

**Unique Thermal Behavior of Acrylic PSAs Bearing Long Alkyl Side Groups and
Crosslinked by Aluminum Chelate**

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Abstract

An acrylic pressure-sensitive adhesive (PSA), bearing octadecyl acrylate, methyl acrylate and acrylic acid groups, and crosslinked by aluminum acetylacetonate (AlACA), displayed behavior unique among acrylic PSAs in that its adhesion, which decreases with an increase in temperature, began to increase again from around 150 °C. In order to understand this behavior, the structure and thermal properties of the PSA were investigated in detail, along with another PSA crosslinked by a covalent crosslinking agent (Az). From thermal mechanical analysis, the PSA with ionic crosslinks (AlACA) showed three softening points at 20, 60, and 160 °C. In comparison, the PSA covalently crosslinked by Az only exhibited two softening points (at 20 and 60 °C). The softening point at 160 °C is clearly related to ionic chelate crosslinking. DSC measurements indicated that the softening point at 20 °C resulted from melting of the ordered octadecyl group, and the softening point at 60 °C was due to an increase in the mobility of the main chain. The temperature dependence of viscoelastic measurements revealed that the viscosity of the PSA crosslinked by AlACA increased at around 160 °C. From these results, we considered that the distinctive adhesion of the PSA crosslinked by AlACA could be due to ligand exchange at the aluminum crosslinking points, which are chelated by carboxy groups built in the main chain.

Keywords: Pressure-sensitive adhesive; Thermosensitive adhesive; Acrylic PSA; Crosslinking; Side-chain crystalline polymer

1. Introduction

A pressure-sensitive adhesive (PSA) is one that adheres instantly to an adherend through the application of light pressure, and detaches easily and without residue by pulling lightly.[1, 2]

Acrylic PSAs are widely used in commercial products and industrial processes, because they are low-cost, self-adhesive and have a high resistance to weathering and water. It is of interest to design acrylic PSAs in such a way that their adhesion can be adjusted according to their chemical structure[3-5] as well as external stimuli such as light[6] and heat[7-9].

An acrylic PSA with a crystalline side group is thermosensitive[7, 10, 11], because the crystalline unit undergoes a reversible order-disorder transition with a change in temperature. Below the transition temperature, the PSA behaves as a hard plastic, because the long alkyl side groups form crystalline aggregates. Above the transition temperature, the side groups change to an amorphous state and become soft and flexible, which leads to an appearance of tackiness.

It is well known that acrylic polymers lacking crosslinks cannot be used as PSAs, since crosslinking provides the thermal and mechanical properties required for thermomechanical stability.[2]

Various multifunctional compounds have been used as crosslinking agents. Some have reactive groups such as aziridine, epoxy, and isocyanate derivatives, which are known to form covalent crosslinks[12, 13]. Aluminum acetylacetonate also functions as a crosslinking agent[14], whose crosslinking reaction takes place at the carboxy groups in the acrylic polymer chain[15]. As the result, an aluminum carboxylate is formed as the crosslink point, and volatile acetylacetone is also produced.

The crosslinking of acrylic PSA with the aluminum chelate gives a satisfactory cohesion increment and the required thermal stability.

Usually, adhesion of acrylic PSAs decreases with an increase in temperature. Even those with crosslinks usually display poor adhesion around 150 °C. Although silicon PSAs can be used in the high-temperature region, they are expensive and rarely used for processes in which Si contamination would be a concern. Therefore, acrylic PSAs, which are reasonably priced and can be used at high temperatures, are in great demand for industrial processes. Hence, our aim is to develop thermosensitive acrylic PSAs that adhere reversibly at a certain temperature, and maintain their adhesion in the high-temperature region. Recently, we discovered that thermosensitive acrylic PSAs crosslinked by aluminum chelate display an unusual characteristic, in that their adhesion increases again from around 150 °C. This is seldom observed in the case of covalent crosslinked PSAs.

The mechanism underlying this behavior and the thermal properties of thermosensitive PSAs are not yet understood. In this paper, we describe the thermal properties of thermosensitive PSAs crosslinked by aluminum chelate, and propose a possible mechanism for their unique activity.

2. EXPERIMENTAL

2.1 Materials

A copolymer consisting of octadecyl acrylate (30 wt%), methyl acrylate (65 wt%) and acrylic acid (5 wt%) was synthesized via radical polymerization, using AIBN as an initiator, in ethyl acetate. The copolymer was used without further purification. The mole fractions of octadecyl acrylate, methyl acrylate and acrylic acid were calculated from elemental analysis to be 0.10, 0.82 and 0.08, respectively. Number- and weight-average molecular weights (M_n and M_w) and polydispersity (M_w/M_n) in THF were 81, 700 kDa and 8.6, respectively. Aluminum(III) acetylacetonate (AlACA) and 2,2-bishydroxymethylbutanol-tris[3-(1-aziridinyl)propionate] (Az) were purchased from Wako and Nippon Shokubai, respectively, and used as crosslinking agents as received. All other chemicals were of reagent grade.

