SYNTHESIS OF 10-CARBOXY-N-DECYL-N, N’-
DIMETHYDECYL-1-AMMONIUM BROMIDE AS ORGANOGELATOR
&
ROOM TEMPERATURE SHAPE MEMORY PROGRAMMING OF STEARIC
ACID/NATURAL RUBBER BILAYER BLEND

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Xiaocheng Chen
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Xiaocheng Chen

Thesis

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ABSTRACT

Quaternary ammonium compounds (QACs) are a mainstay of anti-bacterial materials which are the most effective bactericide agents against microorganisms at a neutral or slightly alkaline PH with generally low concentration. They also have numerous applications as surfactants and disinfectants in a variety of industrial and consumer applications. 10-Carboxy-N-decyl-N, N'-dimethydecyl-1-ammonium bromide is a kind of QACs which has the similar gelation ability as 12HSA because of the ion-pair effect. Nucleophilic substitution was the reaction for synthesizing this quaternary ammonium bromide compound and $^1$H-NMR was used to characterize the final dried products in this thesis. Then the thermal characterizations of samples were measured by TGA, DSC. In order to fabricate QAC organogelators, different solvents were mixed with QAC with different concentration and only DMSO and ethylene glycol succeeded. The final step of this experiment was to observe the crystalline formation process and structure of gels by POM.

The second study focuses on shape memory polymer (SMP), a novel kind of smart material which can remember its original shape and has lots of advantages, such as high elastic but low temperature deformation, low density, low cost, better potential biocompatibility and various external stimuli more than temperature. Bilayer SMP is fabricated by creating inhomogeneous phase of material to achieve deformation purpose without external forces. This thesis first introduces the fundamental understanding of SMPs history, structure, stimulus method and categorization, and the principle of bilayer SMPs. The SMPs were fabricated with commercial readily
cross-linked natural rubber bands and stearic acid in this experiment. Next, the iso-strain stress shape fixity and recovery of SMPs varying with different Stearic Acid wt%, stretch time and stretch strain under cold-drawing conditions are presented. This differs from the typically SMP processing where the sample is heated above the transition temperature of the network fixing the structure of the SMP and offers the advantages of simplified processing and energy savings. The bilayer SMPs are fabricated by gluing two different material rubber bands and then swelling them in stearic acid for different hours. The shape memory effect of bilayer products were described by their curl change.
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CHAPTER I

Synthesis of 10-Carboxy-N-decyl-N, N’-dimethydecyl-1-ammonium bromide as organogelators

1.1 Introduction

In this section, we will briefly introduce some fundamental concepts about organogels, low molecular mass organogelators and quaternary ammonium compounds. The reason why 10-Carboxy-N-decyl-N, N’-dimethydecyl-1-ammonium bromide can be used to fabricate organogels is also discussed.

1.1.1 Organogelators

Gel is generally defined as a semi-solid substance composed of gelator molecules and solvents, the classification of gels is based on the molecules, solvent and the interaction between molecules as shown in Figure 1.1.1.\(^1\)
According to some research review, the interest in “molecular gels” has growing rapidly since 1990 as shown in Figure 1.1.2. The increasing rate of articles number which mentioned “organogel” alone even surpasses the rate of articles containing the word “hydrogels”. In additional, the actual number of publications discussing with organogels and hydrogels is even higher than statistical results shown above, because many of them would use some specific name or other designation instead of these two terms to describe these kinds of materials.

Figure 1.1.1 Classification of gels. Redrawn from reference 1.

Figure 1.1.2 Articles contain “organogel” (shaded columns) or “hydrogel” (solid columns) in the title, key word, or abstract publicized per year from 1990 to 2006, taken with permission from reference 11.
As generally known, when heating up a system consisting of crystalline small molecules (i.e. solute) and a solvent above the melting point (Tm) of the crystal, either a 2-phase, phase separated liquid system would form or the solute would gradually dissolve forming a 1-phase homogenous solution. Normally, when cooling the solution down below the Tm of the solute, the molecules would precipitate in the form of macroscopic crystal. However, there is another type of morphology which does not result in as clear phase separation. In this case the solvent is immobilized by a network of solute crystals and the entire solution forms a solid-like gel instead as Figure 1.1.3 chemically illustrates. The different interactions which associate these molecules together include hydrogen bonding, π-π stacking, Van der Waals, ionic bonding, and metal coordination is a result of chemical diversity in the range of molecules [4, 5]

![Figure 1.1.3 Scheme of gelation mechanism](image)

A substance could be classified as gel if it in accordance two basic characteristics listed below, (1) On the microscopic dimensions, the substance seems to have a continuous microscopic structure which means its structure would not change with variation in the time scale of an analytical experiment. (2) The rheological behavior of
this material is close to a solid despite containing numerous amounts of liquids. Gel stability is influenced by the gap between environmental temperature and gelation temperature (Tg). Besides the usual thermal reversible organogels, there are some other reversible systems which respectively respond to light stimuli, fluoride anions or combination of different stimuli.

1.1.2 Self-assemble low molecular mass organogelators

The low molecular mass organogelator (LMOG) is a specific kind of organogels which are comprised of an organic solvent and low concentration of relatively low molecular mass molecules whose molar mass is $\leq 3000$. Same as other organogelators, they always represent thermally reversible viscoelastic properties from liquid-like to solid-like behaviors. The design strategy of crystalline LMOGs can be developed from the phase diagram of sol-gel system as shown in Figure 1.1.4. Below the liquids line, the system is comprised of homogenous solution of molecules and organic solvent, aggregation and gelation of molecules can only occur upon the liquids line. The ability of transferring from free-flow liquid to non-flow materialsthe LMOGs have versatile applications in many fields, including lubricant, drug delivery agents, templates for assembling nanoparticles, light harvesting complexes, gelelectrolytes, etc.
Figure 1.1.4 Phase diagram of sol-gel system: the minimum gel concentration of molecules vs. temperature in solution. Redrawn with permission from reference 13.

