SYNTHESIS AND CHARACTERIZATION OF
PHOTORESPONSIVE POLYACRYLATES
FOR PRESSURE SENSITIVE ADHESIVES APPLICATION

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SYNTHESIS AND CHARACTERIZATION OF
PHOTORESPONSIVE POLYACRYLATES
FOR PRESSURE SENSITIVE ADHESIVES APPLICATION

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Thesis

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Stimuli responsive polymeric materials can adapt to surrounding environments, which may be sensitive to various factors, such as temperature, electric field, magnetic field, pH or light. Photoresponsive polymers are particularly interesting since light can be controlled spatially and temporally, which makes them potentially useful in many applications such as shape memory materials, surface patterned materials and controlled drug release.

Switchable adhesion exhibits the ability to trigger adhesion in response to environmental changes, for example, temperature, light, pH, solvent, mechanics, and electro or magnetic field. The noteworthy functionality of switchable adhesives has been met with significant interest in many fields of material science and engineering and can find many useful and valuable applications, including the pain-free removal for wound dressing, simplification of separation for material recycle and easily repair or replacement of components in electronics.

In this work, photoresponsive properties are utilized for switchable adhesion, which allows the debonding on demand. A series of novel photoresponsive polyacrylates are designed and synthesized, which are copolymers of n-butyl acrylate, 2-carboxyethyl acrylate and chromophores-contained diacrylate cross-linker. The photoresponsive cross-linker was introduced to achieve the removal of the adhesives since the photoresponsive
linkage can be cleaved upon photo-irradiation. Besides, these polymers were synthesized by emulsion polymerization, which is environmentally-friendly and also facilitates their industrial applications for pressure sensitive adhesives (PSAs) products.
DEDICATION

This thesis is dedicated with gratitude to my parents,

Jinxing Li and Xuemiao Chen,

for their sacrifices to support my study and their steadfast encouragement.
ACKNOWLEDGEMENTS

First, I would like to thank my adviser Dr. Abraham Joy for his guidance in my research. He offered me great help during my study and gave me lots of encouragement for this project.

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At last, I would like to thank my parents for their guidance and support throughout both my study and my life. They have guided me through the winding path of my growth, while giving me enough room to let me make and learn from my own mistakes.
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CHAPTER I

INTRODUCTION

Adhesives with switchable properties\textsuperscript{1-7} allow controlled bonding and debonding on demand. This feature has been met with strong interest in various fields of material science and engineering and can find many valuable and useful applications, including the easily repair of components in bonding structures\textsuperscript{8}, the trauma-free and pain-free removal of wound dressing\textsuperscript{9,10}, or the simplification of recycled material separations\textsuperscript{2}. And pressure sensitive adhesives (PSAs) are adhesives that can wet and bond to surfaces instantaneously when a light pressure is applied. PSAs are one of the main branches of adhesive materials and are widely used in many fields of life science. In the field of medicine, PSAs are generally applied to medical tapes for wound dressing and restoration. However, it is always a painful experience for patients to remove the bandages from the skin after the wound had healed\textsuperscript{11}. For those patients who have softer skins, the surface of skin (or hair) would be possibly peeled along with the medical tapes, which could cause serious skin trauma.

In this work, novel photoresponsive polyacrylates were designed and synthesized for pain- and trauma-free PSAs application by emulsion polymerization of n-butyl acrylate, 2-carboxyethyl acrylate and photoresponsive diacrylate cross-linker. Acrylate copolymer system was used since they are widely applied in skin contact applications
owing to less irritation to skin compared to natural rubber formulations. In addition, the photoactive cross-linker embedded in the polymers will break upon photo-irradiation, which would result in decreased peel strength and therefore facilitates the removal of the adhesives. For the described PSAs system, two photoresponsive cross-linkers, alkoxyphenacyl-based and coumarin-based diacrylate cross-linkers, were synthesized and can undergo chain scission at 300 nm and 254 nm respectively\textsuperscript{12,13}. The coumarin system has an ability to reversibly crosslink at a wavelength of 350 nm\textsuperscript{13}. 
CHAPTER II

BACKGROUND

2.1 Adhesives

Human beings have been known to make use of adhesives since the start of civilization. A glue pot and brush were found to bond veneer to a thin strip of sycamore in Carving in Thebes (ca. 3300 BC). Then in Holland in 1690, the first plant for commercial glue was established\textsuperscript{14}. And according to the records of patents archives, the first patent (No. 183, 024) for adhesive was issued in 1876\textsuperscript{14}. At present, many commercialized adhesive products, especially the pressure sensitive adhesives, such as Scotch® tapes and Easy Peel® address labels, not only make the life and office work more convenient, but also promote the developments of adhesives in many other high-tech products, such as space shuttle and electrical automobiles. Compared to other types of bonding structure, adhesive bonding has advantages and disadvantages\textsuperscript{15}. One superior advantage of adhesive is the possibility to adhere to many different adherend surfaces regardless the shapes and material types. Furthermore, the adhesive bonding is always faster and more economical than the mechanical fastening. Also, adhesives can be easily used as sealant to protect the surface or space from environmental condition. The disadvantages of adhesives are the relatively limited aging period to some extreme environments and sometimes the need for delicate surface preparation.
2.1.1 Classification of adhesives

Adhesives can be defined as substances that are capable of attaching two surfaces together in a stable and permanent manner\textsuperscript{15,16}. There are different types of adhesives and several classification methods for adhesives.

According to the classification of adhesives based on the load-carrying ability, they can be divided into structural and non-structural adhesives. Structural adhesives are normally used below their glass transition temperature, which can carry significant stresses. Usually, the shear strength of structural adhesives is above 6900 kPa (1000 psi) and the strength of structural adhesives does not change significantly with moderate aging. Commonly used structural adhesives are composed of polyurethanes, epoxy, phenolics, acrylates and polyaromatic resins. For non-structural adhesives, they do not have good environmental durability because the non-structural adhesives and their shear strength are lower than 6900 kPa (1000 psi). Non-structural adhesives, composed with natural rubber, synthetic rubbers, polyvinyl acetate, polyesters, silicones, polyolefins, acrylics and some natural resins, are generally used for pressure sensitive adhesives, hot-melts and packaging adhesives.

Another approach to classification of adhesives discerns the application methods and also the curing or setting formation. Different types of adhesives have different steps in the adhesion process. General steps of the formation of bonding are application of the adhesive, wetting the surface and curing or setting to form a bonding. The ways to achieve adhesive setting can be divided into by cooling (hot-melt adhesives), by releasing (solution and emulsion-based adhesives), by in-situ polymer reaction (e.g., UV curable
adhesives, aerobic or anaerobic adhesives) and by application of pressure (typically pressure sensitive adhesives)

Adhesives can also be classified based on their chemical and physical natures. Polymeric materials used for adhesives can be thermoplastic, thermosetting, elastomeric or hybrids. The thermoplastic adhesives are non-cross-linked and reverse to a fluid when heating temperature is higher than glass transition temperature. Differently, the thermosetting adhesives are cross-linked network that cannot melt or be dissolved by solvents. And adhesives made up by elastomer are originated from natural or synthetic rubbers and can be highly elongated. Besides, the hybrid adhesives are mixtures of different types of polymer to adjust the adhesion for specific applications.

2.2 Pressure sensitive adhesives

One class of adhesives that plays an important role in adhesives science and technology is referred to as pressure sensitive adhesives (PSAs)\textsuperscript{15,17}. The PSAs are commonly utilized as the formation of tapes, labels, and protective films. And the market and technology of PSAs products are in rapid expansion in both current and new high-performance areas.

2.2.1 Composition of pressure sensitive adhesives

Pressure sensitive adhesives can adhere to surfaces instantaneously upon application of a light pressure. Different from other types of adhesives, PSAs maintain their fluid state after bonding. And they must remain the tacky status permanently to stick to substrate and possess enough peel and shear strength so that do not leave any residue when peeling from the substrate\textsuperscript{15,18,19}. 