2.2 Preparation of crosslinked PSA film

A given amount of a solution of AlACA in ethyl acetate and the same volume of acetylacetone (used as a retardant) were added to a solution of the copolymer in ethyl acetate. The mixture was shaken for 1 min with a test tube mixer (TAITEC, Se-04), followed by casting onto a polyethylene terephthalate sheet (188 μm thick). The casted mixture was adjusted to a uniform thickness with an applicator and then dried at 80 °C on a hot plate to remove the solvent and excess acetylacetone. The thickness of the adhesive layers after drying was ca. 20 μm . Another PSA film was prepared using the same acrylic copolymer with Az and triethylamine. The films obtained were used for the following measurements.

2.3 Measurements

The gel fraction was calculated from the weight of the insoluble part after soluble

polymers were extracted with hot toluene.

The 180° Peel test was carried out using a Shinto HEIDON 14DR. The crosslinked PSA films with and without preheating treatment were used for the peel test. The preheating treatment was to heat the PSA films at given temperatures, which were higher than the transition temperature of the long alkyl side chain, for 1h in an oven. The crosslinked PSA films with and without the preheating treatment were pasted on a stainless substrate at 40 °C and then heated until measurement temperatures. After 20 min, the PSA films were tested at a peeling rate of 300 mm min⁻¹.

Thermal properties were measured by differential scanning calorimetry (DSC) and thermal mechanical analysis (TMA) using a Shimadze DSC-60, Shimadze TGA-50 and SII SS6000, respectively. The DSC measurement was carried out at a heating rate of 10 °C min⁻¹ in a nitrogen atmosphere unless otherwise noted. The TMA measurements were performed at a heating rate of 5 °C min⁻¹ in air. A quartz probe of 1-mm diameter was used, and the imposed load was 100 mN.

The temperature dependence of the dynamic storage modulus, dynamic loss modulus and loss tangent were measured with a Rheologica Rheopolymer in shear mode. The measurement was performed at a heating rate of 5 °C min⁻¹ under an air atmosphere. The imposed strain, load and frequency were set to be 0.2%, 2.0 N and 1 Hz, respectively.

3 RESULTS AND DISCUSSION

3.1 Design of PSA

The chemical structure of the thermosensitive acrylic PSA we used is shown in Figure 1. The melting point of the long alkyl side group of the PSA can be controlled by adjusting the content of octadecyl acrylate.[16] In this experiment, we used a mole fraction of 0.1 for the octadecyl acrylate, because this sets the melting point of the side group to around room temperature, which is convenient for investigating the thermal properties of the PSA film.

3.2 Gel fraction measurement

The crosslinking efficiency of the crosslinking agents was roughly estimated by gel fraction measurement (Figure 2). The gel fraction increased with an increasing amount of crosslinking agents, and then reached a constant value of 0.87 regardless of the type of crosslinking agent used. Such a high gel fraction at the saturated crosslinking indicates the agents overcrosslinked the PSAs. Besides, an additive amount of 0.18 mol% (0.70 wt%) of Az brought the gel fraction to the constant value, whereas 0.67 mol% (2.0 wt%) of AlACA was required to reach that value. From the additive amounts, the percentages of reacted acrylic acid units were calculated to be 2.3 % for Az and 8.5 % for AlACA, respectively: that is, AlACA required approximately four-fold quantity compared to Az for the overcrosslinking. This result obviously suggests that more efficient crosslinking is achieved with Az than with AlACA. The difference in efficiency is most likely due to the structure of the agents. The reaction point on AlACA is the aluminum atom, which is so small that the crosslinking environment is sterically congested. In contrast, the molecular structure of Az is flexible because of the space between the bifurcation center and the reaction

points.

3.3 Peel test

The temperature dependence of the peel strength of the crosslinked acrylic PSAs with and without preheating treatment in an oven was evaluated by a 180° peel test. The peel test was carried out above 40 °C, since no measurable adhesion occurs below room temperature. This can be attributed to the crystalline aggregate of the long alkyl side group.[12-16] Figure 3 shows plots of the peel strength of the crosslinked PSAs without the preheating treatment as a function of measurement temperatures. As can be seen in Figure 3, the adhesions of the PSAs crosslinked by AIACA and Az decreased with an increase in temperature until 150 °C, which is common for acrylic PSAs. Remarkably, the peel strength of the PSA crosslinked by AIACA increased again from 150 °C. This behavior was scarcely observed in the case of the PSA crosslinked by Az. The adhesion clearly depends on the type of crosslink agent used, since both PSAs consist of the same acrylic copolymer. To explain this behavior, the structure and thermal properties of the PSAs were investigated in detail.

Figure 4 shows plots of the peel strength of the crosslinked PSAs with the preheating treatment as a function of preheating temperatures. The adhesion of the preheated PSA at each measurement temperature was not much different. Even after preheating at 180 °C, the adhesion of the PSA only slightly decreased. This result suggests that the degradation of the PSA at 180 °C is negligible.