Generally, LMOG can be classified into eight different types, Steroid derivatives, anthryl derivatives, gelators containing steroidal and condensed aromatic rings, amino acid-type organogelators, organometallic compounds, miscellaneous types of gelators, and two-component systems. Among all of the different choices, 12-hydroxystearic acid (12HSA) attracts special attentions as the chiral center on the position of 12th carbon lead to its outstanding gelation ability in organic solvents for both D-12-HSA and L-12-HSA. The crystal structure of 12HSA strands was studied by Tetsuro, et al as Figure 1.1.5 shows. It indicates the hydrogen bond sequences are formed by hydroxyl groups of 12HSA along the a-axis, which help the 12HSA molecules stack in a lamellar structure and lead to fibrillar crystal growth. Meanwhile, the structural parameters of 12HSA are functions of cooling rate, the polarity of solvent. By tuning the crystalline structural parameters, the gels could have different optical, rheological and thermodynamic properties.
1.1.3 Quaternary ammonium compounds

With the increasing attention paid to health issues, antimicrobial activity has become a more and more desirable feature when designing and manufacturing medical, personal care and food packaging products to prevent human beings from living environment infections of microorganisms such as yeast, moulds, bacteria, and viruses, etc. \[23\] Antimicrobial methods can be generally sorted into two main types: physical and chemical. Physical processes reach the goal of sterilization goal by killing already existing bacterial spores. On the other hands, chemical agents are used as disinfectant which helps preserve materials from bacterial infection on the basis of killing them. \[24, 25\] One of the most economic and simplest ways to produce anti-bacterial responsive materials is to blend the target polymer with antimicrobial
LMOG. \cite{26} Cationic compounds are strong competitive candidates for antibacterial properties additives because their positive charges on the long carbon chains can attach to surfaces of material which has negatively charged cell of bacteria which inhibit the activity of cells. \cite{27} The main positively charged group structures are the ones contains quaternary ammonium groups, which makes the surfactant quaternary ammonium compounds (QACs). \cite{28} QACs have been widely applied in a variety of industrial and consumer products which makes the it a mainstay of cationic surfactants. \cite{29}

Due to its high polarity, alkyl QACs are able to form micelles at relatively low concentrations. \cite{16} The general chemical structure of QACs is

$$N^+R_1R_2R_3X^-$$

Where R substituent could be an alkyl group as well as a hydrogen atom, and X\(^-\) represents an anion which attach to N\(^+\) group due to ion pair effect. \cite{30} The anti-bacterial activity of quaternary ammonium compounds was first observed in the early 1900s by Jacobs and his associates. \cite{31} Later in 1935, the great application of QAC for pre-operative hand cleaning was firstly reported. \cite{32} According to the report, QACs contains 8–18 carbon atoms and at least one of four R\(_a\) is an alkyl or substituted aliphatic group possessing disinfectant activity. Moreover, optimal anti gram-positive bacteria activity is gained at 12-14 alkyl chain lengths. On the other hand, optimal anti gram-negative bacteria activity is announced at 14-16 alkyl chain lengths. However, QACs with 4 to 18 alkyl chain lengths are virtually inactive. This phenomenon was firstly reported in 2005. \cite{33} It also related to the physical properties
of QACs with the physical relationship between the molecules phase and the external force which comes from the microbial cell membrane.[19] Besides that, the mechanism activities depend on the surface activity of compounds, the solubility of the compound in the medium, and the surface activity of it. [34] Lastly, the micelle formation ability of a compound is conversely closely related to its solubility as well. [35]

Thus, QACs have numerous applications as most useful surfactants, antiseptics and disinfectants in a variety of industrial, agricultural and household applications. [36, 37] These includes microbicides, oxidation inhibitors, laundry saponins, anti-caking agents, size-control agents, satin and water repellents, fabric softener active, anti-static aids, dispersants and other large industrial applications. [38] Moreover, they also have versatile potential applications involving nano-sensors, electronics, and catalysts, as well as delivery or modification agents for paints, food packaging, biomaterials, inks, polymers, drugs, etc [39]

The reason why we choose quaternary ammonium compounds as the low mass molecules for this project is the ion-pair effect between ammonium cation and the bromo anion of 10-Carboxy-N-decyl-N, N'-dimethydecyl-1-ammonium bromide can mimic the hydrogen bonding effect in 12HSA, which helps form physical cross-linking. And it has been reported that when alkyl quaternary ammonium salts which have similar structure to 12HSA can be dissolved in an organic liquid by heating, after cooling down the solution, amines groups of quaternary ammonium salts can aggregate to viscoelastic, thermally-reversible gels at relatively low concentration. [40, 41]
1.2 Experiment section

In this experiment, firstly 10-Carboxy-N-decyl-N, N'-dimethydecyl-1-ammonium bromide was synthesized, and some thermal characterizations of products were done. Then quaternary ammonium compound gel was fabricated and characterized.

1.2.1 Materials

11-Bromoundecanoic Acid (>97.0%, TCI American), N, N-Dimethyldecylamine (>95.0%, TCI American), Acetonitrile (>99.9%, Millipore Sigma), Chloroform-D (>99.8%D, Cambridge Isotope Laboratories), Chloroform (>99.8%, BDH Chemicals), Ethanol (>99.9%, Decon Labs), Butyl Alcohol (>99.4%, EMD Millipore), Ethylene Glycol (>91.18%, Fisher Chemical), Cyclohexane (>99.0%, EMD Millipore), Toluene (>99.5%, Sigma-Aldrich), Ethyl Ether (>99.0%, EMD Millipore), Dimethylformamide (DMF) (>99.9%, BDH Chemicals), Dimethyl Sulfoxide (DMSO) (>99.9%, JT Baker), Styrene (>99.0%, Sigma-Aldrich), o-Xylene (>98.0%, TCI American), Hexane (>98.5%, Sigma-Aldrich), 2-propanol (>99.5%, Sigma-Aldrich), Dodecane (>99.0%, TCI), 1, 4-Dioxane (>99.0%, Alfa Aesar), Heptane (>98.0%, EM Science), Ethyl Acetate (>99.8%, EMD Millipore), Tetrahydrofuran (THF) (>99.9%, Fisher Chemical), Styrene (99.9%, stabilized, ACROS) were used as received.