5
Because no homopolymer can achieve the appropriate balance of adhesion (stickiness) and cohesion (shear strength), PSAs are synthesized by copolymerization with multiple monomers. First, the main composition of PSAs should be the soft monomers, which possess very low $T_g$ to make it tacky enough to stick to the surface. The proper $T_g$ of an optimal PSAs is usually below 0°C and many commercial PSAs products have much lower $T_g$ (i.e., even as low as -60°C)\textsuperscript{15}. Tack and peel strength are imparted by soft or low glass transition temperature monomer (i.e., n-butyl acrylate, 2-ethylhexyl acrylate, acrylic acid, n-octyl acrylate, methyl acrylate and ethyl acrylate). Although large numbers of soft monomers are reported to apply to the synthesis of PSAs, the most commonly used are n-butyl acrylate ($T_g = -54°C$), 2-ethylhexyl acrylate ($T_g = -70°C$) and ethyl acrylate ($T_g = -24°C$). These copolymers with soft monomers have $T_g$ below 0°C and obtain inherent tackiness but are lack of sufficient cohesive strength (shear strength). Thus, incorporation of hard monomers (i.e., ethylene, acrylic acid ($T_g = 106°C$) and acryl amide ($T_g = 179°C$)), which have much higher $T_g$, is needed to enhance the shear strength. The $T_g$s of hard monomers are above 0°C and most of them are much higher than room temperature. In addition, functional monomers, such as acrylic amide, 2-hydroxypropyl acrylate ($T_g = -7°C$) and 2-carboxyethyl acrylate ($T_g = -10°C$), are incorporated for modified adhesion to desired substrates. Also their functional group provide reactive sites for chain crosslinking reactions and thus improve peel and shear strength while can lower the tack simultaneously. And the carboxylic group on the side chain can be modified to link other different type of functional group for specific application.
PSAs formulation can be designed based on specific adhesive application and the adhesion property can be tuned by adjustment of the relative composition of soft monomers, hard monomers and functional monomers. One of the ideal formation of water-based PSA is composed of 70-90wt% soft monomer, 10-30wt% modifying hard monomer, and 3-6wt% functional monomers. The so-called empirical formulation can serve as the starting formulation as the beginning of design of a PSA.

2.2.2 Developments in pressure sensitive adhesives

Pressure sensitive adhesives represent a major field of adhesive materials of industrial and scientific interest. Czech et al. designed and fabricated advanced biodegradable pressure-sensitive double-coated tapes containing starch carrier and water-soluble partially degradable polymer. The described PSAs showed excellent tack and peel adhesion as well as high thermal shear strength. The soil test (degradation) showed total decomposition of the carrier and the water-soluble PSA reached 60% degradation within 28 days. Kajtna et al. synthesized acrylic polymer/montmorillonite (MMT) clay nanocomposite pressure sensitive adhesives (PSA). Modified and unmodified MMT clay were dispersed into monomer which was polymerized using suspension polymerization. The adhesion properties were determined by measurements of tack, peel strength and shear strength. Results showed that the adhesive properties were strongly influenced by the amount and type of MMT clay. Minghetti et al. designed medical water-soluble pressure sensitive adhesive (PSA) incorporated with cellulose ethers or polyvinylpyrrolidone (PVP). The PSA can be easily removed from skin. The water vapor permeability of polymer is high and no primary irritation was observed. Boyne designed a novel acrylic copolymer containing pendant methacrylate groups that undergo
cross-linking upon UV irradiation when combined with a suitable photo-initiator\textsuperscript{24}. The synthesis is shown in the following Scheme 2.1.

Scheme 2.1. Synthesis of Methacrylate functional PSA

The itaconic anhydride containing PSA reacted with 2-hydroxyethyl methacrylate (HEMA) at 50°C in the presence of acid catalyst. Then carbon-carbon double bond was introduced in the side chain. The pendant methacrylate group is capable of cross-linking with a suitable photo-initiator to achieve the deactivation of adhesion upon UV irradiation.

The development of future PSAs are focusing on the incorporation of functionalities, which can enhance the adhesion properties and also provide response to stimuli factors, such as light, temperature and pH\textsuperscript{1}.

2.2.3 Viscoelastic properties of pressure sensitive adhesives

Rheological property plays an essential role in the development of pressure sensitive adhesives (PSAs). Pressure sensitive adhesives are viscoelastic polymeric
materials with both flow properties and elasticity\textsuperscript{15,18}. The flow property dominates the bonding formation between the adhesive and adherent, while the elastic property dominates cohesion of the adhesive itself and the storage of energy. The balance of these properties is the most important to design and develop a pressure sensitive adhesives that meets with specific applications.

Pressure sensitive adhesives are usually applied to a laminate material so that the product can be used for tapes, labels and many other products generally used in daily life\textsuperscript{14,15}. The rheological property of the pressure sensitive product may differ from those pure uncoated adhesives. Besides, it remains difficult to characterize the PSAs and to find out the generally valid data. For the rheological experiment on the rheometer, the thickness for a sample should be thick enough to get reliable storage modulus and loss modulus. But seldom are pressure sensitive adhesives used as thick layers. However, to understand theoretically of the basic adhesive science, the rheology of pure pressure sensitive adhesives will be reviewed in this part.

The property of polymer that can be used for PSAs is based on the viscoelastic, non-Newtonian flow behavior. This kind of macromolecular nature makes polymers potential to be used as adhesives. Based on the viscoelasticity of polymer, adhesives can form bonding in which the adhesive behave like either a fluid or solid. Fluid behavior, which can be characterized as viscosity, has effect on the mobility and thus influences on the adhesion. While the solid behavior, which can be characterized as modulus, has effect on the deformability and thus influences on the cohesion.

In continuum mechanics, Newtonian fluid is defined as a fluid in which the applied stress is linearly proportional to the strain rate\textsuperscript{25}. Compared to Newtonian fluid,
PSAs need to show the opposite characteristics. As aforementioned, polymers that can be used as pressure sensitive adhesive are viscoelastic materials. Viscoelasticity is the property that materials show both viscous and elastic characteristics when applied with stress. For a pressure sensitive adhesive, because of its viscosity, it should be tacky so that adhesive can wet the surface to which it applied and form bonding when a light pressure. On the other hand, the PSA provides sufficient elasticity and cohesion. Although the tackiness is aggressive, the PSA can still be removed from surfaces without leaving any residue. The PSAs require the two contradictory properties together. The delicate balance between viscosity and elasticity is the deciding feature of PSAs. It has been well agreed by many scientists that the viscoelastic properties of the adhesives dominates the performance of PSAs (e.g. peel, tack, and shear).

2.2.4 Peel strength

The peel strength can be measured by peel test by which the average force to part two bonded materials (e.g., tapes, labels and plastic films) can be measured quantitatively at a constant peeling rate. The strength of peeling is calculated during the peel test by divided the average peel force by the unit width of the bonded samples. Adhesive peel test may be performed with 90 degree, 180 degree, T-peel, or Floating Roller\textsuperscript{14}.

In the measurement of the peel strength, both the value of peel force and the mode of peel failure are of importance. Generally, the desired mode of failure is adhesive failure. Other failure types, usually not desired, are cohesive failure (i.e., residues are left on both of the testing substrates), unstable failure (no residue observed but the peeling force oscillate in a large amplitude) or an adhesive transfer (the adhesive transfers from the carrier to the testing substrate).
There are several factors that affect the peel strength as outlined in the Table 2.1. Among all the chemical factors, introduction of high Tg components in polymer will improve the peel strength to a point where the adhesive becomes so stiff that cannot wet the surface and thus the peel strength decreased. Incorporation of carboxylic acid groups can increase the peel strength because of the increased interfacial affinity to the polar surfaces rather than the bulk properties of adhesives. As aforementioned, commonly used monomer to incorporate carboxylic group are acrylic acid, methacrylic acid and 2-carboxyethyl. Generally, low crosslinking density inside the PSAs can improve Peel strength. Zosel et al. reported that a loosely cross-linked network structure with long chain branching can make a good balance between tack and peel strength. But because of the crosslinking density, it is hard to characterize the network morphology. High density of crosslinking makes the adhesive too stiff to adhere to surface and thus, make the peel strength reduce sharply. Plessis et al. have demonstrated that once the gel content is above 36%, the peel strength of BA/AA emulsion-based PSAs decreases. Besides, tackifier, stabilizer and peel modifiers can increase the peel strength.