3.4 Thermal properties

The thermal properties of the acrylic PSAs were investigated by DSC, and TMA. Figure 5 shows the DSC thermogram of the PSA film crosslinked by 1.0 wt% of

AIACA. Broad endothermic and exothermic peaks, based on melting and crystallization of the long alkyl side group, were observed at 23 and 8 °C respectively. The endothermic peak is also accompanied by a shoulder at around 5 °C, which disappears after rapid cooling of the heated sample (see Supplementary data, Figure S1). Broadening of the peaks and the presence of the shoulder indicate a broad distribution of crystalline aggregates that differ by crystallization rates in the PSA.[16] Melting of the side group contributes to the appearance of adhesion, since the peel strength drastically increases above the melting temperature. The melting temperature was higher than the crystallization temperature, but this hysteresis is not unusual[17]. No other peaks appeared between 40 and 200 °C (see Supplementary data, Figure S2). In our measurements, the transition temperatures did not depend on the amounts of crosslinking agents (see Supplementary data, Figure S3). Interestingly, the enthalpies of melting and crystallization of the PSAs decreased significantly after heating up to 170 °C (Figure 5). To investigate this behavior, we measured DSC thermograms of samples preheated at given temperatures (see Supplementary data, Figure S4).

Figure 6 shows plots of enthalpies of melting and crystallization as a function of the preheating temperatures. Preheating above 60 °C led to a decrease in the enthalpies. The decrease was observed even at slower cooling rates of 5 and 2 °C min⁻¹. Intriguingly, the decreased enthalpies partly returned to their original values after aging at 30 °C overnight (see Supplementary data, Figure S5). The DSC behavior suggests the following mechanism. Below 60 °C, the mobility of the main group is not sufficient, so the side group can easily recover its original crystallinity. In contrast, heating above 60 °C causes increased mobility of the main chain, so that the side group needs aging time to recover its original crystallinity. The heating to the

different temperatures may also progressively melt seeds of crystals and make nucleation of crystallinity slower.

Figure 7 shows the results of TMA measurements. Two softening points were observed around 20 and 60 °C. The softening point around 20 °C comes from melting of the side group, and the one around 60 °C is due to the increase in the mobility of the main chain. This result is in good agreement with the DSC measurements. Additionally, an increase in the content of AIACA led to inhibition of the insertion of the probe, suggesting that the film became harder due to an increase in crosslinking.

The PSA crosslinked by 1.0 wt% of AIACA was compared to one crosslinked by 0.3 wt% of Az. Their crosslink efficiencies were assumed to be almost the same, because their gel fractions showed similar values (Figure 2). In Figure 7, both PSAs exhibited softening points, around 20 °C for the melting of the side group and 60 °C for the increase in mobility of the main chain. Remarkably, a drastic increase in the ease of insertion of the TMA probe was observed for the PSA crosslinked by AIACA at around 160 °C. This effect was not observed for the PSA crosslinked by covalent Az, which exhibited only a gentle increase in the ease of probe insertion at high temperatures, so it can be concluded that this is based on ionic crosslinking. The drastic softening most likely contributes to the increase in peel strength observed in the high-temperature region in Figure 3, for the PSA crosslinked by AIACA.

Viscoelastic properties of the acrylic PSAs crosslinked by AIACA and Az were examined by dynamic viscoelastic analysis. Figure 8 shows the temperature dependence of the storage modulus (G'), loss modulus (G''), loss tangent ($\tan\delta$), and $\tan\delta/G'$ of the PSAs. The values of G' for the PSA films drastically decreased between 10 and 30 °C, while the PSAs exhibited a peak maximum at 15 and 20 °C in the G'' and

tan δ curves, respectively. This is closely associated with the melting of the long alkyl side group. Above 40 °C a rubbery plateau region was observed in the G' curves. Both the G' values in the plateau lay around 10^5 Pa, which is clearly compatible with the well-known Dahlquist's criterion[18, 19], suggesting the appearance of tackiness. The peak, the G'' and tan δ curves also showed a plateau between 60 and 120 °C, followed by a decreasing curves after 120 °C. The plateau region is in good agreement with the region in the DSC measurement where the mobility of the main chain increases (Figure 6). Note that the tan δ curve of the PSA crosslinked by AlACA increased slightly above 160 °C, while that of the PSA crosslinked by Az continued to decrease with an increase in temperature. This temperature is close to the drastic softening temperature shown in Figure 7.

The ratio of tan δ to G' is a good gauge of expected adhesive performance.[20, 21] The tan δ/G' for the PSA crosslinked by Az above 110 °C continually decreased, implying that the adhesion decreases with a increase in temperature after 110 °C. In contrast, the tan δ/G' for the PSA crosslinked by AlACA decreased from 110 to 160 °C and then gradually increased after 160 °C, predicting that the adhesion recovers after 160 °C. In our experiment, however, the values of tan δ/G' for the PSAs crosslinked by Az and AlACA were not able to compare, because their crosslink densities were different.

