Amino acid-incorporated polymer network by thiol-ene polymerization

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Abstract. Triallyl L-alanine (A3A) and triallyl L-phenylalanine (A3F) were synthesized by reactions of L-alanine and L-phenylalanine with allyl bromide in the presence of sodium hydroxide, respectively. Thiol-ene thermal polymerization of A3A or A3F with pentaerythritol-based primary tetrathiol (pS4P) or pentaerythritol-based secondary tetrathiol (S4P) at allyl/SH 1/1 in the presence of 2,2'-azobis(isobutyronitrile) produced an amino acid-incorporated polymer network (A3A-pS4P, A3A-S4P or A3F-S4P). Although the thermally cured resins were homogeneous and flat films, the corresponding thiol-ene photopolymerization did not give a successful result. Degree of swelling for each thermally cured film in *N,N*-dimethylformamide was much higher than that in water. The glass transition and 5% weight loss temperatures (T_g and T_5) of A3F-pS4P and A3F-S4P were higher than those of A3A-pS4P and A3A-S4P, respectively. Also, A3F-pS4P and A3F-S4P exhibited much higher tensile strengths and moduli than A3A-pS4P and A3A-S4P did, respectively. Consequently, A3F-pS4P displayed the highest T_g (38.7°C), T_5 (282.0°C), tensile strength (9.5 MPa) and modulus (406 MPa) among all the thermally cured resins.

Keywords: thermosetting resins, biopolymers, alanine, phenylalanine, thiol-ene polymerization

t1. Introduction

Naturally occurring α -amino acid based polymers have gathered considerable attention over recent years as biodegradable, biocompatible and functional materials having various characteristics such as amphoteric nature [1, 2], chiral recognition [3], drug delivery [4, 5], response to stimuli [6–12] and self-organization via supramolecular interactions [13–15]. In past studies, amino acid-based side chain polymers had been mainly synthesized by conventional or controlled free radical polymerizations of amino acids whose *N*- or *C*-terminals are modified with (meth)acrylamide [1–4, 10–12, 14, 16–22] or (meth)acrylate groups [6–9, 23–27]. Amino acid-based main chain polymers had been prepared by ring-opening polymerizations of α -

amino acid *N*-carboxyanhydrides [15, 28–30] or polycondensations of amino acids [31, 32]. Although these strategies had been successfully applied to the synthesis of linear polymers having amino acid moieties, the polymer networks having amino acid moieties in the main chain have not yet been synthesized by the addition polymerizations of amino acids whose *N*- and *C*-terminals are simultaneously modified with substituted olefinic groups. There have been few reports on the synthesis of amino acid-based polymer networks by use of polyaddition reactions. For example, Kiyotsukuri *et al.* [33] reported a polymer network by the reaction of lysine triisocyanate and glutamic acid diethylester hydrochloride. Li *et al.* [34] reported a polymer network by the reaction of a cycloaliphatic epoxy resin with

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DL-lysine, or diglycidyl ether of bisphenol A with L-tryptophan [35]. We also reported a polymer network by the reaction of 4,4'-bismaleimidodiphenylmethane with L-lysine [36].

