Photoadhesive Materials Containing 2-Mercaptopyridyl Moieties

Masahiro Furutani, Daiki Fujihira, and Koji Arimitsu*

Department of Pure and Applied Chemistry, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510, Japan
*arimitsu@rs.tus.ac.jp

2-Mercaptopyridine and its analogues cause a tautomerization reaction between their thiol and thione isomers. The equilibrium state would be changed by the surrounding environment such as polarity. In this study, we have designed and synthesized a vinyl monomer having a 2-mercaptoppyridyl moiety, and prepared a photoadhesive material including the monomer, 2-hydroxyethyl methacrylate, and a photoradical initiator. Photoadhesion between various kinds of adherents was realized using this material with 6.0 J cm⁻² of UV irradiation at a wavelength of 365 nm, recording up to 8.8 MPa of shear strength. The effects and chemical states of 2-mercaptoppyridyl moieties were examined by control and/or XPS spectral measurements. Interestingly, the adhesive strength increased gradually, indicating an autoxidation reaction between two 2-mercaptoppyridyl moieties to form a disulfide bond and cross-linked polymer networks.

Keywords: Photoadhesive material, 2-Mercaptoppyridyl moiety, Tautomerization reaction, Thiol, Thione, Disulfide bond

1. Introduction

Photoadhesion is one of the key technologies for chemical industry [1]. The adhesive process is controlled by light irradiation, which results in quick and locational adhesion under relatively mild conditions. The adhesive mechanism would consist of physical and chemical interactions, which is complicated and still unknown. Anchor effect at irregular interface between adhesive layer and substrate is a description as physical adhesion. On the other hand, chemical adhesive interaction includes covalent bonding, electrostatic interaction, coordination, hydrogen bonding, π-π stacking and so on. Combining these adhesive interactions would realize strong and robust adhesion toward various kinds of substrates, dissimilar materials.

As an attractive chemical structure that enables to adhere dissimilar materials, catechol and its analogues are studied vigorously [2,3]. Wilker et al. copolymerized styrene with 3,4-dimethoxystyrene, and the resulting polymer (33% of catechol groups per unit, \(M_w = 84,200\)) realized 0.7-6 MPa of shear strength on various kinds of adhesive samples (aluminum, steel, polytetrafluoroethylene, poly(vinyl chloride), and red oak) [4]. Naito et al. synthesized methacrylate copolymers bearing with catechol groups, and a mixture of the copolymers showed 2.2-5.2 MPa of shear strength on dissimilar adhesive samples between aluminum, copper, stainless steel, glass, polyethylene, polypropylene, and polyamide [5]. Furthermore, they tried to realize stronger shear strength by formation of covalent bonds between

![](image1.png)

Scheme 1. Tautomerization and redox reactions of 2-mercaptoppyridine.
two catechol groups in the adhesive layer, although use of a strong chemical oxidant or additional heating was required.

On the other hand, our group has featured 2-mercaptopyridine derivatives for photoadhesion of dissimilar materials [6,7]. 2-Mercaptopyridyl (2MP) group has a pyridine-nitrogen atom and a thiol group in the chemical structure, instead of two phenolic hydroxy groups of catechol (Scheme 1). It is expected that these nitrogen and sulfur atoms would interact with substrates of transition metals such as copper [8-10]. 2MP group makes chemical interactions mentioned above, as catechol group does. Furthermore, 2MP group causes a tautomerization reaction between its thiol and thione isomers [11-16]. It is known that the equilibrium state is changed by the surrounding micro-environment of 2MP groups such as polarity, and that the thiol isomer would be subjected to autoxidation with aerial oxygen.

In this article, we have proposed a novel photoadhesive material containing 2MP moieties for adhesion of dissimilar materials. As shown in Scheme 2, vinyl monomer 1 having a 2MP group is copolymerized with 2-hydroxyethyl methacrylate (HEMA) in radical UV curing systems between two adherends, glass and copper, for example. We expected that the 2MP groups would take an appropriate structure according as their micro-environment for generation of the best adhesive strength, at the interface of each adherend and in the adhesive layer. Pang and Gao reported a furan-based elastic thermoset where keto-enol tautomerization reactions were caused with water, to form hydrogen bonds in the polymer bulk [17]. Molinuevo and Cortizo also designed β-ketonitrile tautomeric copolymers and utilized for osteoblastic cell proliferation in the field of bone tissue engineering [18]. However, adhesive materials utilizing tautomerization reactions have not been reported as far as we know.