1.2.2 Instrumentations and Characterizations

The $^1$H NMR spectra were collected on a Varian Mercury 300 MHz spectrometer to characterize the 10-Carboxy-N-decyl-N, N'-dimethydecyl-1-ammonium bromide,
using chloroform-D as the solvent with a concentration of 10mg/ml for the product and a relaxation time of 2s was used. Thermogravimetric analysis (TGA) was performed on a TA instruments TGA 2950, using air atmosphere with a heating rate of 20°C min\(^{-1}\) from 25 °C to 800 °C and the weight of samples are monitored in order to measure the decomposition temperature of the product. The melting and crystalline temperature were characterized by differential scanning calorimetry (DSC) on a Perkin Elmer DSC 8500, using nitrogen as atmosphere with a heating/cooling rate of 10°C min\(^{-1}\) from -50 °C to 150 °C, the DSC tests went 2 cycles in order to eliminate any previous sample history from the measurements. After fabricating a gel with the proper solvent, the gel was characterized by polarized light microscopy (POM) on an Olympus BX60 microscope. On the temperature controller, heating/cooling rate at 2°C / min was set and a heating limit from 30°C to 70°C was used. A 20X objective lens was used to observe the crystalline structure of QAC-based organogels. On the camera panel, the time interval for each picture was 0.5s.

1.2.3 Experimental process

1.2.3.1 Synthesis of 10-Carboxy-N-decyl-N, N'-dimethyldecyl-1-ammonium bromide

As Hoffman’s work in 1999 shows, alkyltrimethyl derivatives can be synthesized by reaction of an alkylamino ester with a bromo acid.\textsuperscript{[42]} Thus, 11-bromoundecanoic acid (2.65g, 0.01mol) was dissolved in acetonitrile (200mL) or acetone (200mL) in a 500mL glass beaker, gently stirred it to help it dissolve more quickly. Then the
solution was poured into a 500ml 1-neck round bottom flask and the beaker was rinsed with 50mL acetonitrile or acetone to ensure all reactants were in the flask. Then N, N-dimethyldecylamine (2.38ml, 0.01mol) was added to the flask with 1mL syringe. A magnetic spin bar was placed in the flask and topped with a reflux condenser, making sure the condenser was tightly connected to the flask. Rubber tubes was attached to condenser to flow water from the bottom to top of the condenser in order to cool the vapor generated during the reaction and allow it flow back into the reactor. The hot plate was wet at 85 °C or 80 °C to figure out the best experimental temperature and stirrer was set at a rate of 500 r/ min. To determine the best experiment factors, the reactions were run under several different conditions in arrangement of reaction temperature and 24/48 hours reaction time. At the end of the reaction, the reactor was allowed to cool to room temperature.

After the reaction, the solution was left overnight in the fume hood to cool to room temperature with aluminum foil wrapped over the top and secured with a rubber band. The cooled flask was placed on a rotary evaporator, where the solvent was removed by vacuum evaporation under room temperature for 2hr until producing a white solid. In order to eliminate the by-products, the product was recrystallized. The crude product was dissolved in an appropriate amount of 1:1 volume ratio mixture solution of di-ethyl ether and methanol at 35 °C which is close to the boiling point of ethyl ether in a 250 mL 1-neck flask. The choice of two recrystallization solvent was derived from Table 1.2.1.
Table 1.2.1 Common solvents for crystallization

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<tr>
<th>Solvent</th>
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<th>Toxicity</th>
<th>Good for</th>
<th>Second solvent for mixture</th>
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<tr>
<td>Water</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>Salts, amides, some carboxylic acids</td>
<td>Acetone, alcohols, dioxane,</td>
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<tr>
<td>Acetic acid</td>
<td>118</td>
<td>+</td>
<td>++</td>
<td>Salts, amides, some carboxylic acids</td>
<td>Water</td>
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<td>Acetonitrile</td>
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<td>+++</td>
<td>Polar compounds</td>
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<td>Methanol</td>
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<td>+</td>
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<td>Water, ethyl ether, benzene</td>
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<td>Ethanol</td>
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<td>Acetone</td>
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<td>+</td>
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<td>Methyl cellosolve</td>
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<td>++</td>
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<td>Water, benzene, ethyl ether</td>
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<td>++</td>
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<tr>
<td>Methyl acetate</td>
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<td>++++</td>
<td>++</td>
<td>General, ester</td>
<td>Water, ethyl ether</td>
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</tbody>
</table>

After all the solid was dissolved, the flask was taken off the heating plate and left it undisturbed until the solution completely cooled down to room temperature, and was then placed it in refrigerator for 48hrs for further recrystallization. The final products were collected on a small Büchner funnel by vacuum filtration, and cold solvent mixture of 1:1 diethyl ether and methanol was used to rinse the round bottom flask. The filtered final product was collected in 20mL glass vials and dried thoroughly to a constant weight at room temperature in a vacuum dry for 24 hrs. The dried powders were weighted to calculate the product yield.
1.2.3.2 Preparation and characterization of 10-Carboxy-N-decyl-N, N'-dimethydecyl-1-ammonium bromide organogelators

20-40 mg of the resulting QAC powders were weighed into a 1 dram screw cap glass vial. Different organic solvents with different QAC solubility and polarity were then added to each individual vial, including toluene, dodecane, o-xylene, benzene, chloroform, ethanol, 2-propanol, DMSO, THF, styrene, ethyl acetate, 1, 4-dioxane, DMF, heptanes, butyl alcohol, benzene, cyclohexane and ethylene glycol. All these solvents were added separately into each vial with a weight ratio of 2 wt% of QAC. All of the vials were heated 90 °C for 1 min to melt the mixture, then the vials were removed from heating plate and the state of the solution in each vial was observed to determine whether it was a 1 phase or 2 phase solution. Next, the vials were left in hood undisturbed overnight to cool down to room temperature and their state was recorded, precipitation, 1 phase liquid or gel. The samples which formed homogenous 1 phase liquid solution were re-prepared using the same solvent but with the QAC weight percent in mixture of 5% and the same procedures were repeated. This time the samples whose viscosity had changed were selected re-prepared with increasing the QAC weight percent gradually up from 10%, 15%, 20%, 25% to 30% until the gels formed. In this way, we can find out the proper organic solvent and concentration for QAC gelation. Formation of gels can be determined macroscopically if the complex in vials would not flow when the vials were inverted upside down.

To prepare the POM samples, a small amount of gels was removed from a vial, which was then placed on the middle of a cleaned, clear glass microscope slide and
gently covered with a cleaned glass slip and then heated up the whole slide on heating plate at 90 °C to melt the gel spread it evenly all over the slides. After the slides cooled down and the gels formed a flat thin film, it was placed on the POM translational stage. The light intensity and focus as well as set the camera parameters were adjusted to insure a clear image. The analyzer was rotated to the minimum intensity degree where the analyzer and polarizer are perfectly perpendicular to each other. The photo parameters of camera were set by taking a “live view” picture and change the software panel to obtain the clearest photo. The start button on the bottom of camera was pressed after the heating plate stayed at 30 °C for 2 min and the heating ramp was started.

