A NOVEL WAY TO REVERSIBLY DETACKIFY PSA COMPOSITIONS USING THERMORESPONSIVE COPOLYMERS

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Introduction

Over the last decade, a number of companies have developed PSA compositions which are capable of being deactivated or detackified and, thus, more easily removed from substrates such as skin. Skin friendly deactivatable adhesives which do not cause trauma on removal from delicate wounds have long been sought after as a means to improve patient comfort.

Various means of deactivating PSA’s have been published, including UV curing, application of heat or cold or by the use of water dispersible components which can be removed by immersing in water (1). A US based corporation has produced PSA compositions based on side chain liquid crystal technology. This relies on a crystallisable side chain which results in detackification on cooling below its melting point (2). The melting point of the side chain, and hence the deactivating temperature, can be tailored to suit the application. Smith and Nephew in the UK have developed a novel light curing PSA composition which can be removed cleanly from the skin (3). The photoinitiator is built into the polymer chain to make it safe for skin contact. The tape can be removed by removing an opaque liner and exposing to ambient light. A number of water deactivatable compositions have also been developed which rely on at least one water soluble component (tackifier or plasticiser) being dispersed on exposure to water (1).

There has been extensive literature on the properties of polymers which display a lower critical solution temperature (LCST). These are polymers which consist of monomers having both hydrophilic and hydrophobic behaviour in aqueous solution. In solution, such polymers are in a fine balance between their hydrophilic and hydrophobic characteristics. A slight change in temperature or pH is often enough to cause the polymer chains to collapse into a globular form and become insoluble. The vast majority of work has concentrated on the n-substituted acrylamides, in particular, n-isopropylacrylamide (NIPAM). Poly(NIPAM) displays a dramatic change from a hydrophilic, highly water soluble polymer with gaussian chain conformation, to an insoluble polymer with a globular chain conformation on raising the temperature above 31°C (LCST). Lightly crosslinked hydrogels based on NIPAM and its copolymers have been extensively studied for potential applications such as self cleaning contact lenses, controlled water release materials in agriculture, rheology modifiers (4) artificial muscle fibres and controlled drug release membranes. There has been significant work carried out on the properties of thermosensitive gels for use as possible drug delivery systems. These include drugs such as sodium salicylate (5), ibuprofen (6) and insulin (7). The interest lies in the response of these gels to small changes in temperature or pH, which cause them to expel aqueous solutions (containing the active material), thus acting as a “smart reservoir.” Such hydrogel-like materials have enormous potential as unique drug delivery systems. It would be of interest to see if it is possible to produce pressure sensitive adhesive
compositions which can be made to swell and de-swell on reaction to an outside stimulus, such as a slight temperature change or shift in pH.

The aim of this brief study was to determine if it is possible to formulate pressure sensitive compositions which display an LCST and can, thus, be swollen into a gel below a critical temperature. The purpose was to produce a PSA which will deactivate in water by swelling, but only when it is exposed to water below a certain temperature, thus, giving a “smart” switchable PSA. In principle, the switching effect should be completely reversible. On heating above the critical temperature, the composition should release absorbed water and regain its pressure sensitivity. We were also interested in looking at pressure sensitive compositions which display different levels of water absorption which could be tailored in combination with temperature sensitivity. Materials like these may have applications as smart drug delivery systems which could potentially be provided in pressure sensitive tape form. The experiments performed in this study are all based on well characterised monomers used in hydrogel research. The significant difference is that they are polymerised with additional monomers and tackifiers which impart good pressure sensitivity to these gel-like materials in their dry state. To illustrate the approach we have taken in making an “LCST adhesive,” we have reproduced in our laboratory some work already published in the literature to highlight the changes in LCST with copolymer composition.