Table 2.1. Factors affecting peel strength

<table>
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<tr>
<td>Chemical</td>
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<tr>
<td>“Soft” monomers</td>
<td>Decrease</td>
</tr>
<tr>
<td>“Hard” monomers</td>
<td>Shows maximum</td>
</tr>
<tr>
<td>Polar monomers</td>
<td>Shows maximum</td>
</tr>
<tr>
<td>Cross-linking agents</td>
<td>Shows maximum</td>
</tr>
<tr>
<td>Tackifier</td>
<td>Shows maximum</td>
</tr>
<tr>
<td>Stabilizers</td>
<td>Shows minimum/maximum</td>
</tr>
<tr>
<td>Peel modifiers</td>
<td>Increases</td>
</tr>
<tr>
<td>Physical</td>
<td></td>
</tr>
<tr>
<td>Adhesive layers thickness</td>
<td>Increases</td>
</tr>
<tr>
<td>Carried thickness/flexibility</td>
<td>Shows maximum</td>
</tr>
<tr>
<td>Dwelling time</td>
<td>Increases</td>
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</table>
Charmeau et al. demonstrated that the peel strengths of the latex films cast from four different particle structures were always lower than the films cast from the solution polymers\textsuperscript{28}. The relatively lower molecular movement and energy dissipation of the film cast from latex can explain this phenomenon. That was due to the soft particles was embedded in to a relatively rigid network in the latex film.

Physical factors affect the peel strength from the adhesive thickness, carrier material and sample preparation. First, peel strength increases along with the increasing of adhesive thickness. Second, the properties of the carrier materials, such as the thickness of carrier and its moduli, will also affect the peel strength complexly, especially for the 180° angle peel test. Benedek and Heymans have emphasized the influence of thickness of carrier on the deformation of backing will have negative effect on the peel force\textsuperscript{15}. The peel force to carrier thickness shows maximum value at a specific carrier thickness. And the carrier modulus is a direct function with peel strength. However it is an indirect function of adhesive modulus with peel strength. Furthermore, sample preparation, such as loading pressure, drying time, dwell time, temperature and humidity, can also affect the peel strength. Dwell time is defined as the time counted from when the adhesive adheres to substrate to the time when start the peel test. Benedek et al. demonstrated that peel strength of emulsion-based PSAs would nearly double when increasing dwell time from 0 to 24hr\textsuperscript{15}. The temperature will influence the rheological property of polymer and thus, has effect on the peel strength.

2.2.5 Shear strength

Shear strength is an indicator of adhesive resistance to applied shear force\textsuperscript{15}. Usually it is referred to as cohesive strength or cohesion of adhesive. Shear strength can
be measured as a force required to pull the PSA parallel to the substrate that the PSA was affixed to with a specific pressure.

Table 2.2. Factors affecting shear strength\textsuperscript{16}

<table>
<thead>
<tr>
<th>Factors</th>
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<tbody>
<tr>
<td>Chemical</td>
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<tr>
<td>“Soft” monomers</td>
<td>Decreases</td>
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<td>“Hard” monomers</td>
<td>Increases</td>
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<tr>
<td>Polar monomers</td>
<td>Increases</td>
</tr>
<tr>
<td>Cross-linking agents</td>
<td>Increases</td>
</tr>
<tr>
<td>Tackifier</td>
<td>Decreases</td>
</tr>
<tr>
<td>Stabilizers</td>
<td>Decreases</td>
</tr>
<tr>
<td>Peel modifiers</td>
<td>Decreases</td>
</tr>
<tr>
<td>Physical</td>
<td></td>
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<tr>
<td>Adhesive layer</td>
<td>Decreases</td>
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<tr>
<td>thickness</td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>Decreases</td>
</tr>
</tbody>
</table>

Shear strength increased as the composition of hard monomer with high Tg increases. And the presence of small molecules (i.e., tackifier, stabilizer and peel modifier) will reduce the shear resistance. The factors that have effect on the shear strength are listed in the Table 2.2.

Shear resistance increases along with the increasing molecular weight. The higher molecular weight, the longer chain length, and the more entanglements and thus, the higher shear strength of PSAs. And the crosslinking density will promote the increase of the shear strength by decreasing the free movement of polymer chains. Plessis et al. showed that PSA with loosely crosslinking density will increase the shear strength\textsuperscript{27}. Thinking about the instantaneously profound effect on tack and peel, the crosslinking density should be controlled.
2.3 Switchable adhesion

Figure 2.1. Adhesion and hierarchical structures: (a) photographs and SEM (scanning electron microscopy) image of sponge\(^{29}\). (b) photographs and SEM image of gecko adhesive structures. (c) photographs and SEM image of sea star adhesive structure\(^{30}\) (d) represented 3D structure of a protein.

Adhesion technology has made a great progress in past decades and has achieved widespread replacement of mechanical fastening with adhesive bonding. However, so far, it is still a challenge to produce adhesives that are sticky on demand. Recent efforts to design and develop novel switchable adhesives are proposed in this part.

Many natural materials, such as proteins, and DNA, exhibit multi-dimensional structures (see Fig. 2.1). The hierarchy of these structures plays an essential role in the determination of the material properties. Switchability, i.e. strong adhesion but also easily detachable, is the most interesting functionality in these hierarchical natural structures. Scientists are trying to mimic these switchable properties by developing stimuli-responsive adhesives, which have response to external chemical or physical signals and switch between bonding and non-bonding state.
2.3.1 Switchable adhesion by chemical functionality

By chemical functionality, adhesion can be switched by responsive molecular interactions, such as electrostatic interaction, hydrogen bonding, hydrophobic interaction. These materials used are stimuli-responsive polymers, which are promising for development of switchable adhesive performance that can respond upon change in temperature change, light, pH change, solvent or biochemical signals\textsuperscript{31-34}.

Phase transition triggered by temperature changing is the principle for designing the thermal switchable adhesion. De. Crevoisier et al. proposed that the switchable adhesive can be developed using the fluorinated liquid crystalline polymer that can undergo a first-order phase transition upon heating or cooling\textsuperscript{35}. Synytska et al. synthesized a series of thermoresponsive polymer brushes with different structure using the poly(N-isopropylacrylamide), PNIPAM, and the poly(oligo(ethylene glycol)methyl ether) methacrylate-\textit{co}-2-(2-methoxyethoxy)ethyl methacrylate, P(OEGMA-MEO2MA), and poly(oligo(ethylene glycol)methyl ether) methacrylate-\textit{co}-oligo(propylene glycol) methacrylate, P(OEGMA-OPGMA)\textsuperscript{36,37}. And all the polymer with different architectures were found to be completely non-sticky when the temperature is below the LCST (Lower Critical Solution Temperature).

The switchable adhesion can also be achieved by photoresponsive properties. Photoactive chromophores and photo initiation are useful tools for the design of ‘switch-off’ bonding. An acrylic based PSAs, which is functionalized with carbon double bond that can be chemically cross-linked to removal easily. The pendant vinyl group photoinitiated by visible light and cross-linked to make adhesive stiff enough and thus, reduce its adhesion. The company Lumina Adhesives\textsuperscript{TM} developed a photoresponsive
pressure sensitive adhesive called ‘Adhelight’ for the light switchable medical tapes application. The adhesive adhere to skin strongly but can be easily removed painlessly without leaving any residue after a few seconds by irradiation with visible light. The commercialized medical tape comprises a transparent film onto which the photo cross-linkable adhesive is laminated. And on top of the transparent film is bonded with a light protective film with a breathable barrier. When it is required to remove the tapes, firstly the protective film is peeled off and adhesive is under exposure of light through the transparent film for several seconds. Then it causes the adhesion to be switched-off and the medical tape can be removed without any pain and residue. This light switchable PSAs with tunable adhesion property can satisfy the need for secure fixing with pain-free and irritation-free removal of wound dressings and other applications where switchable adhesion is needed.