1.3 Result and discussion

1.3.1 Synthesis of 10-Carboxy-N-decyl-N, N'-dimethydecyl-1-ammonium bromide

The reaction scheme for the synthesis of 10-Carboxy-N-decyl-N, N'-dimethydecyl-1-ammonium bromide is shown in scheme 3.1. This is a nucleophilic substitution reaction in which the bromine of 11-bromoundecanoic Acid acts as leaving group is attacked by N, N-dimethyldecylamine. The crude reaction solution is a very light-yellow liquid and the dried final products are white powders.

\[
\begin{align*}
\text{N,N- dimethyldecylamine} + & \quad \text{11-bromoundecanoic acid} \\
\rightarrow & \quad \text{Product}
\end{align*}
\]

Scheme 1.3.1 Reaction scheme of 10-Carboxy-N-decyl-N, N'-dimethydecyl-1-ammonium bromide
The experiments were conducted under several different reaction conditions to determine the best reaction conditions for this experiment to maximize the product yield, which was calculated by dividing final dried product weight with the sum of two reactants. Firstly, different solvents were used, chloroform, methanol, THF, acetone and acetonitrile. It was observed that the reaction only successfully yielded the product with acetone and acetonitrile as the reaction solvent. The next step was to compare the efficiency of these two solvents for the reaction and choose the better one. Then the experiment was repeated with different combination of temperature and time. The results are shown is Table 1.3.1.

Table 1.3.1 Yield degree of 10-Carboxy-N-decyl-N, N’-dimethydecyl-1-ammonium bromide under different reaction conditions

<table>
<thead>
<tr>
<th>Reaction condition</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature/°C</td>
<td></td>
</tr>
<tr>
<td>Time/hour</td>
<td></td>
</tr>
<tr>
<td>200ml Solvent</td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>24</td>
</tr>
<tr>
<td>Acetone</td>
<td>9.53%</td>
</tr>
<tr>
<td>80</td>
<td>24</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>28.61%</td>
</tr>
<tr>
<td>85</td>
<td>24</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>61.47%</td>
</tr>
<tr>
<td>85</td>
<td>48</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>69.58%</td>
</tr>
</tbody>
</table>

From table 1.3.1, it is clear that as the solvent for this reaction, acetonitrile acts better than acetone when other parameters stay same. The yield of products after recrystallized increases dramatically when raising the react temperature with the same solvent, and it keeps increasing when the react time becomes longer. Thus, the
reactions conditions used in following experiments are using acetonitrile as solvent, reacting at 85 °C for 48 hours.

The chemical structures of all the reactants and product were confirmed by 300MHz 1H NMR spectra. The 1H NMR spectra of the two reactants and 10-Carboxy-N-decyl-N, N’-dimethyl ammonium bromide in Chloroform-D is shown in Figure 1.3.1(a) (b) (c). From this picture, the characteristic peak position of the methylene groups adjacent to the quaternary ammonium nitrogen is 3.38 ppm, the integral of this area is 5.8, which is close to the expected number of 6 hydrogens. Other characteristic peaks show the reasonable shift from the original reactants.

Figure 1.3.1(a) 1H NMR spectra of 11-bromoundecanoic acid in Chloroform-D.
Fig 1.3.1(b) 1H NMR spectra of N, N-Dimethyldecylamine in Chloroform-D.

Fig 1.3.1(c) 1H NMR spectra of final product in Chloroform-D.
1.3.2 Thermal characterization of 10-Carboxy-N-decyl-N, N'-dimethydecyl-1-ammonium bromide

The decomposition temperature of the dried final products was conducted by TGA using an air atmosphere. The weight and derivation weight change percent were measured as a function of temperature. The result is shown in Figure 3.2. The peaks of the derivative of the weight change indicate the main decomposition temperatures of the material.

![TGA curve of 10-Carboxy-N-decyl-N, N'-dimethydecyl-1-ammonium bromide](image)

Figure 1.3.2 TGA curve of 10-Carboxy-N-decyl-N, N'-dimethydecyl-1-ammonium bromide

It can be inferred from Figure 3.2 that the first thermal decomposition temperature occurs at 253.03 °C, which gives a general heating range for DSC. Below 100 °C, the weight loss is trivial which shows the existence of remaining water in the sample can be ignored. It also shows that after the first decomposition peak, the decomposition rate slows down but there are still two peaks respectively appears at 416.81 °C and
468.96 °C. The reason for this kind of discontinuous weight loss is complex; it may be explained by partial decomposition or structure change of 10-Carboxy-N-decyl-N, N'-dimethyldecyl-1-ammonium bromide. For example, it is known the quaternary ammonium compounds have lower thermal stability than the corresponding, but a full description would require further investigation.

Then DSC was used to measure the melting temperature ($T_m$) and crystalline temperature ($T_c$) of the dried final product. Each aluminum sample pan contains 3-5 mg sample. The result is shown in Figure 3.3.

![DSC curve for 10-Carboxy-N-decyl-N, N'-dimethyldecyl-1-ammonium bromide](image)

As Figure 1.3.3 shows, the melting temperature of the product is 88.88 °C and the crystallization temperature is 52.13 °C. It is noticed that beside the sharp melting temperature peak at 88.88 °C, there is another small peak at 84.27 °C. The two melting temperature peaks may be explained by different crystalline phases existing
in sample powders, such as $\alpha$, $\beta$, $\gamma$ crystalline phases, but the real and deeper causes still need to be explored. The melting and crystal temperature characteristic temperatures can decide a general temperature range when fabricating organogelators.

1.3.3 Fabrication of 10-Carboxy-N-decyl-N, N'-dimethydecyl-1-ammonium bromide organogel

Firstly, it is important to find a proper solvent which can form a gel. The solutions of 10-Carboxy-N-decyl-N, N'-dimethydecyl-1-ammonium bromide in different temperature were recorded in Table 1.3.2 and Figure 1.3.4.