3.5 Possible mechanisms of drastic softening and recovering peel strength

We considered two mechanisms for the softening of the PSA crosslinked by AlACA: decomposition or ligand exchange of the Al crosslink points. However, decomposition can be excluded from consideration, because influence of the preheating

treatment to the adhesion of the PSAs was negligible (Figure 4). Ligand exchange between the chelated carboxy group and the remaining carboxy group seems likely in the case of ionic chelate crosslinking. According to literature, ligand exchange of aluminum complexes with bidentate ligands such as oxalate[22] and acetylacetonate[23-25], in an organic solvent, takes place very slowly around room temperature and is only activated above 150 °C. Therefore, the softening at 160 °C observed in the TMA measurement could be due to ligand exchange inspired by the activated motion of the main chain (Figure 9). Similar behavior is typical of a polymer crosslinked by hydrogen bonding, whose crosslink is reversible by heating, and has been studied theoretically[26, 27] and experimentally[28-31].

We therefore propose a possible mechanism for the increase in adhesion in the high temperature region as follows: the PSA crosslinked by AlACA behaves as a common crosslinked acrylic PSA below 160 °C, but above 160 °C heat and the sufficient mobility of the main chain could encourage ligand exchange at the Al crosslink points. This ligand exchange could cause an increase in tackiness, which would contribute to the increase in adhesion of the PSA in the high-temperature region.

4. Conclusion

A thermosensitive PSA crosslinked by AIACA displayed unique behavior in that its adhesion increased at around 160 °C in the peel test. We investigated the structure and thermal properties of the PSA, as well as one covalently crosslinked by Az, in order to explain this unusual activity. Gel fraction measurement revealed that the crosslinking efficiency of Az is better than that of AIACA. From the peel test, TGA, DSC, TMA and temperature dependence of the viscoelastic analysis, we found that i) melting and crystallization of the long alkyl side group cause reversible switching of adhesion using heat; ii) the mobility of the main chain is activated between 60 and 120 °C; iii) sufficient motion of the main chain may encourage ligand exchange at the Al crosslink points; iv) the increase in adhesion of thermosensitive PSAs in the high-temperature region could be due to an increase in tackiness caused by ligand exchange.

We expect that our results will improve fundamental knowledge about thermosensitive PSAs and the design of acrylic PSAs with thermal stability in the high-temperature region.

Acknowledgement

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Figure captions

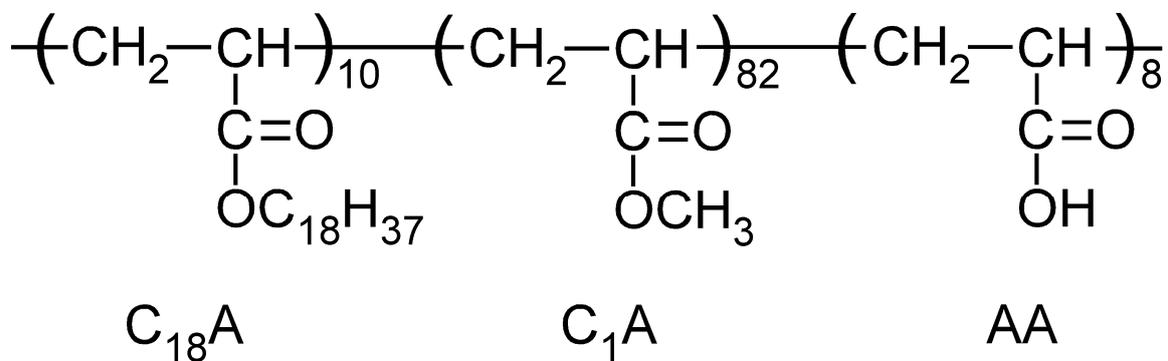


Figure 1. The chemical structure of the thermosensitive acrylic PSA used.

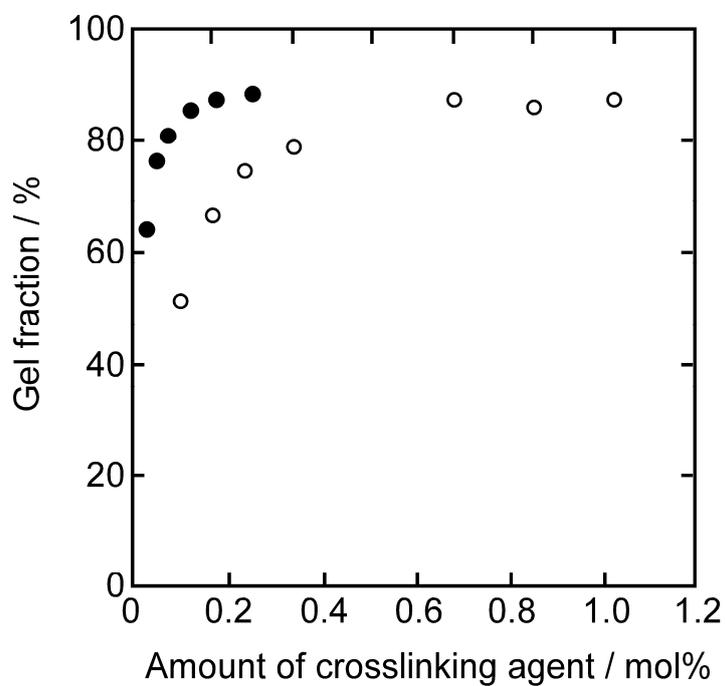


Figure 2. Plots of gel fractions of PSAs as a function of the amount of crosslinking agents: AlACA (○) and Az (●).

