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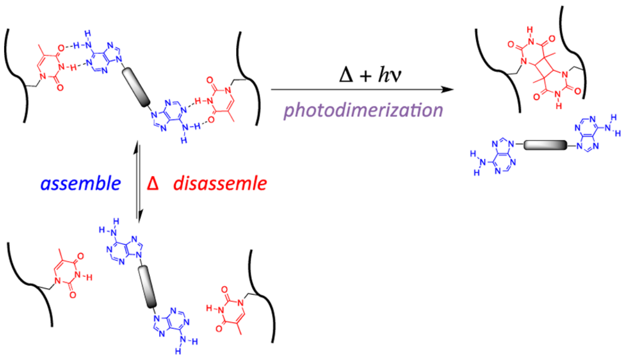
Adhesive Materials Utilizing a Thymine–Adenine Interaction and Thymine Photodimerization

Nobuhiro Ishikawa, Masahiro Furutani, and Koji Arimitsu*

Department of Pure and Applied Chemistry, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510, Japan

Supporting Information



ABSTRACT: A cross-linking reagent having two adenine units was mixed with polymers bearing thymine units to form adhesive materials utilizing both intermolecular hydrogen bonding and in situ formation of covalent bonds. In the case of 58 mol % of adenine units relative to thymine units, formation of intermolecular hydrogen bonds because of a thymine–adenine interaction was observed at room temperature using FT-IR. The peel strength became weak with heating above 60 °C, indicating breakup of intermolecular bonds between thymine and adenine units. On the other hand, UV–vis spectral measurements showed that heating at 80 °C with 254 nm light irradiation facilitated the photodimerization reaction between thymine units even in the presence of adenine cross-linking reagents. This result was consistent with a large value for the peel strength (6.5 N/10 mm) after the dual treatment, heating at 80 °C with 400 mJ/cm^2 of UV irradiation.

Pressure-sensitive adhesives (PSAs) have been used in many fields, such as automobiles, electronics, and medical.[1−5] The macroscopic properties of PSAs are determined by the microscopic molecular behaviors of the polymers in bulk as well as on the interface. Molecular weight and entanglement between polymers are known to be important factors to be considered, particularly the cross-linking state.

Recently, it has been reported that chemical units for noncovalent interactions were incorporated into a soft material to change the properties of the bulk by temporal cross-linking.[6−8] These units were introduced at side chains or termini of main chains to form reversible polymer networks. Copolymers and telechelic polymers having interacting moieties, such as ureidopyrimidinone (Upy)[9−15] and 2,6-bis(1′-methylbenzimidazolyl)pyridine (Mebip),[14,16] were designed. Fiore et al. reported adhesive materials consisting of polymers having Upy or Mebip at their termini and controlled the adhesive properties by UV irradiation.[14] Zimmerman et al. coupled complementary artificial nucleobases with silane coupling reagents and used them for adhesion glass substrates.[17] Long et al. designed polymers having adenine or thymine units and mixed these polymers to examine adhesive properties, although the peel strength was relatively weak.[18]

On the other hand, there is another type of adhesive material that changes its properties by in situ formation of covalent bonds. Kavitha and Singha reported functional polymers that change the peel strength by a progression of Diels–Alder reactions between side chains of the polymers.[19] Nakasuga et al. proposed an adhesive system consisting of an acryl PSA, an epoxy resin, and a UV cationic catalyst where photo-cross-linking reactions between epoxy resins proceeded in the acryl PSA matrix to increase the peel strength.[20] However, to the best of our knowledge, there is no example where adhesive properties are controlled with both temporal noncovalent interactions and covalent bonds formed in situ by external stimuli. Recently, PSAs have been required to use for adhesion of micrometer-sized narrow spaces of fine electronic parts. It is worth acquiring a liquid-like property during heating, which is accomplished by deformation of noncovalent interaction at high temperature. Furthermore, additional UV irradiation forms covalent bonds, leading to ultimate strong adhesion.