Table 1.3.2 Statuses of 2 wt% QAC in different solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>at 100°C</th>
<th>room temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 liquid</td>
<td>2 liquids</td>
</tr>
<tr>
<td>Hexane</td>
<td>●</td>
<td></td>
</tr>
<tr>
<td>Dodecane</td>
<td>●</td>
<td></td>
</tr>
<tr>
<td>Heptane</td>
<td>●</td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td>●</td>
<td></td>
</tr>
<tr>
<td>1,4-dioxane</td>
<td>●</td>
<td></td>
</tr>
<tr>
<td>o-Xylene</td>
<td>●</td>
<td></td>
</tr>
<tr>
<td>Chloroform</td>
<td>●</td>
<td></td>
</tr>
<tr>
<td>Styrene</td>
<td>●</td>
<td></td>
</tr>
<tr>
<td>2-propanol</td>
<td>●</td>
<td></td>
</tr>
<tr>
<td>Ethanol</td>
<td>●</td>
<td></td>
</tr>
</tbody>
</table>
Table 1.3.2 shows that with 2 wt% QAC in solvents, none of them could form a gel after cooling down to room temperature, thus we choose the seven solvents which formed 1 phase homogenous solution to test for gelation at higher concentration. In this way, chloroform, 2-propanol, ethanol, butyl alcohol, DMF, ethylene glycol and DMSO were picked out. Then the weight percent of quaternary ammonium bromide compound in solution was increased to 5wt% and 10wt% as fig 3.5(a), (b) shows.
Fig 1.3.5(a) Appearance of 5 wt% QACs in different solvents. From 1 to 6, it respectively added 2-propanol, chloroform, butyl alcohol, DMF, ethylene glycol and DMSO into vial. (b) Appearance of 10 wt% QACs in different solvents. From 1 to 5, it respectively added 2-propanol, chloroform, butyl alcohol, ethylene glycol and DMSO into vial.

As two pictures show upside, when the concentration of 10-Carboxy-N-decyl-N, N'-dimethydecyl-1-ammonium bromide raise up to 5%, the vial with DMF inside start to precipitate, while the solution with ethylene glycol and DMSO start to become opaque and the viscosity increased. When the QAC weight percent went up to 10%, the one with ethylene glycol and DMSO become more viscous while others remained transparent solution. We continued increasing the weight percent QAC in DMSO and ethylene glycol until gelation, which appeared at 10% for ethylene glycol and 15% for DMSO. Moreover, when the contents of QAC increase, the state of the solution becomes more and more solid-like as Figure 3.6 (a), (b) shows.
1.3.4 Characterization of 10-Carboxy-N-decyl-N, N'-dimethydecyl-1-ammonium bromide organogels by polarized optical microscopy

Polarized optical microscopy (POM) was used to observe the microscopic structure of the organogels with different solvents and different 10-Carboxy-N-decyl-N, N'-dimethydecyl-1-ammonium bromide concentration. The temperature range for POM is from 30° C to 70° C at a rate of 2° C min⁻¹. The pictures in Figure 1.3.7(a), (b) were screenshots of the process of how QAC crystals are formed in DMSO and ethylene glycol solutions. The second rows present the exact point where crystalline firstly emerged.
Figure 1.3.7 (a) Crystallization of QAC in DMSO solution

Figure 1.3.7(b) Crystallization of QAC in ethylene glycol

The formation of crystal can be observed in both Figures 1.3.7 (a) and (b). In Figure 1.3.7(a), the $T_c$ for QA in DMSO decrease with increase of quaternary
ammonium weight percent, and the crystal can grow into a fiber-like structure in 15wt% and 20wt% QAC/DMSO mixture. Normally crystallization happens in two or three dimensional, whereas the fiber-like crystalline structure of QA organogels must only enhanced growing along one axis and attenuated growing along another axis. However, in Figure 3.7(b) the crystalline temperatures in ethylene glycol stay constant with variation in 10-Carboxy-N-decyl-N, N'-dimethydecyl-1-ammonium bromide concentration. And only small scattered crystals without specific shape can be observed.

1.4 Conclusion

10-Carboxy-N-decyl-N, N'-dimethydecyl-1-ammonium bromide was synthesis by nucleophilic substitution reaction using 11-bromoundecanoic acid and N, N-dimethyldecylamine. The best yield happens when using acetonitrile as solvent, reacting at 85 °C for 48 hours. The first decomposition temperature for the compounds is 253.03 °C and the melting temperature is 88.62 °C. After trying various types of solvents, it was found that DMSO and ethylene glycol could be gelled with this compound. The DMSO start to gel at 15 wt% QAC and ethylene glycol start to gel at 10 wt% QAC. Then the crystal structure and formation process were studied by POM, the pictures shows that $T_c$ in DMSO decrease with increase QAC wt% and the crystal tend to be a fiber-like structure. While $T_c$ in ethylene glycol stays at a relatively stable value and the only small scattered crystals without specific shape were observed.
CHAPTER II

Room temperature shape memory programming of stearic acid/natural rubber bilayer blends

2.1 Introduction

2.1.1 Brief history of Shape-Memory Polymer

The generally definition of a SMP is a novel class of material whose deformed shape can be fixed into a temporary shape with application of force, and would remain the shape stably until it is exposed to a suitable external stimulus which can trigger the material to recover to its original shape on demand.\[^{43}\] This specific behavior of SMP is called Shape Memory Effect (SME). The first concept of SME is proposed by L.B. Vernon and H.M. Vernon in terms of “elastic memory” which means a deformed elastic material can resume its original shape by heating up, this idea was mentioned in a dental material patent in 1941.\[^{44}\] After this early discovery, people started to use covalently cross-linked polyethylene making heat-shrinking tubes and films by means of ionizing radiation which revealed the commercial value of shape-memory polymers in 1960s. The mechanism of the heating shrinkable product is that the permanent shape of material is also fixed by covalent cross-links and it can resume its original shape when heating upon recover temperature which is controlled
by the melting point of the polyethylene crystal, this effect is similar with the thermally induced SME.\cite{45} It is usually thought that the first official use of the SMP term was adopted under trade name of Polynorbonene to describe those specific materials by CDF Chimie Company and then commercialized by Japan Nippon Zeon Company in 1984.\cite{46} From hereafter, we ushered in an era that significant advances about SMPs have been made and dozens of publication talking about SMPs appearing yearly as shown in Figure 2.1.1

![Figure 2.1.1 Literature analysis for period 1970–2006: according to the result of literature search for “shape-memory polymer” White–publications in English, black–publications in Japanese, taken with permission from reference 48.](image)