Other type of adhesives can be switched reversibly by the change of pH. Keddie et al. published switchable mechanical and adhesive properties of a P(BuA-co-AA) latex film. Probe-tack measurements showed the latex film originated from low-pH dispersion has higher adhesion energy compared to film form the high-pH dispersion.

Minko et al. developed solvent-responsive switchable adhesive based on polymer brushes mixture. Adhesion of mixed polymer brushes can be tuned by exposing to selective solvents. Creton et al. reported the adhesive properties of another mixed polymer brushes made with functionalized polystyrene and poly(2-vinylpyridine). Immersed in selective solvents can vary the chain organization of brushes mixture. The exposure can achieve switchable adhesion.
2.3.2 Switchable adhesion by physical topography functionality

Pioneering research in switchable adhesion by using topography started in the beginning of 21st century. Del et al. published the first patterned surface for switchable adhesion. Since then, adhesive topography designed by response to stimuli, such as light, temperature, mechanical stretching and electric/magnetic field, promotes the development in the field of switchable adhesives.

2.4 Emulsion polymerization

Emulsion polymerization is a kind of heterogeneous polymerization which is widely used in making various commercialized polymers such as poly(vinyl acetate), polychloroprene and poly(methyl methacrylate).

2.4.1 Emulsion polymerization system

The main components for emulsion polymerization consist of initiator, monomer, emulsifier and water. Other components can also be present in the system such as stabilizer, chain transfer agent or buffering agents.

1. Monomer: It is usually oil-soluble and can undergo radical polymerization. If the monomer has a good solubility in water, the reaction kinetics would be similar to that of solution polymerization.

2. Water: Dispersion medium.

3. Initiator: It can be either thermal initiator or redox initiator that is water-soluble.

4. Emulsifier: Surfactants are used which enable a fast reaction rate and minimize coagulation in the reactor. Commonly used surfactants include sodium dodecyl sulfate (SDS) and fatty acids.
2.4.2 Mechanism of emulsion polymerization

As shown in Figure 2.2, when the concentration of surfactant in water is above critical micelle concentration (CMC), surfactant can interact to form small colloidal clusters which are termed micelles. When the monomer is added dropwise into a mixture of water and emulsifier, most of the monomer is dispersed as monomer droplets and the size depends on the stirring rate. Due to the hydrophobic effect, the monomer droplets formed were surrounded and stabilized by emulsifiers. The hydrophilic part of emulsifiers contacts with the water phase and the hydrophobic part contacts with the oil phase formed by monomers. Only a very small amount of monomers dissolves in the continuous water phase, which then enters the interior hydrophobic parts of the micelles.

The water-soluble initiators are dissolved in water phase where the initiating radicals are produced. The initiating radicals can enter the micelles and initiate the
polymerization. As the polymerization proceeds, the monomer in the micelles will be consumed and replenished by the monomer droplets. On the other hand, polymerization can also take place in water phase due to the small amount of monomers in water. When the monomer polymerizes in water phase, the propagating radical will precipitate from water phase. There are two mechanisms for particle nucleation, micellar nucleation and homogeneous nucleation. The micellar nucleation (also termed heterogeneous nucleation) occurs when the radicals enter the micelles from water phase to initiate chain propagation. For homogeneous nucleation, the oligomeric radicals are precipitated from the water phase and stabilized by emulsifier. After that, monomer is absorbed to form polymer latex particle.

2.4.3 Advantages of emulsion polymerization

Emulsion polymerization has several advantages including (1) The heat dissipation problem can be solved by using water as the reaction medium. (2) The viscosity of the reaction system remains close to that of water and does not depend on the molecular weight of the polymers. (3) For the product of emulsion polymerization, it can be readily used for many applications such as adhesives and coatings. (4) The rate of polymerization is fast and the molecular weight is high.

2.4.4 Film formation of emulsion-based pressure sensitive adhesives

For most application of emulsion-based PSAs, latex is coated to form a thin film onto a substrate. The morphology of the dry latex film plays a central role in determining the properties of dry film, such as mechanical strength and permeability. The morphology is governed by the process of film formation. That means it is of importance to understand the film formation process and figure out the structure-property relationships.
of adhesive film. By understanding the process of film formation process, we can control and design high performance PSAs latex.

Figure 2.3 Process of film formation of emulsion-based pressure sensitive adhesives

The process of film formation plays a central role in determining the adhesion and cohesion property of emulsion-based PSAs film. Mechanical properties, thermal properties and permeability are the commonly investigated latex film properties. Compared with the PSAs film originated from the solution cast, Young’s modulus of latex film were higher than the film resulting from the solution polymerization with same composition.
The film formation process (see Fig. 2.3) is the transformation from a polymeric emulsion to an adhesive film along with the water evaporation. The first stage is that water evaporates and brings latex particles to a closer contact. And the close contact of particles will prevent the water diffusing from the particle layer and thus, decrease the rate of water evaporation. Richard et al. developed several drying models offering a potential theoretically understanding of the latex film formation process\textsuperscript{46}. In the second stage, preliminary film of deformed particles is formed with relative weak mechanical architecture. Each particle consists of a hydrophobic polymeric core and a hydrophilic shell formed from the surfactant to stabilize the particle in water phase. Two factors, drying temperature as driving force and the Tg of polymer as resisting force, govern this stage. In the final stage, a further coalescence of the latex particles form the thin adhesive layer finally. The cohesive strength increases by the inter-diffusion of particles that adjacent to each other. The molecular weight of polymer, particle structure, temperature and other small molecules (i.e., surfactant and solvent) dominate this final formation of latex film. The inter-particle chain movement and entanglement is usually presented by Gennes’ reptation model. Also the inter-particle cross-linking can lead to a cross-linked film formation, which influences the inter-diffusion of latex film. Klein el al. have reported the utilization of 1wt\% of isobutoxy methyl acrylamide as cross-linker in BA/AA and 2-EHA/AA emulsion-based pressure sensitive adhesives. And the data showed that the loose inter-particle crosslinking does help to improve the PSA performance.
2.5 Photoresponsive polymer

Photoresponsive polymers are one type of stimuli responsive polymers, whose properties can be tuned upon photo-irradiation. Due to the spatial and temporal control of the light, photoresponsive polymers have gained increasing attention in recent years and have been widely used for many applications such as photoactive shape memory material\textsuperscript{47}, actuators\textsuperscript{48}, surface patterned materials\textsuperscript{49} and controlled drug release\textsuperscript{50}.

2.5.1 Developments in photoresponsive polymer

There are three types of photoresponsive polymers: the first type is polymers with photoresponsive species in the side chain; the second one is polymers with end-functionalized photoactive unit; and the third being the photoresponsive species positioned in the polymer backbone.

Scheme 2.2. Synthesis of a hyperbranched polyester functionalized with 4-methylcoumarin units
For example, Shi has reported a hyperbranched polyester functionalized with 4-methylcoumarin units that can undergo photo-cross-linking and photocleavage\textsuperscript{51}. The novel polymer was synthesized by thiol-ene addition reaction of thiol-modified hyperbranched polyester with a coumarin based vinyl monomer (Scheme 2.2).

Coumarin end-functionalized polycaprolactones has been designed by Priestly et al\textsuperscript{52} as a detectable drug carrier. The interparticle assembly can be tuned reversibly by the photoirradiation due to the cyclodimerization and cleavage between coumarin based end group (Scheme 2.3.).

Scheme 2.3. Synthesis of coumarin end-functionalized polycaprolactones

Sun et al. synthesized a novel polycarbonate with alkoxyphenacyl based chromophore in backbone for potential application in drug delivery system\textsuperscript{12,53} (Scheme 2.4). The polycarbonate incorporated with photoactive moiety can be used for controlled
drug release. The controlled release was demonstrated by the release of Nile Red from nanoparticles of this polymer.