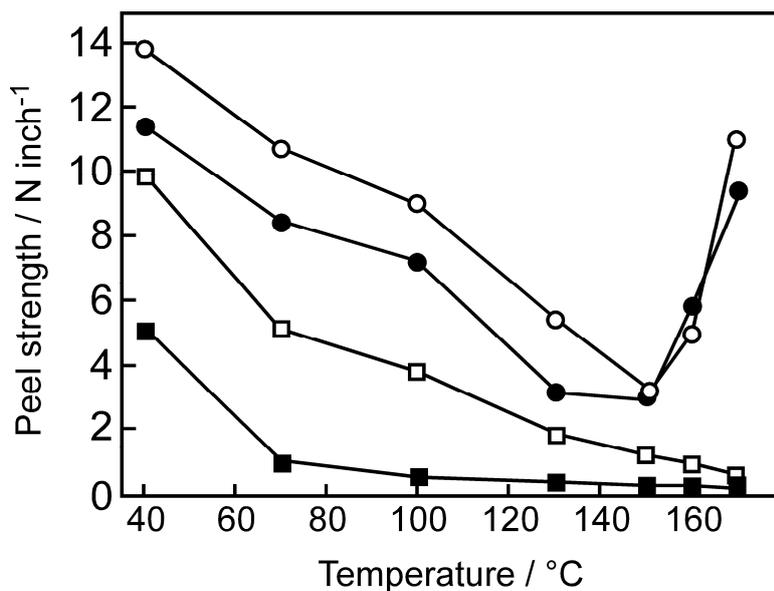


Figure 3. Plots of peel strength of PSAs crosslinked by 0.5 wt% of AlACA (○), 1.0 wt% of AlACA (●), 0.3 wt% of Az (□), and 1.0 wt% of Az (■) without preheating treatment.

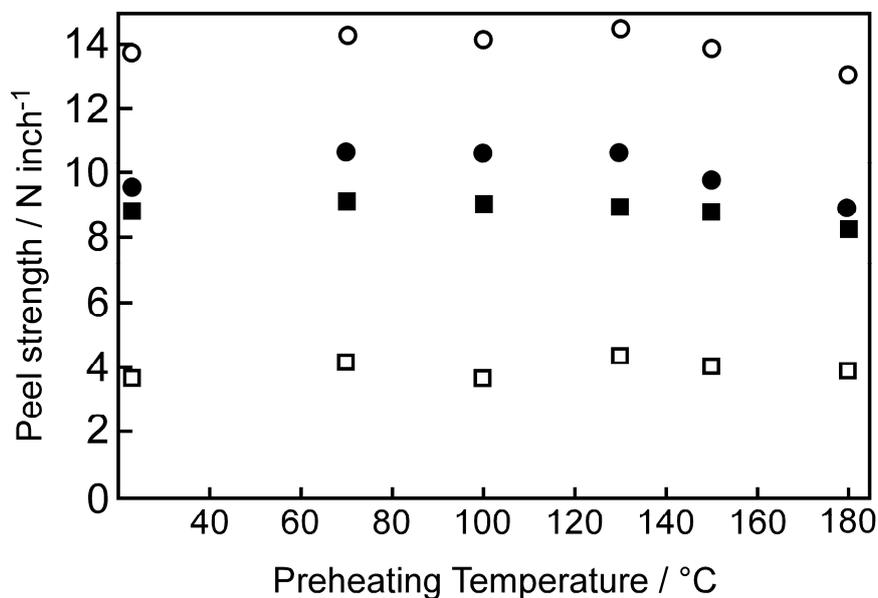


Figure 4. Plots of peel strength of PSAs crosslinked by 1.0 wt% of AlACA at 40 (○), 100 (■), 150 (□), and 180 °C (●) after preheating treatment at given temperatures.