This dramatic increase was corresponded to the rapid development of multifunctional polymers which also contain SME and the discoveries of other trigger stimuli more than heat. Furthermore, the development in product manufacturing industry was intensified and several products have entered the market, especially in the textiles area.\cite{47} Interestingly, nearly half of these are published in Japan and was
mainly driven by the company Mitsubishi Heavy Industries before 2000. Except for the polymers mentioned above, many other linear and phase-segregated multi-block copolymers, such as polyurethanes, poly (trans-isoprene) and styrene-butadiene copolymers can be found in the shape-memory polymer related literatures.\[^{[48]}\]

2.1.2 Structure of Shape-Memory Polymer

Firstly, we briefly introduce the structure of Shape-Memory Alloy (SMA) whose phase structure is analogous to SMP. Here, the SME is based on a thermoelstic phase transition between Martensitic and Austenite phase.\[^{[49]}\] Austenite is the stronger and cubic symmetry phase of SMA, while Martensite is the relatively soft, lower symmetry and easier deformed phase. The onset of the forward transformation begins at the martensite start temperature (Ms) and ends at the martensite start temperature (Mf), the entire process produces a temporary shape at low temperatures. Upon re-heating, the martensite starts to transform into the austenite phase when temperature exceeds the austenite start temperature (As), thus the deformed shape will automatically recover to its initial shape without any external deformation. And this transition would end at the austenite finish temperature (Af). The entire process is called reverse transformation as shown in Figure 2.1.2.\[^{[50]}\]
In analogy with SMA, on the microscopic level, thermo-responsive SMP is composed of two-phase copolymer structures, this is a phase separation structure since the two segments are incompatible. The soft segment is usually amorphous with a glass transition temperature \( T_g \) or semi-crystalline with a melting temperature \( T_m \) whose hydrogen bonds can be broken upon heating, both of the two temperatures are called transition temperature \( T_t \). The hard segment is a physically or chemically cross-linked network connected by covalent bonds. The former structure can undergo a temporary deformation in shape memory cycle and is able to drive shape recovery to the original shape when a proper stimulus is applied. On the other hand, the latter one prevents shape deformation when external force applied, the permanent deformation it forms can be remained when releasing load even upon heating.
2.1.3 Shape Memory cycle processing

For a typical thermally Shape Memory cycle, firstly, the program starts with a deformation of SMP at a temperature above the of the $T_1$. Holding the load constant, then drop the temperature below $T_g$ or $T_m$. The elastic deformation of soft segments and the permanent elongation of hard segments work together to freeze a temporary shape after releasing load. When the deformed material is reheated above its transition temperature, the soft segments in SMP can be molten and then freed towards the original shape. \cite{54, 55} However, the hard segments in polymer will remain the permanent deformation because the covalent bonds in polymer network have been broken and rearranged with application of stress which makes the structure change irreversibly.\cite{56, 57}

It should be noted that unlike the SMP programming step above, the deforming process of Shape-Memory Alloys can be operated at a room temperature which is relatively lower (so called “cold-drawing”) and then resume its original shape upon heating. \cite{58} The cold-drawing microstructure evolution can be learned from the
research Wang et al. did in 2010. The object of study is a poly (ester urethane) SMP with poly (ε-caprolactone) (PCL) as soft segments and urethane as hard segments. During the initial extension period, the amorphous PCL chains are oriented along the stretching direction while the hard segments and crystalline PCL phase keep their original state unchangingly. With the increase of stretch extent, the two unchanging segments soon gain a high degree of orientation. Meanwhile, the hydrogen bonds between the urethane are weakened with the application of uniaxial stretch and crystalline PCL undergoes stress-induced disaggregation and crystallizes again. When heating up, the microstructure change in the SMP system will reverse.

Figure 2.1.4 Illustration of the microstructure change of the PEU SMP during the Cold Drawing and the Recovery Processes. Taken with permission from reference 60.

Compared with the traditional SMPs programming procedure, the cold-drawing method is much easier and can save more energy. What’s more, the study of Katzenberg also reveals that shape memory natural rubber can reach fully shape recovery within a specifically narrow trigger range when being cold-programmed. In view of so many advantages, we decide to focus on the cold-drawing programming of SMPs in this study.
2.1.4 Trigger method

The usual actuation methods of SMPs can be heat, electricity, light, moisture, PH, magnetism. \cite{64,65} In fact, all the different trigger methods of SMPs can be ascribed to heat intrinsically; merely the heat-produce method is indirect. For example, moisture responsive SMP can be triggered by immersing it into water without heating. \cite{73} This can be explained by the relationship between $T_g$ and the amount of water SMP absorbs during the immersing. The water imbibed by SMP can be divided into free water and bound water. The former one has no influence on SMP property and can be removed by heating upon the vapourization temperature, however the bound water can weaken the hydrogen bonding effect thereby reduce $T_g$ of material, which makes it possible to trigger shape recovery at room temperature. \cite{66}

In order to meet different shape-memory trigger demand, the elastic property of soft segments in SMP is required to be a function of the corresponding trigger method and it should be named related with its particular stimulus. \cite{67} For instance, if a material undergoes shape recovery when external temperature is changed, it can be named as a thermally induced SMP.

2.1.5 Bilayer shape memory material

For complex systems, such as bilayer material, the deformation such as bending or twisting might be caused by inhomogeneous volume change. \cite{68} Generally, there are two types inhomogeneous deformation: one material in inhomogeneous field, and multiple materials in inhomogeneous field.
With the structure of bilayer shape memory materials, it’s possible to fabricate triple-shape memory effect (TSME) which means the SMPs has the ability to memorize two temporary shapes during the one programming process. TSM polymers provide an additional dimension for SMPs which bring it great application potential in medical science, actuators, and recoverable coatings.

2.2 Experimental section

2.2.1 Materials
Stearic Acid (>98.0%, TCI American), Isopropyl alcohol (IPA) (>98.0%, BDH chemicals), size 64 (80mm x 6 mm x 1.0mm) size 8 (22 mm x 0.7 mm x 1.0mm) Pale Crepe Gold® (i.e. soft rubber bands) and Advantage® (i.e. stiff rubber bands) (Alliance® Rubber Company), Loctite 2g Plastics Bonding System were used as received.