2. Experimental

2-Mercaptonicotinic acid, 4-vinylbenzylamine, 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (WSCl HCl), 4-dimethylaminopyridine (DMAP), nicotinic acid, benzoic acid, 2-hydroxyethyl methacrylate (HEMA), nitric acid, and 2,2-dimethoxy-2-phenylacetophenone (Omnirad 651, former Irgacure 651) were purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). 1-Hydroxycyclohexyl phenyl ketone (Omnirad 184, former Irgacure 184) was purchased from Sigma-Aldrich Japan K. K. (Tokyo, Japan). Tetrahydrofuran (THF), dichloromethane, chloroform, and methanol were purchased from FUJIFILM Wako Pure Chemical Corporation (Osaka, Japan). All reagents were used without further purification.

CaF$_2$ substrate was purchased from Pier Optics Co., Ltd. (Gunma, Japan). Copper (Cu) and aluminium (Al) substrate (oxidized, 0.3 mm in thickness) were purchased from SANSYO Co., Ltd. (Tokyo, Japan). Treated Cu substrate was prepared with nitric acid to obtain non-oxidized Cu surface [19]. Glass substrate (1 mm in thickness) was purchased from Matsunami Glass Ind., Ltd. (Osaka, Japan).

$^1$H-NMR and $^{13}$C-NMR spectra were recorded using a JEOL JNM-AL300. ESI-MS measurements were performed using a JEOL JMS-T100CS. FT-IR spectral measurements were performed using a JASCO FT/IR-6600. ATR attachment (ATR PRO ONE with a germanium prism, PKS-G1, JASCO Corporation) was used as necessary. Photoadhesion experiments were performed with an LED lamp, LPUV365/2501-00 (IWASAKI Electric Co., Ltd.). UV-Vis spectra were obtained using a Cary8454 (Agilent Technologies Japan, Ltd.). Shear stress was recorded using MCT-1150 (A&D, Co., Ltd., tensile rate: 10 mm/min). XPS spectral measurement was performed using an AXIS-NOVA (Kratos Analytical Ltd.), employing Al Kα X-rays as the exciting source. The binding energies were referenced to the C 1s binding energy, set at 284.8 eV.

Synthesis of 1. To a dried flask were added 2-
mercaptopnicotinic acid (0.50 g, 3.2 mmol), WSCI HCl (0.74 g, 4.0 mmol), THF (30 mL) and dichloromethane (40 mL) under nitrogen atmosphere, which was stirred at room temperature for 1 h. To the solution were added 4-vinylbenzylamine (0.64 g, 4.8 mmol) and DMAP (0.47 g, 4.0 mmol), followed by stirring overnight at 0°C. After filtration, the filtrate was purified by column chromatography (chloroform : methanol = 40 : 1, v/v) to obtain 1 in 15% yield as a yellow solid (0.13 g). 1H-NMR (300 MHz, CDCl3): δ 4.71 (d, 2H, J = 7.2 Hz), 5.23 (dd, 1H, J = 0.80, 15 Hz), 5.73 (dd, 1H, J = 0.80, 24 Hz), 6.70 (dd, 1H, J = 15, 24 Hz), 6.94 (m, 1H, Py-H), 7.38 (m, 4H, Ar-H), 7.60 (m, 1H, Py-H), 8.87 (m, 1H, Py-H), 11.1 (t, 1H, J = 7.2 Hz), -C(=O)-NH-), 12.3 (br, 0.6H), -NH-C(=S)-). 13C-NMR (75 MHz, CDCl3): δ 42, 113, 113, 126, 128, 133, 136, 138, 141, 142, 164, 174. ATR-FT-IR (powder, cm−1): 1130, 1240, 164, 174. 1H-NMR (300 MHz, CDCl3): δ 4.50 (d, 2H, J = 8.0 Hz), -CH2-), 5.23 (dd, 1H, J = 0.80, 15 Hz, -CH2), 5.80 (dd, 1H, J = 0.80, 24 Hz, -CH2), 6.72 (dd, 1H, J = 15, 24 Hz, -CH2), 7.31 (d, J = 11 Hz, 2H, Ar-H), 7.44 (d, J = 11 Hz, 2H, Ar-H), 7.52 (m, 1H, Py-H), 8.24 (m, 1H, Py-H), 8.72 (m, 1H, Py-H), 9.06 (m, 1H, Py-H), 9.25 (t, 1H, J = 8.0 Hz, -C(=O)-NH-). HR-ESI-MS [M+Na]+: m/z calcd. for C15H14N2O1Na1: 293.07245; found: 293.07159.