Scheme 2.4. Synthesis of alkoxyphenacyl based photoresponsive polycarbonate
CHAPTER III

EXPERIMENTAL

3.1 Materials and instrumentation

Materials: Dichloromethane (SIGMA-ALDRICH, 99.5%), methanol (SIGMA-ALDRICH, 99.5%), hexane (SIGMA-ALDRICH, 99.5%), ethyl acetate (SIGMA-ALDRICH, 99.5%), toluene (MACRON, AR), acetone (SIGMA-ALDRICH, 99.5%), acetonitrile (SIGMA-ALDRICH, 99.5%), n-butyl acrylate (TCI, 99.0%), 2-caboxyethyl acetate (POLYSCIENCE), sodium dodecyl sulfate (98.5%), 4,4′-azobis(4-cyanovaleric acid) (SIGMA-ALDRICH, 98.0%), sodium bicarbonate (SIGMA-ALDRICH, 99.5%), 3-bromopopan-1-ol (CHEM-IMPEX INT’L INC.), 18-crown-6 (ACROS ORGANICS, 99%), potassium carbonate anhydrous (EMD, GR ACS), sodium sulfate (SIGMA-ALDRICH, 99.0%), phenyl-λ³-iodanediyl bis(2,2,2-trifluoroacetate) (MATRIX SCIENTIFIC, 97%), 4-chloromethyl acetoacetate (ALFA AESAR, 97%), p-toluenesulfonic acid (Oakwood Chemical), resorcinol (SIGMA, 99%), acryloyl chloride (ALDRICH, 97%), hydroquinone bis(2-hydroxyethyl) ether (ACROS, 99.0%), silica gel (SORBTECH, catalog mubmer # 30930M-25, porosity: 60Å, particle size: 40-63μm, bulk density: 0.4g/ml)

Analytical methods: NMR was recorded on a Varian NMRS 300 MHz instrument. \(^1\)H NMR chemical shifts were reported in ppm relative to the \(^1\)H signal of solvent residual.
The size distributions of emulsions were determined by dynamic light scattering (DLS) using a Malvern Instruments Zetasizer Nano ZS. TA XT plus texture analyser was used to measure the peel and shear strength.

3.2 Synthesis of crosslinkers

Photoresponsive crosslinker and non-photoresponsive crosslinker were synthesized. The photoresponsive crosslinkers, alkoxyphenacyl and coumarin based crosslinkers, were synthesized respectively. And the non-photoresponsive crosslinker was synthesized as model crosslinker.

3.2.1 Synthesis of non-photoresponsive crosslinker

In a 100 ml round-bottom flask equipped with a magnetic stir bar, hydroquinone bis(2-hydroxyethyl) ether (2.0 g, 10.0 mmol) was dissolved in anhydrous dichloromethane (20 ml). Triethylamine (4.18 ml, 30.0 mmol) was added and the solution was cooled in ice bath for 0.5 hour. Then acryloyl chloride (3.29 ml, 40.0 mmol) was added slowly by a syringe pump. The reaction was carried out at room temperature overnight. After that, the insoluble by-product of triethylamine chloride was removed by filtration and the filtrate was washed with brine solution for 3 times and deionized water for 2 times. The organic layer was then dried over anhydrous sodium sulfate and concentrated under reduced pressure. The product was purified by column chromatography to give a white color solid (1.38 g, 45% yield).

\[ ^1H \text{NMR (300 MHz, CHLOROFORM-}d\text{)} \text{ppm} \]

\[ 4.04 - 4.26 (m, 4 \text{H}) \]

\[ 4.40 - 4.56 (m, 4 \text{H}) \]

\[ 5.85 (dd, J = 10.54, 1.46 \text{Hz}, 2 \text{H}) \]

\[ 6.04 - 6.27 (m, 2 \text{H}) \]

\[ 6.47 (d, J = 1.46 \text{Hz}, 1 \text{H}) \]

\[ 6.42 (d, J = 1.46 \text{Hz}, 1 \text{H}) \]

\[ 6.86 (s, 4 \text{H}) \]
3.2.2 Synthesis of alkoxyphenacyl-based photoresponsive crosslinker

The synthesis of alkoxyphenacyl-based photoresponsive crosslinker undergoes three steps and get pure compound.

3.2.2.1 Synthesis of 1-(4-(3-hydroxypropoxy)phenyl)ethan-1-one (AJ2)

In a 200ml round-bottom flask equipped with a magnetic stir bar, 4-acetylphenol (10 g, 73.4 mmol), 18-crown-6 (0.29 g, 1.10 mmol), potassium carbonate (13.17 g, 95.5 mmol) were added. The flask was evacuated and refilled with nitrogen for three times. Then anhydrous acetone (25 ml) was added and the solution was stirred for 30 min. After that, 3-bromopopan-1-ol (12.25 g, 88.1 mmol) was added and the reaction was refluxed for 24 hours. The reaction mixture was filtered and the filtrate was washed by acetone for 3 times. Filtrate was dried and purified by column chromatography to give a white solid (13.12 g, 92%).

\[1 \text{H NMR (300 MHz, CHLOROFORM-}d) \square \text{ppm} \]

- 2.08 (quin, \( J = 5.93 \) Hz, 2 H)
- 2.56 (s, 3 H)
- 3.88 (t, \( J = 5.86 \) Hz, 2 H)
- 4.20 (t, \( J = 6.00 \) Hz, 2 H)
- 6.87 - 7.01 (m, 2 H)
- 7.85 - 8.02 (m, 2 H)

3.2.2.2 Synthesis of 2-hydroxy-1-(4-(3-hydroxypropoxy)phenyl) ethan-1 - one (AJ5)

In a 500 ml round bottom flash equipped with a magnetic stir bar, AJ2 (4.0 g, 20.6 mmol), [bis(trifluoroacetoxy)iodo]benzene (13.28 g, 30.9 mmol), trifluoroacetic acid (1.58 ml, 20.6 mmol), acetonitrile (82.4 ml, 20.6 mmol) and water (16.5 ml, 20.6 mmol) were added. The reaction was carried out at 45 °C for 24 hours. Then the acetonitrile and trifluoroacetic acid were removed under reduced pressure. The residue was extracted by ethyl acetate for three times. Then the solvent was removed under reduced pressure and the compound was purified by column chromatography to give a white solid. (2.62 g, 60%)
1H NMR (300 MHz, CHLOROFORM-d) \( \delta \) ppm 2.08 (quin, \( J = 6.00 \) Hz, 2 H) 3.55 (br. s., 1 H) 3.88 (t, \( J = 6.00 \) Hz, 2 H) 4.21 (t, \( J = 6.15 \) Hz, 2 H) 4.77 - 4.87 (m, 2 H) 6.98 (m, \( J = 8.78 \) Hz, 2 H) 7.13 - 7.51 (m, 1 H) 7.26 (s, 1 H) 7.89 (m, \( J = 8.78 \) Hz, 2 H)

3.2.2.3 Synthesis of alkoxyphenacyl-based diacrylate crosslinker

In a 100 ml round-bottom flask equipped with a magnetic stir bar, AJ5 (2.1g, 10.0 mmol) was dissolved in anhydrous dichloromethane (30 ml). Triethylamine (4.18ml, 30.0 mmol) was added and the solution was cooled in ice bath for 0.5 hour. Acryloyl chloride (3.29 ml, 40.0 mmol) was added slowly by a syringe pump under stirring. The reaction was carried out at room temperature overnight. After that, the insoluble by-product of triethylamine chloride was removed by filtration and the filtrate was washed with brine solution and deionized water and dried over anhydrous Na2SO4. Then the solution was concentrated under reduced pressure and the compound was purified by column chromatography to give a white solid (0.99 g, 31%).