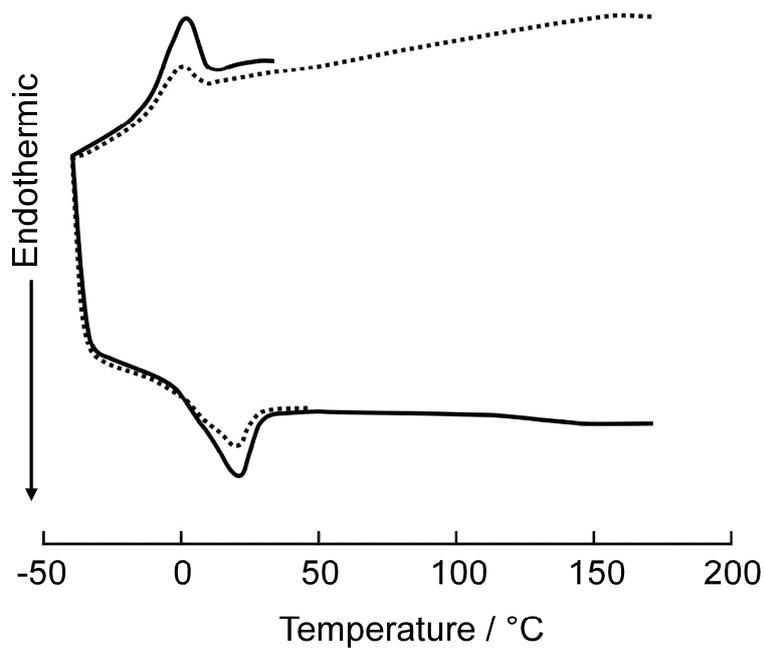


Figure 5. DSC thermograms of PSA crosslinked by 1.0 wt% of AIACA: 1st scan (solid line), 2nd scan (dotted line).

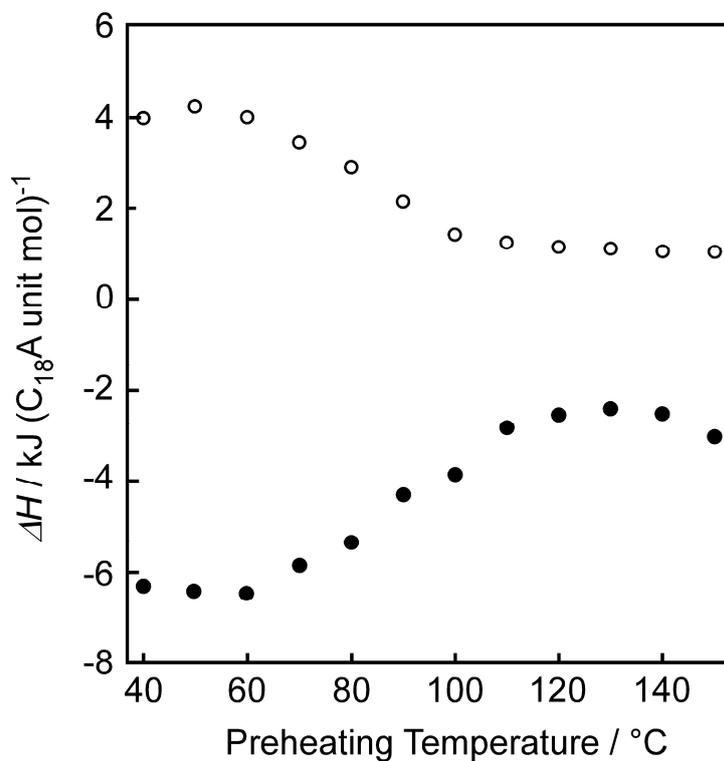


Figure 6. Plots of enthalpies of melting and crystallization of the long alkyl side group of PSA crosslinked by 1.0 wt% of AIACAAs a function of preheating temperature.

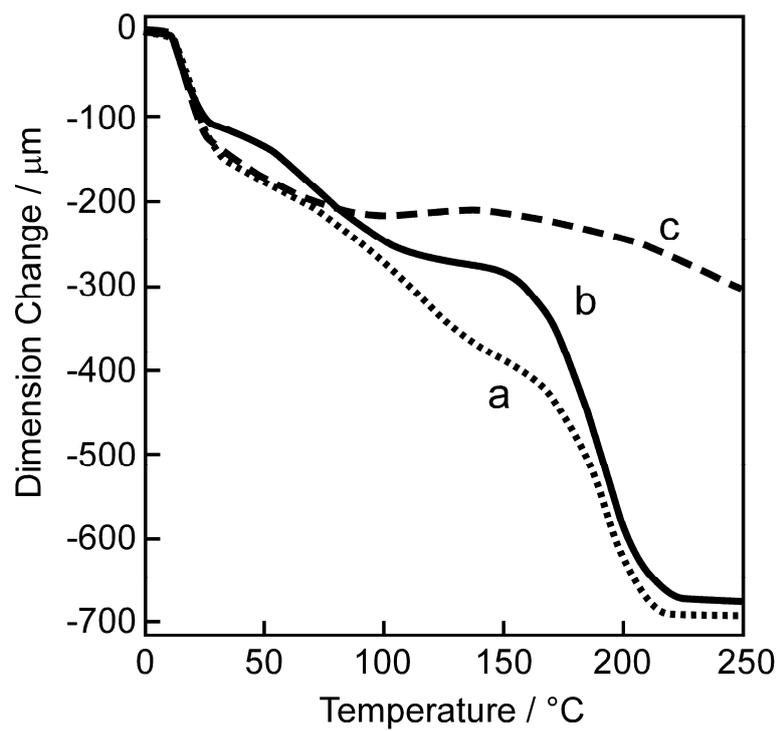


Figure 7. TMA curves of PSA crosslinked by 0.5 (a) and 1.0 wt% of AlACA and 0.3 wt% of Az (c).