Synthesis of 2. To a dried flask were added benzoic acid (0.41 g, 3.4 mmol), WSCI HCl (0.69 g, 4.0 mmol), DMAP (0.47 g, 4.0 mmol), followed by stirring overnight at 0°C. After filtration, the filtrate was purified by column chromatography (chloroform : methanol = 20 : 1, v/v) to obtain 2 in 53% yield as a pale yellow solid (0.38 g). 1H-NMR (300 MHz, CDCl3): δ 4.50 (d, 2H, J = 8.0 Hz, -CH2-), 5.23 (dd, 1H, J = 0.80, 15 Hz, -CH2), 5.80 (dd, 1H, J = 0.80, 24 Hz, -CH2), 6.72 (dd, 1H, J = 15, 24 Hz, -CH2), 7.31 (d, J = 11 Hz, 2H, Ar-H), 7.44 (d, J = 11 Hz, 2H, Ar-H), 7.52 (m, 1H, Py-H), 8.24 (m, 1H, Py-H), 8.72 (m, 1H, Py-H), 9.06 (m, 1H, Py-H), 9.25 (t, 1H, J = 8.0 Hz, -C(=O)-NH-). HR-ESI-MS [M+Na]+: m/z calcd. for C15H14N2O1Na1: 261.10038; found: 261.10070.

Consumption of functional groups before and after radical copolymerization. Vinyl monomer 1 (1.3 mol%) was added to HEMA. Ominrad 651 (10 wt%) was then added to the mixture, followed by agitation for homogenization. The mixture was spin-coated (1000 rpm, 20 s) on a CaF2 substrate, sandwiched with another CaF2 substrate. FT-IR spectral measurements were performed before/after UV irradiation at a wavelength of 365 nm (50 mW cm−2, 6.0 J cm−2). In another experiment, vinyl monomer 1 (50 mol%) was added to HEMA. Ominrad 184 (10 wt%) and the minimum amount of THF were then added to the mixture, followed by agitation for homogenization. The mixture was dropped on a CaF2 substrate, sandwiched with another CaF2 substrate. UV-Vis spectral measurements were performed before/after UV irradiation at a wavelength of 365 nm (50 mW cm−2, 6.0 J cm−2).

Photoadhesion of dissimilar materials. Vinyl monomer 1 or 2 (0 or 1.3 mol%) was added to HEMA. Irgacure 651 (10 wt%) was then added to the mixture, followed by agitation for homogenization. Each mixture was dropped on a substrate (glass, Cu, treated Cu, or Al), sandwiched with another glass substrate. The adhesive area was 30 mm2. UV irradiation at a wavelength of 365 nm (50 mW cm−2, 6.0 J cm−2) was performed toward over the glass substrate. Resulting photoadhesive samples were subjected to shear stress measurement (tensile speed: 10 mm min−1). The measurement was repeated three times for each adhesive sample.

Amount of 1 toward HEMA. Vinyl monomer 1 (0-5.0 mol%) was added to HEMA. Irgacure 651 (10 wt%) was then added to the mixture, followed by agitation for homogenization. THF was used when the mixture was not homogenized without solvent. Each mixture was dropped on a substrate (glass or Cu), sandwiched with another glass substrate. The adhesive area was 30 mm2. UV irradiation at a wavelength of 365 nm (50 mW cm−2, 6.0 J cm−2) was performed toward over the glass substrate. Resulting photoadhesive samples were subjected to shear stress measurement (tensile speed: 10 mm min−1). The measurement was repeated three times.