1H NMR (300 MHz, CHLOROFORM-d) \( \delta \) ppm 2.20 (quin, \( J = 6.22 \) Hz, 2 H) 4.14 (t, \( J = 6.15 \) Hz, 2 H) 4.37 (t, \( J = 6.29 \) Hz, 2 H) 5.39 (s, 2 H) 5.79 - 6.00 (m, 2 H) 6.06 - 6.35 (m, 2 H) 6.37 - 6.62 (m, 2 H) 6.86 - 7.03 (m, 2 H) 7.82 - 7.99 (m, 2 H)

3.2.3 Synthesis of coumarin-based photoresponsive crosslinker

The synthesis of coumarin-based photoresponsive crosslinker undergoes four steps and get the pure compound.

3.2.3.1 Synthesis of 4-(chloromethyl)-7-hydroxy-2H-chromen-2-one (C1)

In a 500 ml round-bottom flask equipped with a magnetic stir bar, resorcinol (10.0 g, 90.9 mmol), 4-chloromethyl acetoacetate (13.96 ml, 100 mmol), p-toluenesulfonic acid (3.6 g, 20.9 mmol) and toluene (120 ml) were added. A Dean-Stark apparatus was
connected to the round bottom flask and the reaction was refluxed for 1 hour. Water was removed during the reaction. After that, the reaction soluiton was concentrated and the product was purified by column chromatography to give a white solid (9.6 g, 52%).

3.2.3.2 Synthesis of 7-hydroxy-4-(hydroxymethyl)-2H-chromen-2-one (C3)

In a 500 ml round-bottom flask equipped with a magnetic stir bar, C1 and 300 ml water was added and refluxed for 3 days. Then, the reaction solution was filtered while hot and cooled down to room temperature to give a white crystal (95%). The product was dried under vacuum overnight. The product was used without further purification.

3.2.3.3 Synthesis of 4-(hydroxymethyl)-7-(3-hydroxypropoxy)-2H-chromen-2-one (C4)

In a 50ml round-bottom flask equipped with a magnetic stir bar, C3 (1.0 g, 5.2 mmol), 18-crown-6 (0.7 g, 2.6 mmol), potassium carbonate (2.0 g, 14.5 mmol) were added. The flask was evacuated and refilled with nitrogen for three times. Then anhydrous acetone (15 ml) was added and the solution was stirred for 30 min. After that, 3-bromopopan-1-ol (0.96 ml, 10.8 mmol) was added and the reaction was refluxed for 24 hours. The reaction solution was filtered and the filtrate was washed by acetone for 3 times. Then the filtrate was concentrated under reduced pressure and the product was purified by column chromatography to give a yellow solid (1.07 g, 82%).

$^{1}$H NMR (300 MHz, DMSO-$d_6$)  
\[
\begin{align*}
\delta &\text{ ppm} \\
1.88 &\text{ (t, } J=6.29 \text{ Hz, 2 H)} \\
3.56 &\text{ (q, } J=5.85 \text{ Hz, 2 H)} \\
4.15 &\text{ (t, } J=6.29 \text{ Hz, 2 H)} \\
4.56 &\text{ (t, } J=5.12 \text{ Hz, 1 H)} \\
4.72 &\text{ (d, } J=4.68 \text{ Hz, 2 H)} \\
5.59 &\text{ (t, } J=5.56 \text{ Hz, 1 H)} \\
6.29 &\text{ (s, 1 H)} \\
6.87 - 7.04 &\text{ (m, 2 H)} \\
7.61 &\text{ (d, } J=8.78 \text{ Hz, 1 H)}
\end{align*}
\]
3.2.3.4 Synthesis of coumarin-based crosslinker

In a 100 ml round-bottom flask equipped with a magnetic stir bar, C4 (2.0 g, 8.0 mmol) was dissolved in anhydrous dichloromethane (20 ml). Triethylamine (2.78 ml, 20.0 mmol) was added and the solution was cooled in ice bath for 0.5 hour. Acryloyl chloride (2.58 ml, 32.0 mmol) was added slowly by a syringe pump. The reaction was carried out at room temperature overnight. After that, the insoluble by-product of triethylamine chloride was removed by filtration and the filtrate was washed with brine solution and deionized water and dried over anhydrous Na$_2$SO$_4$. The solution was concentrated under reduced pressure and the product was purified by column chromatography to give a yellow solid (0.97 g, 34%).

$^1$H NMR (300 MHz, CHLOROFORM-$d$) ppm 2.15 - 2.29 (m, 2 H) 4.14 (t, $J = 6.15$ Hz, 2 H) 4.38 (t, $J = 6.29$ Hz, 2 H) 5.36 (d, $J = 1.17$ Hz, 2 H) 5.86 (dd, $J = 10.25$, 1.46 Hz, 1 H) 5.99 (dd, $J = 10.25$, 1.17 Hz, 1 H) 6.07 - 6.19 (m, 1 H) 6.19 - 6.31 (m, 1 H) 6.36 (s, 1 H) 6.43 (dd, $J = 17.27$, 1.46 Hz, 1 H) 6.55 (dd, $J = 17.27$, 1.17 Hz, 1 H) 6.77 - 6.96 (m, 2 H) 7.43 (d, $J = 8.49$ Hz, 1 H)

3.3 Emulsion polymerization

Emulsions were synthesized with photoresponsive crosslinker and non-photoresponsive crosslinker, respectively.

3.3.1 Emulsion polymerization with non-photoresponsive crosslinker

Polymers with different amount of model cross-linker (0.1%, 0.2%, 0.3% and 0.5% mole fraction) were synthesized to obtain the ideal polymer properties. As an example, the synthesis of polymers with 0.5% cross-linker is as follows: in a 50 ml round-bottom flask equipped with a magnetic stir bar, water (6 ml) and sodium dodecyl sulfate (16.2 mg)
were added. A mixture of n-butyl acrylate (1.86 g, 14.5 mmol, 89.5%), 2-caboxyethyl acrylate (0.23 g, 1.6 mmol, 10%) and model cross-linker (24.8 mg, 0.081 mmol, 0.5%) was added dropwise. Then a stock solution (1 mL) of 4,4'-azobis(4-cyanovaleric acid) (3.4 mg) and sodium bicarbonate (3.6 mg) was added. After degassing for 30 minutes, the reaction was carried out at 70°C for 10 hours.

3.3.2 Emulsion polymerization with alkoxyphenacyl-based photoresponsive crosslinker

Polymers with different amount of cross-linker (0.1%, 0.2%, 0.3% and 0.5% mole fraction) were synthesized to obtain the optimal polymer properties. As an example, the synthesis of polymers with 0.5% cross-linker is as follows: in a 50 ml round-bottom flask equipped with a magnetic stir bar, water (6 ml) and sodium dodecyl sulfate (16.2 mg) were added. A mixture of butyl acrylate (1.86 g, 14.5 mmol, 89.5%), 2-caboxyethyl acrylate (0.23 g, 1.6 mmol, 10%) and alkoxyphenacyl-based cross-linker (25.8 mg, 0.081 mmol, 0.5%) was added dropwise. Then a stock solution (1 ml) of 4,4’-azobis(4-cyanovaleric acid) (3.4 mg) and sodium bicarbonate (3.6 mg) was added. After degassing for 30 minutes, the reaction was carried out at 70°C for 10 hours.

3.3.3 Emulsion polymerization with coumarin-based photoresponsive crosslinker

Polymers with different amount of cross-linker (0.1%, 0.2%, 0.3% and 0.5% mole fraction) were synthesized to obtain the optimal polymer properties. As an example, the synthesis of polymers with 0.5% cross-linker is as follows: in a 50ml round-bottom flask equipped with a magnetic stir bar, water (6 ml) and sodium dodecyl sulfate (16.2 mg) were added. A mixture of butyl acrylate (1.86 g, 14.5 mmol, 89.5%), 2-caboxyethyl acrylate (0.23 g, 1.6 mmol, 10%) and coumarin-based cross-linker (29.0 mg, 0.081 mmol, 0.5%) was added dropwise. Then a stock solution (1 mL) of 4,4’-azobis(4-cyanovaleric acid)
(3.4 mg) and sodium bicarbonate (3.6 mg) was added. After degassing for 30 minutes, the reaction was carried out at 70°C for 6 hours.