Herein, we propose a novel concept for PSAs utilizing both noncovalent and covalent cross-linking. Thymine is well-known to be one of the nucleobases to form multiple intermolecular hydrogen bonds with adenine. It is also known that two thymine units can dimerize under 254 nm light irradiation.[21,22] Covalent bonds derived by the photodimerization reaction are thermally stable, which is difficult to accomplish by using Diels–Alder reactions. Applying the two different interactions in a PSA, two types of stimuli, heat and light, would be used to change the adhesive properties drastically. Copolymer **1** has thymine units at the side chain, and it was mixed with cross-linking reagent **2** having two adenine units (Scheme 1). The resulting mixture is expected to work as a PSA, because a polymer network would be formed by intermolecular hydrogen bonding between **1** and **2** (thymine–adenine interaction, Scheme 1a). The temporal cross-linking would be reversibly

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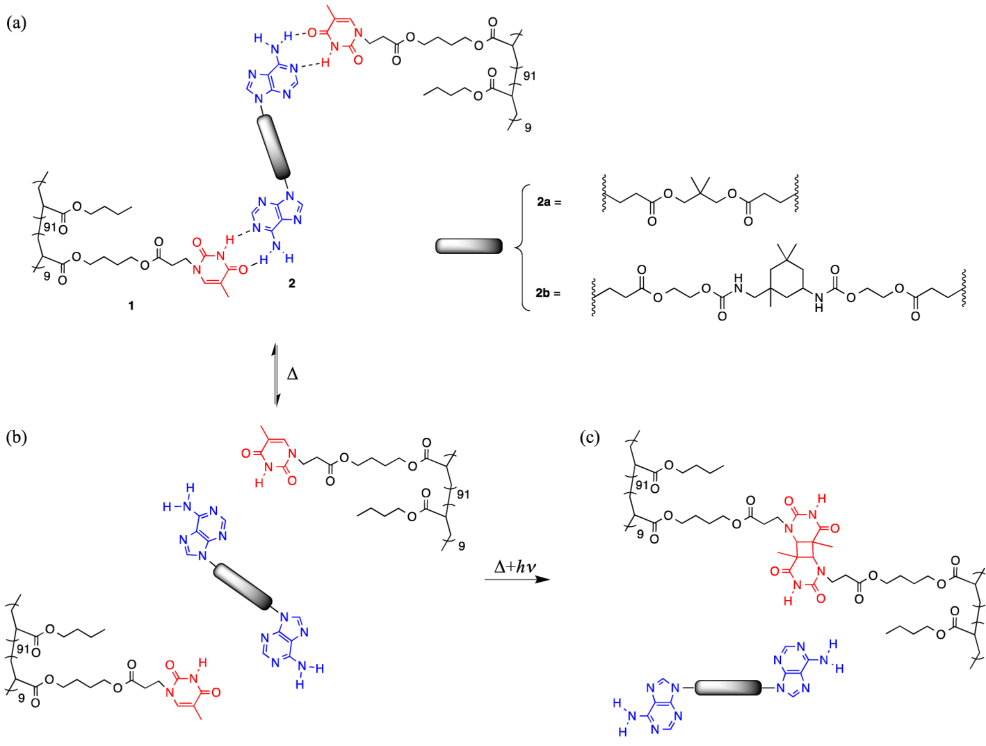
Scheme 1. Covalent and Noncovalent Interaction between Copolymer 1 and Crosslinking Reagent 2 in a PSA Matrix[a]



[a](a) Mixing **1** with **2**, (b) heating the mixture, and (c) heating the mixture with UV irradiation.

broken by heat, leading to a decrease in the cohesive force (Scheme 1b). On the other hand, heat treatment plus UV irradiation on the mixture would facilitate photodimerization reactions between thymine units of copolymer **1**, resulting in the formation of covalent cross-linking points for a strong cohesive force (Scheme 1c).

Copolymer **1** was synthesized using radical polymerization of butyl acrylate (BA) and thymine acrylate (Tac). The ratio of BA/Tac was estimated to be 91/9 using ^{1}H NMR spectroscopy. The molecular weight (M_n) and polydispersity index (M_w/M_n) were 8.0×10^4 and 4.1, respectively. The relative high value of polydispersity index would be because the thymine copolymer **1** synthesized by free radical polymerization has somewhat basicity that results in relative strong interaction with the solid phase of GPC column.[18] Cross-linking reagents **2a** and **2b** were synthesized from adenine and the corresponding bifunctional acryl monomers. While symmetric **2a** showed poor solubility toward general organic solvents, asymmetric **2b**, having an isophorone skeleton, showed good solubility.