Experimental

A series of copolymers based on NIPAM and acrylic acid were prepared as well as copolymers based on NIPAM and n-tert-butylacrylamide (NTBA). Copolymer based on NIPAM and acrylic acid were polymerised in water using ammonium persulphate and a tetramethylethylenediamine accelerator. Copolymers of NIPAM-co-NTBA were produced in a mixture of acetone and water using the same polymerisation conditions. The aim of this study was to test the consistency of the polymerisation procedure with published literature (8). Copolymers of NIPAM and NTBA are brittle materials and have Tg’s greater than 100°C. In order to introduce pressure sensitivity, the Tg of the resultant copolymers needs to be well below 0°C. Certain polyethylene glycol oligomers (PEG) have inherent pressure sensitivity, as well as low Tg, and were, thus, used as a copolymer to reduce Tg and impart film forming properties to the compositions. A series of compositions based on PEG and NIPAM were polymerised in a solution of ethanol and water using potassium persulphate initiator at 72°C for eight hours. The PEG’s chosen were a blend of acrylated oligomers designed to impart a good balance of tack and cohesion. A very small amount of difunctional monomer was added to give some slight crosslinking.

A series of copolymer PSA compositions were produced using UV curing of 100% solids mixtures. This was achieved by dissolving NIPAM and NTBA in warm PEG oligomer with a small amount of crosslinking difunctional monomer and adding a free radical UV photoinitiator. Compositions based on NIPAM, PEG and the cationic monomer, N,N’-dimethylaminopropylmethacrylamide (DMAPMA), were also produced in order to investigate the effect pH has on water uptake. A ratio of PEG oligomer to acrylamide of at least 4:1 was chosen to give a modulus suitable for pressure sensitive properties. These compositions could be further tackified by predissolving tackifying resins such as

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\begin{align*}
&H_2C=CH-C(\underset{\text{O}}{\overset{\text{O}}{\underset{\text{CH}_3}{\text{N}}}})CH_2\text{CH}_3 \quad H_2C=CH-C(\underset{\text{O}}{\overset{\text{O}}{\underset{\text{CH}_3}{\text{N}}}})C(\underset{\text{O}}{\overset{\text{O}}{\underset{\text{CH}_3}{\text{N}}}})CH_2\text{CH}_3 \quad H_2C=CH-C(\underset{\text{O}}{\overset{\text{O}}{\underset{\text{CH}_3}{\text{N}}}})CH(CH_3)\text{CH}_2
\end{align*}
\]

\text{N-isopropylacrylamide} \quad \text{N-tert-butylacrylamide} \quad \text{N,N’dimethylaminopropylmethacrylamide}
Swelling studies were carried out over a range of temperatures from 0°C to 80°C by immersing the produced polymer disks and films in deionised water. The samples were allowed to equilibrate until no further water absorption could be detected. Samples were weighed by firstly removing surface water with an absorbent paper and quickly weighing. The effects of pH and ionic strength of water were carried out by immersing samples of NIPAM-co-NTBA-co-PEG in NaCl solutions and samples of NIPAM-co-PEG-co-DMAPMA polymer in buffer solutions of pH 4, 7 and 10.

**Results and Discussion**

Figure 1 shows the results of our swelling experiments on a series of NIPAM-co-acrylic acid gels. The swelling ratio is defined as the weight of the wet sample divided by the weight of the dry polymer. The data, as expected, show a clear LCST which increases in temperature as the mole fraction of acrylic acid is increased. What is also observed is a broadening in the LCST as the copolymer becomes more complicated. The critical temperature for pure NIPAM is quite sharp, with an LCST around 35°C, slightly higher than recorded in the literature (8). The increase in LCST with increasing acrylic acid content is as expected and is consistent with literature findings. Addition of polar or highly soluble monomer will tend to increase the polymer’s affinity for water and, thus, tend to increase the critical point. While this is an interesting effect, a more interesting and less studied phenomenon is in lowering the LCST to a point where the critical point is at or below room temperature. In principle, addition of a less polar monomer than NIPAM to NIPAM should reduce the LCST below 35°C. In this study we chose n-tert-butylacrylamide (NTBA) as a co-monomer. Normally, NTBA is completely insoluble in water but can be solubilised by copolymerising with a more water soluble monomer such as NIPAM or acrylic acid. This in principle should lower the LCST of NIPAM below its homopolymer value (9). A series of copolymers of NIPAM-co-NTBA were prepared and their LCST measured by cloud point determination on warming an aqueous solution of the polymer. Figure 2 shows the cloud point temperatures of the NIPAM-co-NTBA copolymers in de-ionised water as a function of copolymer composition. The cloud points show an almost linear decrease as the NTBA mole percent is increased. Extrapolating the data to pure NTBA homopolymer would give an LCST of around -20°C, which is of course only theoretical. High levels of NTBA would be expected to make the copolymer completely insoluble.