2.2.2 Preparation of shape memory polymers and bilayer SMPs.

The preparation of SMP used batches of 15 size 8 commercial natural rubber bands
swollen in molten stearic acid. Stearic acid was melted in 20 ml glass vials at 75°C using a thermostatic aluminum heating plate. Each batch of rubber bands was weighed to establish the starting weight and then immersed in molten stearic acid for different swell times of: 0.5, 1, 2, 3, or 4 hours. After removing the rubber bands from the stearic acid, they were immediately dipped them into room temperature IPA for 1 minute to wash off the stearic acid on the surface of samples. Then all rubber bands were stretched and scraped slightly to remove any other residual stearic acid. Finally, the stretched rubber bands were immersed in 75°C hot water to eliminate the deformation caused by swelling and stretching, and then dried them in air overnight and weighed. According to the weight of the samples before and after swelling, we can easily calculate the stearic acid weight percent (SA wt %) of SMP as:

$$SA\text{ wt}\% = \frac{g_{\text{swell}} - g_{\text{neat}}}{g_{\text{swell}}} \times 100\%$$

Where $g_{\text{neat}}$ and $g_{\text{swell}}$ correspond to the weight of the batches of the initial and swollen rubber bands.

For bilayer SMP fabrication, first we cut both soft and stiff size 64 commercial rubber bands into 40mm long pieces and marked the inner side of original rubber ring with a permanent marker. Next the two part cyanoacrylate adhesive was used to glue together two rubber bands, 10 different types of samples were fabricated, inner side of soft rubber with inner side of soft rubber, outer side of soft rubber with outer side of soft rubber, inner side of soft rubber with outer side of soft rubber, inner side of stiff rubber with inner side of stiff rubber, outer side of stiff rubber with outer side of stiff rubber, inner side of stiff rubber with outer side of stiff rubber, outer side of stiff rubber with outer side of stiff rubber, inner side of soft rubber with outer side of stiff rubber, inner side of soft rubber with outer side of stiff rubber.
rubber with inner side of stiff rubber, inner side of soft rubber with outer side of stiff rubber, outer side of soft rubber with inner side of stiff rubber, outer side of soft rubber with outer side of stiff rubber. The bilayer rubber bands were all left in air overnight for totally cementation and weighed to determine the “neat” weight for each bilayer sample. Then the swelling process was repeated for all of the bilayer rubber bands and single layer size 64 rubber pieces as described above. For swelling was conducted at 80°C and swelling times of 1, 2, 3, 4 hours. Finally, the swelled rubber bands were weighed and the SA wt% after swelling was determined.

2.2.3 Characterization of Shape memory effect for one layer SMPs

The most common quantification of SME is to determine the shape fixity (F) and shape recovery (R). F is the percentage of applied strain the SMP could store after programming; R represents the degree SMP could recover its original shape after programming. These two parameters are calculated from a uniaxial tensile deformation using equations below [74],

\[
F = \frac{\varepsilon_f}{\varepsilon_a} \times 100\%
\]

\[
R = \frac{\varepsilon_f - \varepsilon_r}{\varepsilon_f - \varepsilon_i} \times 100\%
\]

\[
\varepsilon_k = \frac{l_k - l_i}{l_i} \quad k = f, r, a, i
\]

l_f-fix length  l_r-recovery length  l_a-applied length  l_i-initial length.

In order to acquire all four lengths needed for characterizing R and F, room temperature deformation was performed by a Mark-10 Force Gauge Model at room temperature with two hook clamps to set the rubber bands and stretch the sample at a average rate of 4mm/s with the rotate handle, 0.01 newton (N) was used as force
gauge in the experiments. Then the recovery of deformed sample was triggered in a 75°C hot water for 1min. Two lines were marked on every sample with a distance between them of approx. 10mm to set the initial length. The fixed length of every deformed specimen was measured after leaving to relax in air for 24 hours. Three different stretch tests were conducted. For each test it was repeated three times to measure the shape fixity and recovery.

2.2.3.1 Different natural rubber bands, apply same force with varying SA wt%  
A force 10N was applied to stretch both soft and firm rubber bands with varying SA wt%, The samples were held at the applied strain for 1h and then removed from the test apparatus. The samples were left out to relax in air for 24h before the fixity measurement.

2.2.3.2 Soft natural rubber bands, apply different strain with varying SA wt%  
The samples were stretched to 200% or 300% and held for 1 hour for different SA wt% soft samples.

2.2.3.3 Soft natural rubber bands, same strain, same SA wt% with varying stretch time  
Soft rubber bands with 57 wt% stearic acid were stretch to 200% strain. The time the sample was held in the stretched state was varied from 1min to 49 hours.
2.2.3.4 Crystalline orientation of deformed SA/ size 8 rubber bands

The crystal orientation for deformed shape memory samples were characterized by small angle X-ray scattering (SAXS). The size 8 shape memory rubber bands were stretched to 100%, 200%, 300%, 400% strain for 10min and to 300% for 1min, 10min, 100min, and 1000min. All the samples were removed from the testing apparatus and left at room temperature overnight and then cut in 2mm long samples from the middle of sample section between the two contact points with the Mark-10 machine. Each sample was placed one by one on the sample stage of SAXS, where the samples was oriented with the stretching direction horizontal or parallel to the fround with the sample lying across the centered on the open circle on the sample holder.

2.2.4 Shape memory effect of bilayer SA/ rubber bands blends.

After swelling, both one layer (i.e. individual rubber bands) and bilayer rubber bands bent. Moreover, all one layer rubber bands bent towards their inner side and all soft/stiff bilayer rubber bands bent towards the soft rubber side. To observe the shape memory effect (SME) of bilayer rubber bands, each sample was pressed flat by a iron plate at room temperature for 1 hour to fix their shape and then immersed into 80°C hot water to trigger the shape recovery. This shape memory programming is shown in Figure 2.2.1.

![Figure 2.2.1 Shape memory programming for bilayer rubber bands.](image)
2.3 Result

2.3.1 Content of Stearic Acid

Using the SA wt% formula mentioned in chapter 2.2.3, we calculated the SA wt% the natural rubber bands absorb for different swelling time at the same temperature. The results are displayed in Fig 2.3.1 In this swelling system, NR acts as a base material, filled with SA.

![Figure 2.3.1 SA wt% swelled in size 8 rubber bands for different swell time](image)

According to Figure 2.3.1, it is directly observed that the longer natural rubber bands swell in stearic acid, the more stearic acid will be absorbed. Moreover, the soft rubber bands always adsorb more stearic acid than the stiff ones at the same swelling time.