3.4 Characterization of emulsion

Typical characterization techniques of the emulsions are Dynamic Light Scattering (DLS) for particle size, solid content, and monomer conversion. The particle size of each emulsion was measured by using Dynamic Light Scattering. Monomer conversion was assured by nuclear magnetic resonance (NMR). And the solid content was determined by measurement of weight before and after the drying process at room temperature for 24h in vacuum oven.

Solid content (wt%) = \( \frac{W_2}{W_1} \times 100\% \)

where \( W_2 \) is the weight of dried polymer after vacuum drying and \( W_1 \) is the weight of the emulsion before vacuum drying.

3.5 Characterization of photo-switchable performance

As mentioned before, the typical characterizations of PSAs are tack, peel and shear strength. In this project, peel test was chose to characterize the adhesion property, whereas the lap shear test was used to evaluate the cohesion strength.

3.5.1 Sample preparation

The emulsion sample was prepared onto quartz plates, which is UV transmissible so that the irradiation test can be measured. Quartz plates were put on to a horizontal desk and pipetted with 150µl emulsion on the fix area (25mm*20mm). The emulsion was spread to form a homogeneous emulsion film and then dry at room temperature for 24h. After the sample is dry, the preliminary sample was vacuumed in vacuum oven at 37°C.
for 2h to remove the water thoroughly. Thickness of these samples varies from 85-96µm and they are further used for peel test and lap shear.

3.5.2 Shear and peel test

Lap shear and peel test were both measured on the TA. XT *Plus* texture analyser. For the experiments of each emulsion-based PSAs, either for peel or shear test, ten samples were prepared based on different test standard. Five samples of them were tested without irradiation and the other five left were first irradiated for 5 minutes and then continue for specific testing. The irradiation experiments were conducted by a Rayonet reactor at 300nm (16 tubes, 5.34mW/cm2).

For the lap shear of each emulsion, the ten dry samples are covered with another quartz plate and clamped for 45min, respectively. Then the clamps were removed. Five samples were placed under irradiation for 5min and the other five were not. And the shear rate used was 5mm/s at room temperature.

For the 180° peel test, the peel strength of PSAs was measured at a peel rate of 25mm/s. A 25mm wide PET film was adhered to the dry sample with finger pressure. The peel test sample was irradiated from the back of quartz plate for 5 min. After 2 min dwell, the peel of the PET film was performed. And the other samples without irradiation were tested in the same procedures except the irradiation step.

3.6 Rheological test

An Rheometer (Aris GII) with parallel plate geometry (8mm in diameter) was used for the rheology measurement. The storage modulus and loss modulus were measured and recorded at 25°C in oscillatory mode from 0.5 to 100 Hz with a constant strain of 0.5%.
CHAPTER IV

RESULTS AND DISCUSSION

4.1 Characterization of crosslinker

Photoresponsive crosslinker and non-photoresponsive crosslinker were synthesized. The photoresponsive crosslinkers, alkoxyphenacyl and coumarin based crosslinkers, were synthesized respectively. And the non-photoresponsive crosslinker was synthesized as model crosslinker.

4.1.1 Characterization of non-photoresponsive crosslinker

Figure 4.1. $^1$H NMR spectra of (1,4-phenylenebis(oxy))bis(ethane-2,1-diyl) diacrylate (model cross-linker)
The synthesis of photoresponsive cross-linker is costly and time-consuming. Therefore a model diacrylate cross-linker was synthesized and used to optimize the adhesive properties. The model cross-linker contains a benzene ring, which has a similar structure to that of the chromophore-contained cross-linker. The model cross-linker was synthesized using a one-step reaction, which is outlined in Scheme 4.1. The reaction of acryloyl chloride with hydroquinone bis(2-hydroxyethyl) ether in the presence of triethylamine provide the product in approximately 45% yield.

The chemical structure of the compound was confirmed by $^1$H NMR spectroscopy. As shown in the NMR spectra, the peaks marked with c, d and e correspond to the protons in the vinyl groups. The peak at around 6.8 ppm corresponds to the benzene ring in the compound.

4.1.2 Characterization of alkoxypheacyl based photoresponsive crosslinker

Scheme 4.2. Synthesis of Alkoxypheacyl based Crosslinker, reaction condition: (a) $\text{K}_2\text{CO}_3$/18-crown-6, acetone reflux. (b) trifluoroacetic acid, CH$_3$CN, H$_2$O. (c) CH$_2$Cl$_2$, room temperature.
Figure 4.2. $^1$H NMR spectra of 2-hydroxy-1-(4-(3-hydroxypropoxy)phenyl) ethan-1-one (AJ5)

Figure 4.3 $^1$H NMR spectra of 3-(4-(2-(acryloyloxy)acetyl)phenoxy)propyl acrylate (AJ5 cross-linker)
The synthesis of alkoxyphenacyl cross-linker consists of three steps (Scheme 4.2). First, the hydroxyacetophenone was chain extended by reacting the phenolic hydroxyl group with 3-bromopropanol. The next step involves the α-hydroxylation of the ketone group under acidic condition using [bis(trifluoroacetoxy)]Iodobenzene to give the alkoxyphenacyl diol. At last, the reaction of alkoxyphenacyl diol with acryloyl chloride generated the alkoxyphenacyl cross-linker in approximately 31% yield. The low yield was because the hydroxyl groups in the alkoxyphenacyl diol were not completely acryloylated, which was confirmed by thin-layer chromatography (TLC). The structure of the cross-linker was confirmed by $^1$H NMR spectroscopy. The peaks marked with c, d, e, f, g and h correspond to the protons in the vinyl groups. The peaks at around 6.9 and 7.9 ppm correspond to the protons in the benzene ring.

4.1.3 Characterization of coumarin based photoresponsive crosslinker

Scheme 4.3. Synthesis of Coumarin-based Crosslinker, reaction condition: (a) p-Toluenesulfonic acid, toluene, and reflux. (b) H$_2$O, reflux (c) K$_2$CO$_3$/18-crown-6, acetone reflux. (d) CH$_2$Cl$_2$, room temperature.
Figure 4.4. $^1$H NMR spectra of 4-(hydroxymethyl)-7-(3-hydroxypropoxy)-2H-chromen-2-one

Figure 4.5. $^1$H NMR spectra of 3-((4-((acryloyloxy)methyl)-2-oxo-2H-chromen-7-yl)oxy)propyl acrylate
The synthesis of coumarin-based crosslinker consists of five steps (Scheme 4.3). The first step is the Michael Addition of resorcinol with 4-chloromethyl acetoacetate. Then the chloride of compound (1) undergoes substitution reaction and converts to hydroxyl. Then compound (2) was chain extended by reacting with 3-bromopropanol to form a diol. The diacrylate cross-linker was obtained by the reaction of compound (3) with acryloyl chloride. The cross-linker (4) was purified by column chromatography. The yield of the coumarin-based cross-linker is 34%. The low yield was because the hydroxyl groups in the coumarin diol were not completely acryloylated, which was confirmed by thin-layer chromatography (TLC). The $^1$H NMR spectra accords with the structure of coumarin based cross-linker. The peaks from c to h are the protons in the vinyl group on both side of the cross-linker. And the peak a, b and i correspond to the three protons in coumarin.