Autoxidation of 2-mercaptopyridyl groups in the adhesive layer. Vinyl monomer 1 (1.3 mol%) was added to HEMA. Irgacure 651 (10 wt%) was then added to the mixture, followed by agitation for homogenization. The mixture was dropped on a glass substrate, sandwiched with another glass substrate. The adhesive area was 15 mm2. UV irradiation at a wavelength of 365 nm (50 mW cm−2, 6.0 J cm−2) was performed toward over the glass substrate. Resulting photoadhesive samples were allowed to stand for 0-4 weeks, and then subjected to shear stress measurement (tensile speed: 10 mm min−1). The measurement was repeated four times.

Chemical states of 2-mercaptopyridyl groups in the adhesive layer. To HEMA were added vinyl monomer 1 (1.3 mol%) and Irgacure 651 (10 wt%), followed by agitation for homogenization. The mixture was dropped on a treated Cu substrate, sandwiched with another glass substrate. The adhesive area was 30 mm2. UV irradiation at a wavelength of 365 nm (50 mW cm−2, 6.0 J cm−2) was...
performed toward over the glass substrate. Resulting photoadhesive samples were subjected to shear stress, to obtain two fractured photoadhesive samples on the glass and treated Cu substrates. Then, the chemical state on nitrogen and sulfur atoms in each sample was examined by XPS spectral measurements.

3. Results and discussion

3.1. Consumption of functional groups before and after radical copolymerization

Before and after UV irradiation, polymerizable functional groups (vinyl and methacryl groups) were monitored by FT-IR spectral measurements (Fig. 1). Peaks assigned to these functional groups were observed around 1640-1650 cm\(^{-1}\), and these peaks disappeared mostly after 6.0 J cm\(^{-2}\) of UV irradiation. On the other hand, as shown in Fig. 2, a broad peak was observed at 387 nm in UV-Vis spectral measurements. The peak intensity was not changed, even after the same UV irradiation. Photoadhesion of two CaF\(_2\) substrates was confirmed. This peak would be assigned to absorption of the thione-structure of 2MP moieties \(\text{n-}\pi^*\) electronic transition [14,16]. These spectral results indicate that vinyl monomer 1 copolymerized with HEMA through a photoradical polymerization reaction, and that 2MP moieties were introduced into the polymer side chains without undesirable reactions.

3.2. Photoadhesion of dissimilar materials

Using a mixture consisting of HEMA, 1 and Omnirad 651, photoadhesion of glass, Cu, treated Cu or Al substrates with another glass substrate was examined. The results are shown in Fig. 3. Up to 6.04 MPa of shear strength was recorded on the glass-glass adhesive samples, which was better than other samples using metal substrates. This would be due to strong interaction between hydroxy groups of both the adhesive layer (from HEMA) and the surface of glass substrate. Cohesive failure was observed on the all glass-glass samples. Comparing among glass-metal adhesive samples, glass-Cu (or treated Cu) samples recorded better shear strength than glass-Al ones. This indicates that 2MP moieties from 1 would contribute to the adhesion force through thiol-transition metal interaction [10,16,20,21], even though interfacial fracture was observed on the Cu side.

Comparing samples of HEMA+1 with HEMA+2, HEMA+1 samples were superior (or comparable) to HEMA+2 samples. Slight difference was observed in the glass-glass samples, which implies that the 2MP moieties from 1 would interact with hydrophilic glass surface in their polar form, thione-structure. On the other hand, effect of thiol groups in their thiol-structure on adhesive strength would be observed clearly in the results on glass-Cu (or treated Cu) samples. The results without vinyl monomers (HEMA only) would indicate indirectly the copolymerization of 1 (or 2) with HEMA. Each vinyl monomer is integrated into polymer chains, and the side chains would contribute to interaction between polymers, or a polymer chain and substrate surface.
It is found that 1-2 mol% of 1 toward HEMA was the optimal amount, for both glass-glass and glass-treated Cu adhesive samples (Fig. 4). Comparing results between glass-glass and glass-treated Cu samples, 2MP moieties seem to interact stronger with Cu substrate than with glass substrate.