In order to make a pressure sensitive composition, the modulus of the composition would have to fall within the Dahlquist criterion. The acrylamide based polymers produced so far are all high Tg copolymers and are incapable of being pressure sensitive. Polyethylene glycol oligomers were chosen as the third component as they form low Tg homopolymer, can be intrinsically tacky and are a good solvent for acrylamide monomers and for certain tackifying resins. The modulus can be modified simply by changing the levels of PEG in the composition to give a modulus in the correct range for pressure sensitivity. A series of copolymers based on NIPAM-co-NTBA-co-PEG were produced using free radical polymerisation in solvent and also as 100% solids reactions using UV initiation. Addition of a third co-monomer like PEG would be expected to broaden any visible LCST transition and increase it in temperature, due to the polar nature of PEG. Figure 3 shows the result of swelling experiments for a series of copolymers as a function of temperature. The samples all show an intrinsic tack and LCST behaviour. The NIPAM-co-PEG copolymer shows a critical point around 70°C. Addition of NTBA appears to reduce the LCST but not significantly. There is also an overall reduction in the equilibrium.
water uptake as the level of NTBA is increased. This is probably due to decreased solubility with increasing NTBA content.

A comparison of polymer produced from solvent and as 100% solids did not show significant differences in LCST behaviour. This is an interesting result, as the methods of polymerisation are quite different, resulting in different copolymer composition and molecular weights. It has been shown that polymers based on NIPAM show LCST behaviour relatively independent of molecular weight, which would explain our findings (10).

It is interesting to note that the LCST behaviour appears to be active at 70°C but also apparent at lower temperatures, as noted by the slope in the swelling curves around 30°C. To try and accentuate this phenomenon, we deliberately varied the initiator concentration to try and form more homopolymer and copolymer of the acrylamides during the polymerisation. The results can be seen in Figure 4. The graph shows a swelling behaviour associated with multiple LCST’s at around 70°C, 30°C and also at 10°C. This is most likely due to the formation of NIPAM homopolymer and NIPAM-co-NTBA copolymer which is showing LCST behaviour at 30°C and 10°C respectively. This is mainly observed when there is a significant amount of NTBA in the copolymer. The ability to introduce different critical temperatures into the composition opens some interesting possibilities into tailoring the water absorption and desorption properties of a pressure sensitive copolymer.

A study was also carried out to investigate the effect of electrolyte and pH on the swelling behaviour of these gels. NIPAM and NTBA based gels would not be expected to show a pH response as there are no ionic groups present (11). Studies on swelling behaviour at pH 4 and pH10 revealed no obvious difference in swelling behaviour (Figure 5). DMAPMA is a cationic monomer with a protonated tertiary amine group. In an attempt to introduce a pH based LCST, copolymer based on NIPAM-co-DMAPMA-co-PEG was produced and the swelling behaviour studied (Figure 6). What was observed was a slight change in LCST at temperatures around 40°C resulting in a 10 degree shift in critical point as the pH was increased. Only a very small amount of DMAPMA was required to induce a pH response. High concentrations of DMAPMA tended to destroy the thermal LCST behaviour of the composition and gave uniform swelling at all temperatures. Copolymer of NIPAM-co-NTBA-co-PEG did not show any temperature changes to its LCST when immersed in NaCl solutions (Figure 4). Only dehydration with increasing salt concentration was seen, which was not unexpected.