4.2 Characterization of emulsions

Table 4.1 Emulsions library and characterizations data

<table>
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<tr>
<th>Mono</th>
<th>0.0%</th>
<th>0.1%AJ</th>
<th>0.2%AJ</th>
<th>0.3%AJ</th>
<th>0.1%M</th>
<th>0.2%M</th>
<th>0.3%M</th>
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<td>55%</td>
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</tr>
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<tr>
<td>Model Crosslinker</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>0.1%</td>
<td>0.2%</td>
<td>0.3%</td>
</tr>
<tr>
<td>Photoresponsive Crosslinker</td>
<td>--</td>
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<td>0.2%</td>
<td>0.3%</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Conversion</td>
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<td>100%</td>
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<tr>
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<td>38.2%</td>
<td>39.1%</td>
<td>39.5%</td>
<td>41.2%</td>
<td>39.5%</td>
<td>40.2%</td>
</tr>
<tr>
<td>Particle size (nm)</td>
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<td>60</td>
<td>55</td>
<td>63</td>
<td>74</td>
<td>94</td>
<td>186</td>
</tr>
</tbody>
</table>

The monomers used for the system consist of n-butyl acrylate, 2-carboxyethyl acrylate and the alkoxyphenacyl-based photoresponsive crosslinker. Poly(n-butyl acrylate), which has a low glass transition temperature (Tg) was selected as the major component of the polymer due to its inherent tackiness. And the 2-carboxyethyl acrylate which has a carboxyl group is added to improve the peel and shear strength. 4,4′-
Azobis(4-cyanovaleric acid) was selected as the water-soluble initiator, which was neutralized by 3.5 eq sodium bicarbonate to increase the solubility in water.

The polymerization with different mole fraction of model cross-linker (0.1%, 0.2%, 0.3%, 0.5% and 1%) was first attempted to explore the ideal percentage of the crosslinker for the desired polymer properties. It was observed that the polymer lost stickiness when the percentage of crosslinker was above 1%. Based on the previous results from the model polymerization, polymerization with photoresponsive cross-linker (0.1%, 0.2%, and 0.3% mole fraction) was attempted and adhesion properties of these polymers would be compared. Then the emulsion with same amount of alkxoyphenacyl-based photoresponsive crosslinker (0.1%, 0.2%, and 0.3% mole fraction) were synthesized.

The conversion of monomer demonstrated by NMR is 100% conversion. The solid content of the emulsions varies around 40% slightly. The particle size of the emulsion was determined by dynamic light scattering (DLS). And the size of the particles with alkxoyphenacyl and coumarin cross-linkers is 55 nm and 94 nm, respectively (Table 4.1). The particle size will have a significant influence on the adhesion properties. It has been reported that the shear strength of the adhesives increased with decreasing particle size due to the tighter packing during the drying process. Therefore the obtained particle size would be promising and the adhesion properties of the emulsion would be characterized by peel and lap shear test.

4.3 Characterization of photo-switchable PSAs

To demonstrate the reduced adhesion caused by photoresponsive breaking of crosslinking point (Fig. 4.6), a comparison of groups with the replacement of photoresponsive crosslinker by non-photoactive crosslinker was synthesized and measured.
To demonstrate the concept of reduced adhesion by breaking crosslinking moiety via photoresponsive chain scission (Fig. 4.6), the polymer crosslinked by alkoxyphenacyl based photoresponsive crosslinker was first to be characterized by lap shear and peel test before and after irradiation.

Figure 4.6 The degradation of photoresponsive PSAs

4.3.1 Rheology of PSAs

One interesting phenomenon in the emulsion polymerization process should be mentioned is that when the crosslinker amount is higher than the 0.5 (mol)%, the emulsion obtained is always has significant coagulation after polymerization at 60 °C for 6h. And the emulsion cannot be used for the next sample preparation for peel and shear. So the authors determined to fix the amount of crosslinker at 0.1 (mol)%, 0.2 (mol)%, 0.3 (mol)% and one emulsion without any crosslinker as control. On one hand, the low degree amount of crosslinker could introduce enough cohesion of polyacrylate. On the
other hand, the photoresponsive property can be incorporated by the photoactive crosslinker and the relatively low amount of crosslinking density can have less negative effect on the adhesion property of polyacrylate.

Figure 4.7. Rheological test

Once the polyacrylate crosslinking, it is possible that the crosslinked network is too stiff to be used as pressure sensitive adhesives. To demonstrate the crosslinked polyacrylate can be used as PSAs based on Dahlquist criterion, rheological properties were characterized. To promote the wetting ability and contact between adhesive and substrate, PSAs should have a dynamic elastic modulus below the Dahlquist criterion (shear modulus $G' \leq 3 \times 10^5$ Pa at 1 rad/s). In the Fig. 4.7, samples with 0.0 (mol)%, 0.1 (mol)%, 0.2 (mol)% and 0.3 (mol)% model crosslinker are characterized. The shear modulus increases as the amount of crosslinker increases because the crosslinking degree could make polymer stiff. But the shear moduli of crosslinked polyacrylates are still blow the Dahlquist criterion, which indicates that the crosslinked polyacrylates can be used as
PSAs although the crosslinked network inside polymer make the polymer a little bit stiffer. And the samples with AJ5 croslsinker will also be characterized.

4.3.2 Shear test

All the lap shear data are shown in Fig. 4.8 and 4.9. For the sample with 0.3% photoreponsive crosslinker (column of $R_{0.3\%}$) the shear force decreases 62.5% compared to the sample without 5 min irradiation with 300nm UV light. Whereas the sample with 0.3% non-photoresponsive crosslinker (column of $N_{0.3\%}$) does not show any significant reduce of shear force after UV irradiation. Actually, all the samples with different amount of non-photoresponsive crosslinker do not show too much change of shear force before and after the irradiation and are within the limits of error.

Figure 4.8. Shear strength of photoresponsive PSAs before and after irradiation. The shear area of each sample was 25mm×20mm.
Figure 4.9. Shear strength of non-photoresponsive PSAs before and after irradiation. The shear area of each sample was 25mm×20mm.

For the shear force data of samples with photoresponsive crosslinking network, the decreasing trend of shear force, before and after irradiation, becomes obvious as the amount of photoresponsive crosslinker amount increases from 0.1%, 0.2% to 0.3%. But the shear force does not show significant increasing tendency along with the increasing crosslinking degree because the crosslinking degree is not too high to show an effect on the shear force.
4.3.3 Peel test

Figure 4.10. $180^\circ$ Peel force of non-photoresponsive and non-crosslinked PSAs

Figure 4.11. $180^\circ$ Peel test at different peel rate of non-photoresponsive and non-crosslinker PSAs
Until now, only the peel test result of sample with 0.0% of crosslinker was obtained. The result (Fig. 4.10) shows there is only slight reduce of peel force after irradiation under 300nm UV for 5 min. Peel tests under different peel rate, 0.1mm/s, 1mm/s, 5mm/s and 25mm/s, are shown in the Fig 4.11. The tendency of peel test under these different rates is that the higher peel rate leads to higher peel force. Further peel tests of samples with different amount of either photoresponsive or non-photoresponsive crosslinker will be done before the graduation.
CHAPTER V

CONCLUSION

In this work, two photoresponsive crosslinkers, alkoxyphenacyl based and coumarin based diacrylate crosslinkers, were synthesized and these photoresponsive crosslinkers were utilized to synthesize crosslinked photoresponsive acrylic polymers for the photoresponsive pressure sensitive adhesives (PSAs) application. The described polymer system was composed of n-butyl acrylate, 2-carboxyethyl acrylate and the chromophore-based diacrylate crosslinker.

Acrylic polymers with different fraction (0.0%, 0.1%, 0.2%, 0.3% and 0.5%) of photoresponsive crosslinker were synthesized via emulsion polymerization, for which the resultant emulsion can be readily used for PSAs. It was observed that polymers with less than 1% crosslinker were stickier. The particle size of the emulsion was around 70 nm, which was confirmed by dynamic light scattering (DLS). The shear strength of PSAs crosslinked by photoresponsive crosslinker shows as high as 63.6% reduction of shear strength after UV irradiation, while the PSA crosslinked by non-photoresponsive crosslinker does not show any significant reduction of shear strength. And the reduction percent of shear strength increases along with the increasing amount of photoresponsive crosslinker from 0.1%, 0.2% to 0.3%.
The future work will be focused on the characterization of the adhesion properties by peel test of the described polymer systems with three different crosslinker contents. In addition, the percentage of other monomers in the polymer system would also be varied to optimize the adhesion properties of PSAs.
REFERENCES


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