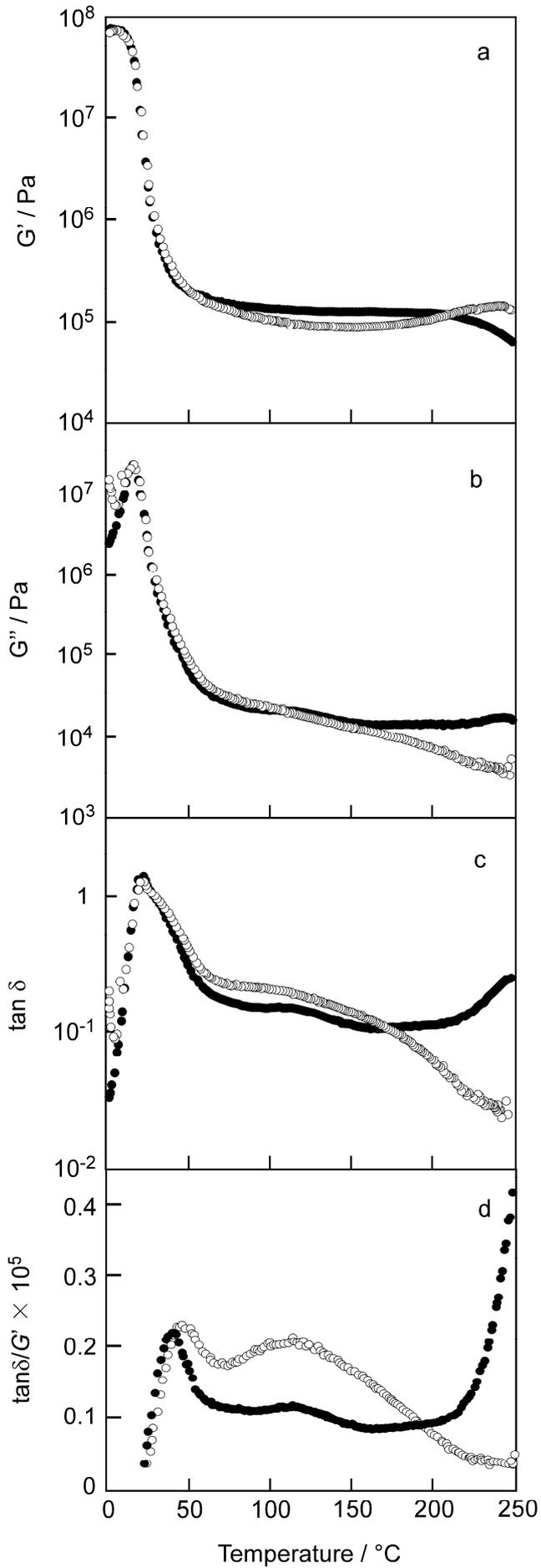


Figure 8. Temperature dependence of storage modulus (a), loss modulus (b), loss tangent (c), and $\tan \delta / G'$ (d) of PSAs crosslinked by 1.0 wt% of A1ACA (●) and 0.3 wt% of Az (○).

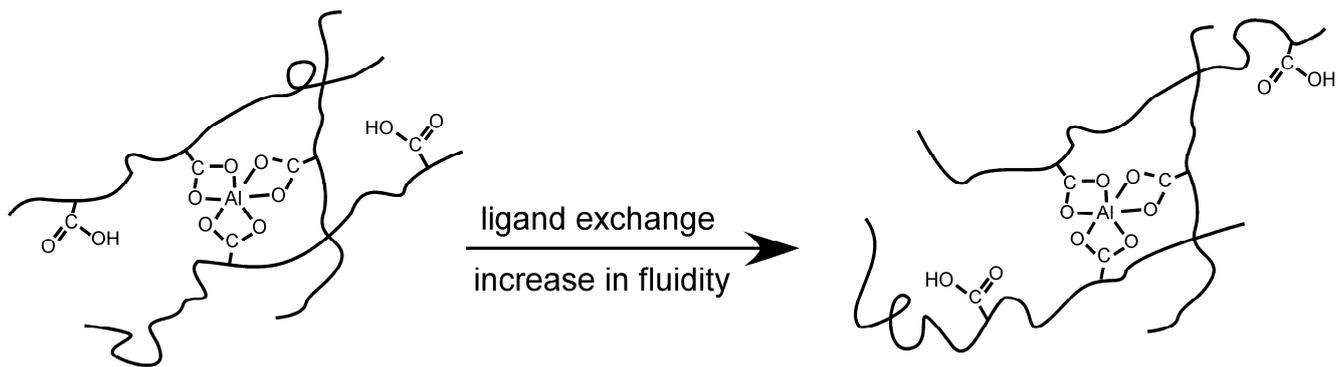


Figure 9. Schematic drawing of possible ligand exchanges between chelated carboxy group and remaining carboxy group.