The swelling curves and visual appearance of the one and two layer size 68 rubber bands are shown in Figure 2.3.2.Similar to the previous result, the stearic acid weight
percent also increases with increased swelling time. However, the SA weight percent of the bilayer rubber bands was not an average value of the soft and stiff one layer samples, but lower.

![Stearic acid wt% graph]

Figure 2.3.2 SA wt% swelled and shape change of size 68 one layer and bilayer rubber bands

In order to solve this problem, a hypothesis was made, that the glue between two layers influences stearic acid adsorption. To test our hypothesis, we measure SA wt% at 2 hours of swelling for the soft-soft bilayer, stiff-stiff bilayer and soft-stiff bilayer rubber bands. The result is shown in Figure 2.3.3.
According to Figure 2.3.3, it shows that the SA wt% of soft-stiff bilayer rubber bands stay in the middle of soft bilayer and stiff bilayer rubber bands, which certified our hypothesis.

2.3.2 Shape-Memory Properties

Shape memory effect can be characterized by two shape memory properties: shape fixity and shape recovery. These two parameters were measured under different deformation conditions, and results were compared as function of SA wt%, stretch time and stretch strain.
2.3.2.1 Shape memory properties as a function of SA wt%

Firstly, with increasing SA wt%, the general trend in the shape fixity for both soft and firm rubber bands is increase fixity with increased SA wt% when the same stretching force was applied as Figure 2.3.4 presents. This result is because the crystal structure holds the temporary shape after the force was removed. At low SA wt% the crystal network is no able to resist deformation and therefore the sample retracts resulting in lower fixity. The fixity of the stiff rubber bands is lower than the soft rubber bands. This is attributed to the lower swelling in the stiff rubber band.

Fig 2.3.4 Shape fixity and recovery for soft and firm rubber bands with 10N applied.

When it comes to shape recovery, the result doesn’t show a monotonic increase along with SA wt%, but reaches the best recovery at 3 hours swell time which represents about 57% SA wt%. This may be explained that parts of covalent bonds in natural rubber network were damaged when too much stearic acid filled in and this kind of deformation is irreversible. It should be noted that the SME of firm rubber based samples is obviously worse than the soft ones, so the following experiments
only focuses on soft rubber bands. One another point to note here is the x-axis title is swell time, because same swell time brings different SA wt% to soft and firm samples.

2.3.2.2 Shape memory behavior as a function of applied strain and SAwt%

One another thing we interested in is how the stretch strain level influences SME, therefore in section the effect of varying the applied train on the soft rubber bands was studied and is shown in fig 2.3.5.

![Fig 2.3.5 Shape fixity and recovery for soft rubber bands with different strain applied.](image)

Generally, the shape fixity at 200% strain is better than 300% strain but the difference between them is not that large. On the other hand, the shape recovery of both sets is about 90% and 300% strain have better shape recovery.
2.3.2.3 Variation of shape memory properties with time under strain

In the last part of experiments, the effect of holding time under 300% strain on the SME was studied. All the fixity and recovery data are plotted on a log time axis plot in Figure 2.3.6.

Figure 2.3.6 Shape fixity and recovery of 57 wt% SA soft rubber bands with 300% stretch strain
From the plot above, although it can show the tendency of how the shape fixity and recovery change with stretch time increasing, both shape fixities and recovery are poor values due to the large strain applied, so replace the fixity and recovery with fixed and residual strain to show a reasonable amount as Figure 2.3.7 shows.

![Figure 2.3.7 Fixed and residual strain of 57 wt% SA soft rubber bands](image)

According to Figure 2.3.7, the fixed strain increases along with stretch time increasing until 26 hours stretch, after 26 hours the fixed strain started to fluctuate but still stay at a relatively stable level. On the other hand, the residual strain also has the same tendency but the growth rate is smaller than the fixed strain. With the longer time stretching, it is likely that some stress relaxation occurs which would account for this phenomenon.
2.3.3 Characterization of crystalline orientation of deformed SA/ size 8 rubber bands

The pictures of SAXS were processed with saxsgui software to target the circle center and make the orientation more obviously. The crystalline orientation morphology is shown in Figure 2.3.8 and azimuthally averaged 2D images of intensity is shown in Figure 2.3.9.

![Figure 2.3.8 Crystalline orientation nanography of shape memory rubber bands](image)

Figure 2.3.8 Crystalline orientation nanography of shape memory rubber bands
Figure 2.3.9 Visualized 2D images of shape memory rubber bands SAXS data

From the two figures above, we can easily tell that the orientation degree increases with increasing holding time under strain and the applied strain. For undeformed samples, there were no orientation shown as the diffraction rings are uniform and the integral intensity is constant vs. the azimuthal angle. The orientation degree increases with the deformation time and strain increasing according to the increase of the integral intensity.

2.3.4 Shape memory effect of bilayer SA/ rubber bands blends

As shown in chapter 2.3.1, the soft rubber can always swell more stearic acid than the stiff rubber. Thus if we glue soft and stiff rubber bands together and then swell them in stearic acid, there would be a SA wt% gradient of the swollen bilayer materials, which indicates a different volume change between these two layers and leads the bilayer materials bended as shown in figure 2.3.2. Then take the bilayer rubber bands for shape memory experiment. The shape memory circle was
programmed as Figure 2.3.10 shows.

![Figure 2.3.10 shape memory effect of bilayer SA/ NR blends](image)

From result shown upward, the bent bilayer material could fix a temporary shape by pressing at room temperature until stimuli its recovery by heating it up. When put the fixed bilayer rubber bands into hot water, it can immediately turn back to its original shape with little curvature loss. This indicated that this bilayer product has pretty good thermal shape memory property.

2.4 Conclusion

On the basis of all the experiments shown it is obvious that the SA wt% influences a lot on the shape memory properties. Generally, shape fixity and recovery of a SMPs become better when increases with a maximum at 57 SA wt%. In addition, applied strain and hold time under strain also impact on the properties to some extent. We also have made some analysis on the microscopic level by SAXS. It shows that the orientation degree of stearic acid crystal in rubber bands increases with the applied strain and hold time under strain. Then bilayer rubber bands were fabricated by gluing
two rubber bands together and then swelling in stearic acid for different hours. The SA wt% for one layer and bilayer samples indicates that the glue used to adhere two rubber bands influence the stearic acid swelling efficiency. Moreover, the result shows that the stearic acid wt% gradient between two layers would lead to bend, if this bending is programmed to flat at room temperature, then it is able to recover to its original shape with thermal stimuli.
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