3.3. Autoxidation of 2MP groups in the adhesive layer

Interestingly, in the case of adhesive samples fabricated with vinyl monomer 1, the adhesive strength increase gradually, as shown in Fig. 5. It is known that thione and thiol isomers of 2-mercaptopyridines are in equilibrium, and the thiol isomer would be oxidized to the corresponding disulfide compound (PySSPy) under a mild condition [22]. In our case, the 2MP moieties would be also oxidized for several weeks by dissolved oxygen in the adhesive layer, forming a cross-linked polymer network where PySSPy bonds work as cross-linking points. After three weeks later, 8.80 MPa of shear strength was recorded that is the maximum strength in this study.

3.4. Chemical states of 2MP groups in the adhesive layer

XPS spectral measurements were performed on a fractured glass-treated Cu photoadhesive sample of HEMA+1, to investigate chemical states of 2MP groups in the adhesive layer and at the interface of each substrate. Again, interfacial fracture on the Cu side was observed. Nevertheless, nitrogen and sulfur atoms were detected from both substrates. Rate of atomic concentration of these elements toward carbon on the treated Cu side was ca. 10 times larger than on the glass side. This indicates a strong interaction of 2MP groups toward treated Cu substrate rather than glass substrate.

Figure 6 shows the spectra in the N1s region. Peaks are classified into three kinds of binding energies, around 399, 400, and 402 eV. At first, the peak around 399 eV (399.5 eV in Fig. 6(a)) would correspond to the pyridine-nitrogen atom in PySSPy bonds [7,23]. The second peak around 400 eV (400.5 and 399.7 eV) could be assigned to
thioamide-nitrogen atoms of the thione-structure of 2MP groups, compared with binding energy for amide-nitrogen atoms [24]. The last peak around 402 eV (401.6 eV in Fig. 6(b)) would be for electron-deficient pyridine-nitrogen atoms due to neighbor electron-withdrawing groups, or coordination toward metals.

On the other hand, the corresponding spectra in the S2p region are shown in Fig. 7. Values of binding energy for S2p3/2 are shown in Fig. 7. Peaks at 163.3 and 161.9 eV in Fig. 7(a) (for the glass side) would be assigned to the sulfur atoms in PySSPy bonds and in thiocarbonyl groups of thione-structure of 2MP groups, respectively [7,25]. For the treated Cu side, a peak at 161.6 eV in Fig. 7(b) would be also assigned to the thiocarbonyl-sulfur atoms (nearly 162 eV). The last peak at 157.3 eV in the same Figure would be for electron-rich sulfur atoms, or thiolate-sulfur atoms of thiol-structure of 2MP groups, probably generated through thiol-Cu interaction.

Results in Figs. 6 and 7 imply the existence of thione-structure of 2MP groups and PySSPy bonds on the glass side. In the adhesive layer, 2MP groups take thione-structure, which is consistent with the result of UV-Vis spectral measurements in Fig. 2. PySSPy bonds were formed probably due to autoxidation in air. For the treated Cu side, 2MP groups take both thione- and thiol-structures, and both of them would interact with Cu surface.

From the experimental results in this section and Section 3.3, 2MP groups seem to change their chemical state with their micro-environment, as shown in Fig. 8. At a hydrophilic interface (e.g. glass side), 2MP groups form thione-structure, because they would be surrounded with hydroxy groups. In the middle of adhesive layer, 2MP groups would choose thione-structure at first, due to surrounding hydroxy groups from HEMA. However, they transform gradually to PySSPy
through thione-to-thiol tautomerization and subsequent autoxidation reactions. Lastly, at a relatively-hydrophobic metallic interface (e.g. Cu side), they exist as thiol-structure as thiolate, to generate thiol-metal interaction.

4. Conclusion

In conclusion, we have proposed a novel photoadhesive material including 2-mercaptopyridyl (2MP) groups that cause tautomerization and autoxidation reactions according as their surrounding micro-environment. Photoadhesion of dissimilar materials is accomplished by using a radical UV curing system, with 0.7-6 MPa of shear strength. The adhesive strength could be increased through formation of PySSPy cross-linking bonds under a mild condition. In our group, use of this material as both dismantlable and reusable (rebonding) adhesive is undergoing, by utilizing chemical properties of disulfide bonds, i.e. bond-exchange reactions [6,26].

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