Unique Thermal Behavior of Acrylic PSAs Bearing Long Alkyl Side Groups and Crosslinked by Aluminum Chelate

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Supplementary Data

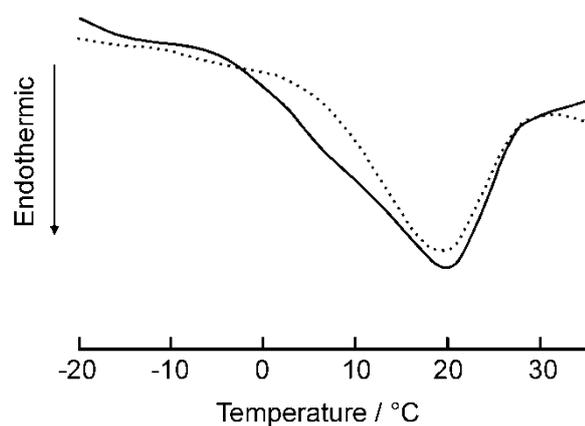


Figure S1. DSC thermograms of PSA crosslinked by 1.0 wt% of Alac: before rapid cooling (solid line) and after rapid cooling (dotted line).

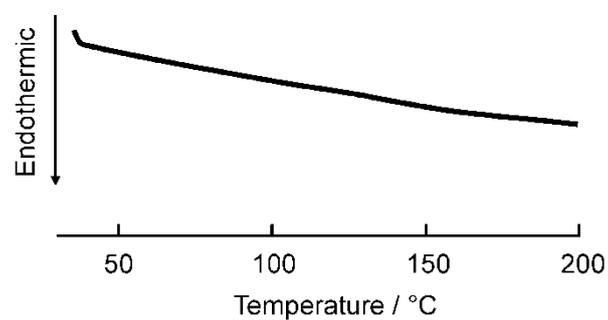


Figure S2. DSC thermogram of PSA crosslinked by 1.0 wt% of Alac.

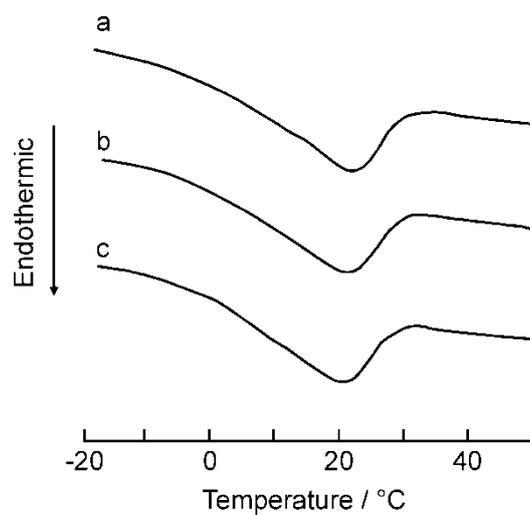


Figure S3. DSC thermograms of PSA crosslinked by 0.5 (a), 1.0 (b), and 2.0 (c) wt% of Alac.

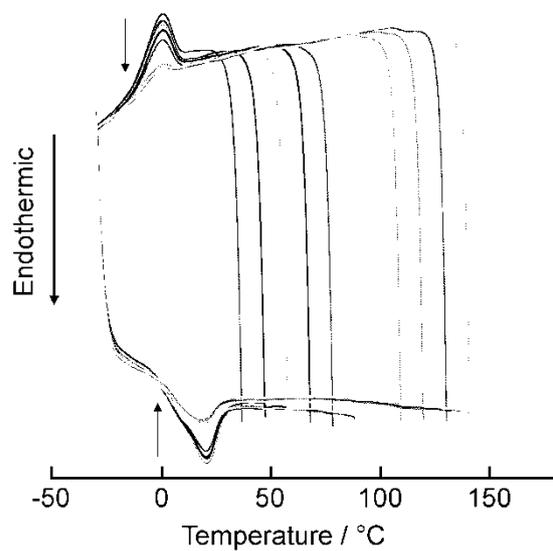


Figure S4. Preheating dependence of DSC thermograms of PSA crosslinked by 1.0 wt% of Alac.

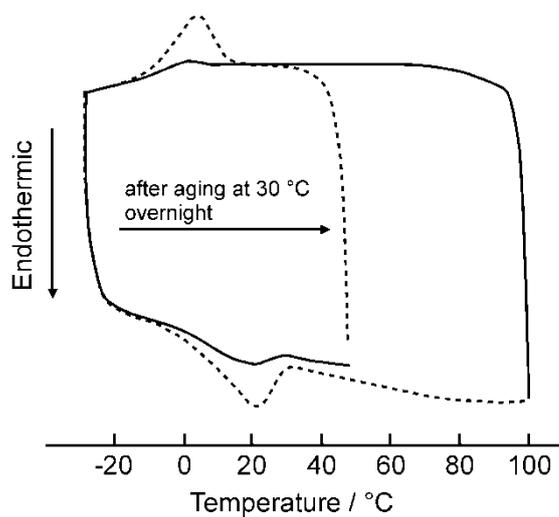


Figure S5. DSC thermograms of PSA crosslinked by 1.0 wt% of Alac after heated at 100 °C (solid line) and the heated sample after aging at 30 °C overnight (dotted line).