To monitor the thymine−adenine interaction, FT-IR measurements were performed with films of **1** containing **2b** (Figure 1). Content rate of the adenine unit of **2b** was 0, 29, or 58 mol % relative to the thymine unit of **1**. In the case of 0 mol % of the adenine unit, a broad shoulder peak was observed around 1700 cm^{-1}, which was assigned to carbonyl groups of free thymine units of **1**. Increasing the number of adenine units, the peak was shifted to the lower wavenumber region. Furthermore, in UV−vis measurements (Figure S1, see Supporting Information), a peak of **1** at 269 nm was blue-shifted after mixing **2b**. These results indicate that thymine units of **1** interact with adenine units of **2b** to form intermolecular hydrogen bonds.[23−25]

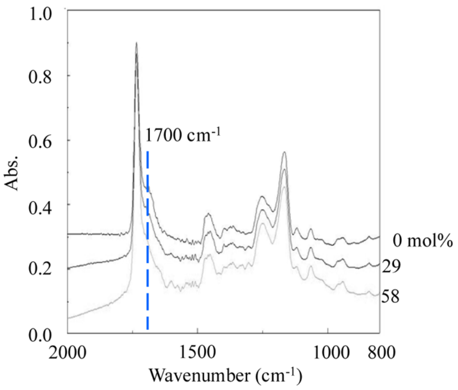


Figure 1. FT-IR spectral changes of films of **1** containing **2b** (0, 29, and 58 mol % of adenine units relative to thymine units of **1**).

The peel strengths of mixtures of **1** and **2b** became stronger with increasing amount of **2b** at room temperature (Figure 2). This is probably because the thymine−adenine intermolecular interaction between **1** and **2b** is stronger than the noncovalent interactions between thymine units of **1**.[26] The effect of temperature on the peel strength was examined at various temperatures (40, 60, and 80 °C). The as-prepared adhesive sheets were placed at each temperature for 3 min, followed by the peel strength test. Although the peel strengths became weak at higher temperatures, the decreasing rates were somewhat suppressed in the presence of **2b**. As an exception, the highest value was recorded at 40 °C in the case of 0 mol % of adenine units, however, cohesive failure was observed. Peel strength of PSAs is influenced by temperature. There is a small transition temperature region where peeling mode is changed from adhesive failure to cohesive failure. Around this temperature region, PSAs begin to show high peel strength according to increasing temperature.[27] Copolymer **1** would have its transition temperature region around 40 °C, resulting in the

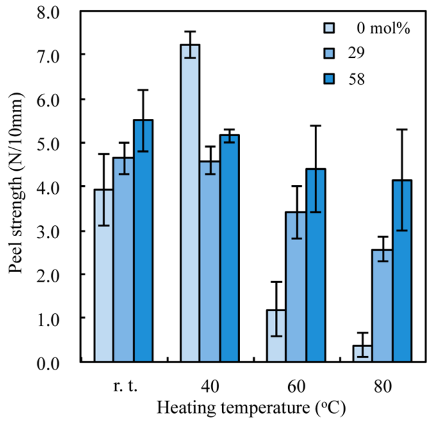


Figure 2. Peel strength of adhesive films of **1** at room temperature, 40, 60, and 80 °C. Adenine units of **2b** were 0, 29, and 58 mol % relative to thymine units of **1**. The peel angle and peel speed were 180° and 300 mm/min, respectively.

high peel strength. At 60 and 80 °C, on the other hand, deformation of molecular interaction would be caused to decrease the peel strength.