**Pressure sensitive compositions**

The pressure sensitive compositions produced in this study display an unusual behaviour in the presence of water and can show several temperature dependant transitions. The most obvious application for such adhesives is in their ability to absorb several times their dry weight in water in a very short space of time. Thus, any pressure sensitive properties are quickly lost after exposure to water. Since the compositions are intrinsically temperature sensitive and not simply sensitive due to one water swellable component, it should be possible to restore tack by increasing the temperature of the tape or the water in which it is immersed. As a simple experiment, we have taken a sample of adhesive coated onto polyester film with a 50 micron thickness and immersed it cold water. Within seconds the adhesive has swollen into a gel and has lost all of its pressure sensitive properties. We then take the same sample and immerse it in water above the critical temperature (70°C) to deliberately thermally “shock” the adhesive and observe what happens. On immersion, the tape immediately turns white. This is due to the absorbed water phase’s separating out of the gel as the LCST is exceeded. Over the space of 1-2 minutes, the tape goes clear again as most of the absorbed water is expelled. On removing the tape from
water and quickly drying the surface moisture away, the adhesive has regained most of its tack. This procedure can be repeated several times and the tape will always regain its tack on immersing above its LCST.

The physical properties of these compositions are listed in Table 1. Peels of 25 oz/inch are easily obtained by adjusting the composition with a suitable compatible tackifier. One drawback of such compositions is that a hydrophilic film former is required, which results in moisture uptake over time. However, a water uptake up to 50% will still yield reasonable pressure sensitive properties. This may be an advantage in using such adhesives as smart reservoirs which can be forced to release their contents on a slight increase in temperature. For example, on moving the adhesive from room temperature to the temperature of the skin. Adhesive stored between release liner does not appear to absorb ambient moisture to any noticeable level even after several years.

Although this is a simple study using materials that have been well characterised by the scientific community, it does highlight that pressures sensitive adhesives with unique properties can be made fairly easily. Other materials that display an LCST behaviour which would be more suitable for medical applications include certain cellulose derivatives.

Summary

It has been shown that it is possible to make pressure sensitive compositions which show a strong swelling behaviour in contact with water which is also temperature sensitive. It is possible to adjust the swelling behaviour of these gel like adhesives by adjusting the copolymer composition and the polymerisation conditions. Pressure sensitive adhesives like these may be of interest as de-tackifying adhesives or potentially as drug reservoirs which release their aqueous content on warming.

References

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Table 1. Typical peel and tack results for a composition based on NIPAM-co-PEG copolymer tackified with terpene phenolic resin.

<table>
<thead>
<tr>
<th>Peel from Glass</th>
<th>Peel from Stainless steel</th>
<th>Loop tack</th>
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<tr>
<td>26 oz/inch</td>
<td>20 oz/inch</td>
<td>1800 grams</td>
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Figure 1. Swelling ratio of N-isopropylacrylamide-co-acrylic acid copolymers in water as a function of temperature. Different mole ratios of acrylic acid were added to change the lower critical solution temperature.
**Figure 2.** Cloud point temperatures for copolymers of N-isopropylacrylamide-co-N-tert-butylacrylamide as a function of copolymer composition. Composition is in mole %.

**Figure 3.** Swelling ratio of NIPAM-co-NTBA-co-PEG pressure sensitive compositions as a function of temperature. The ratios refer to the weight ratio of NIPAM to NTBA in each copolymer respectively. The amount of PEG in the copolymer is kept constant.
Figure 4. Swelling ratio of a NIPAM-co-NTBA-co PEG pressure sensitive copolymer against temperature in NaCl solution. The initiator level has been altered to induce lower temperature transitions.

Figure 5. Swelling ratio for a pressure sensitive copolymer based on NIPAM-co-NTBA-co-PEG at different pH.
Figure 6. Swelling ratio for a pressure sensitive copolymer based on NIPAM-co-DMAPMA-co-PEG at pH of 4, 7 and 10.
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