction

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Figure 27 Gas chromatography of oleic alkyd/acrylic system after reaction

Peak Info for Oleic after reation

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Figure 28 Gas chromatography of linoleic alkyd/acrylic system after reaction

Peak information for linoleic after reaction

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Figure 29 Gas chromatography of linolenic alkyd/acrylic system after reaction

Peak information for linolenic after reaction

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