The photodimerization reaction of **1** was investigated with 254 nm light irradiation in the presence of **2b**, 58 mol % of adenine units relative to the thymine units. A sample film was kept at 80 °C during the UV irradiation. The peak intensity at 260 nm that is assigned to free thymine units was monitored using UV−vis spectral measurements and FT-IR spectral measurements. As shown in Figure 3, the peak intensity decreased upon increasing the total irradiation energy, which indicates that the photodimerization reaction proceeded as expected. A similar spectral change was observed on a film of **1** without **2b** (Figure S2), and the diminution rate was much larger than in the presence of **2b**. These would probably be because the noncovalent interaction between thymine and adenine units disturbed the photodimerization reaction even at 80 °C.[28,29] FT-IR spectral measurements under the same conditions also support the photodimerization of thymine units of **1** even in the presence of **2b** (Figures S3 and S4).

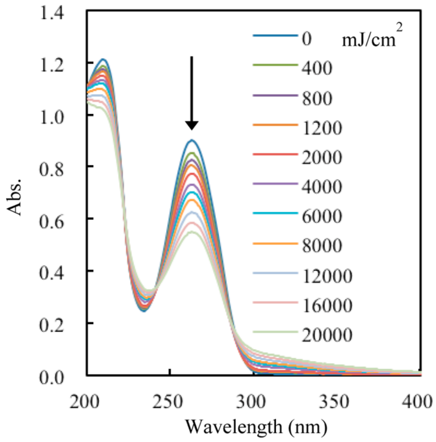


Figure 3. UV−vis spectral changes of a film of **1** containing **2b** (58 mol % of adenine units relative to thymine units of **1**) during 254 nm light irradiation. The film was heated at 80 °C under measurement.

To examine the effect of cross-link formation by the photodimerization reaction on the macroscopic properties of the PSAs, we carried out another peel strength test on films of **1** containing **2b**. UV irradiation was performed on the sample films with the temperature maintained at 80 °C, followed by the mechanical test at room temperature. As shown in Figure 4, the peel strength increased according to the amount of **2b**. The maximum value of 6.5 N/10 mm was obtained in the case of 58 mol % of adenine units with 400 mJ/cm^2 of irradiation energy, and an adherent failure was observed. The photodimerization reaction would contribute to the formation of cross-linking bonds, resulting in enhancement of the cohesive property. However, with more than 600 mJ/cm^2 of irradiation energy, the strengths were decreased. One reason could be that too many cross-linking points were generated in the matrix of **1**, leading to a reduced interfacial coherence.[30] In the cases of 0 and 29 mol % of adenine units, the peel strengths were not changed so much with the amount of irradiation energy.

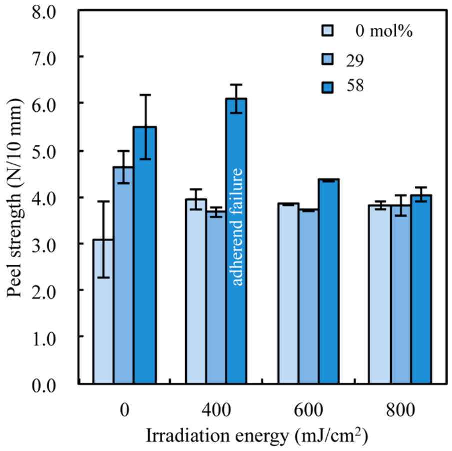


Figure 4. Peel strength of adhesive films of **1** containing **2b** (0, 29, and 58 mol % of adenine units relative to thymine units of **1**) at room temperature. Before measurement, 254 nm light irradiation was performed at 80 °C. The peel angle and peel speed were 180° and 300 mm/min, respectively.

In summary, we prepared a novel adhesive material utilizing not only temporary bonding between thymine and adenine units, but also irreversible bonding by the photodimerization reaction between thymine units. This material, consisting of copolymer **1** and cross-linking reagent **2b**, showed an adhesive property like PSAs at room temperature, although this decreased at higher temperatures. On the other hand, the peel strength was increased even at 80 °C by simultaneous UV irradiation. This study would be expected to supply a new concept for intelligent adhesive reagents applied for a variety of industrial processes.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Preparation of copolymer, cross-linking reagent, and experimental methods. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.5b00359.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: arimitsu@rs.noda.tus.ac.jp.

Notes

The authors declare no competing financial interest.

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