Recently, radical-mediated thiol-ene 'click' reactions have attracted increasing attention as a method for the production of crosslinked polymer networks with various frameworks and functional groups [37–40]. The radical thiol-ene reaction can be initiated by a variety of techniques including under traditional thermal conditions with common azo species such as 2,2'-azobis(isobutyronitrile) (AIBN) or via photochemical methods, with or without added photoinitiator. Thiol-ene polymerization is characterized by advantages such as an inherently rapid reaction rate, reduced oxygen inhibition, high regioselectivity and low polymerization shrinkage. Furthermore, as the reaction is initiated by the formation of primary radicals by the decomposition of an initiator and subsequent production of a thiyl radical by the abstraction of a hydrogen radical from the thiol group, monomers containing functional groups (OH, CO₂H, NH₂ etc.) with a hydrogen that is less easily abstracted than the hydrogen of a thiol group can be polymerized without protecting the functional groups. In past studies, several research groups reported on the syntheses of bio-based polymer networks by thiol-ene polymerizations. For example, Echeverri *et al.* [41] reported elastomeric networks from maleated soybean-oil glycerides by thiol-ene coupling. Ortiz *et al.* [42] reported polymer networks prepared by thiol-ene photopolymerizations of allyl-etherified sucroses. We also reported trehalose- and eugenol-incorporated polymer networks by thiol-ene photopolymerizations [43, 44]. In the past studies, thiol-ene reactions have been applied to the modification of unsaturated amino acids [45] and to the synthesis of peptide-functionalized conjugates [46], but amino acid-based polymer network has not been prepared by use of thiol-ene polymerization to the best of our knowledge. In this study, triallyl L-alanine (A3A) and triallyl L-phenylalanine (A3F) whose *N*- and *C*-terminals are simultaneously modified with allyl groups were conveniently synthesized by one-pot reactions of L-alanine and L-phenylalanine with allyl bromide, respectively (Figure 1), and thermal and mechanical properties of polymer networks prepared by thiol-ene reactions of A3A and A3F with tetrathiol compounds were investigated.

Figure 1. Synthesis of A3A and A3F

2. Experimental section

2.1. Materials

L-Alanine and L-phenylalanine were purchased from Tokyo Kasei Kogyo Co. Ltd. (Tokyo, Japan). Pentaerythritol-based primary tetrathiol (pS4P, pentaerythritol tetrakis(3-mercaptopropionate)) was purchased from Sigma-Aldrich Corporation (St. Louis, MO, USA). Pentaerythritol-based secondary tetrathiol (S4P, pentaerythritol tetrakis(3-mercaptopbutyrate), trade name: Karenz MT™ PE1) was kindly provided by Showa Denko K. K. (Tokyo, Japan). The chemical structures of pS4P and S4P are shown in Figure 2. As photo-initiators, 1-hydroxycyclohexyl phenyl ketone (Irgacure® 184, mp. 45–49°C, UV/VIS absorption peaks in methanol: 246, 280, 333 nm), phenyl bis(2,4,6-trimethylbenzoyl) phosphine oxide (Irgacure® 819, mp. 127–133°C, UV/VIS absorption peaks in methanol: 295, 370 nm), 2-hydroxy-1-[4-(2-hydroxyethoxy)phenyl]-2-methyl-1-propanone (Irgacure® 2959, mp. 86.5–89.5°C, UV/VIS absorption peak in methanol: 276 nm) were purchased from Toyotsu Chemiplas Corporation (Tokyo, Japan). (±)-Camphorquinone (Wako Pure Chemical Industries Ltd., Osaka, Japan) was also used as a photo-initiator. Allyl bromide, sodium hydroxide, AIBN, dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF) and acetone were purchased from Kanto Chemical Co., Inc. (Tokyo,

Figure 2. Chemical structures of pS4P and S4P

Japan). All of the commercially available reagents were used without further purification.

2.2. Synthesis of *N,N,O*-triallyl-L-alanine (A3A)

To a solution of L-alanine (0.891 g, 10.0 mmol) in DMSO (30 mL), pulverized sodium hydroxide (2.64 g, 66.0 mol) was added, and the resulting mixture was stirred for 10 min. Allyl bromide (3.99 g, 33.0 mol) was dropwise added over a period of 30 min at room temperature. After the addition, the mixture was stirred for 24 h at room temperature and filtered. Dilute hydrochloric acid was added to the filtrate, and then extracted with chloroform. The organic layer was washed with water five times, dried over sodium sulfate and concentrated in vacuo to produce A3A as a brown liquid (1.08 g) in 52% yield: ^{13}C -NMR (400 MHz, CDCl_3 , δ , ppm): 14.94 (C-9), 53.63 (C-4), 57.38 (C-7), 64.76 (C-1), 116.87 (C-6), 118.24 (C-3), 132.17 (C-2), 136.41 (C-5), 173.52 (C-8). Anal. calcd. for $\text{C}_{12}\text{H}_{19}\text{O}_2\text{N}$: C, 68.87%; H, 9.15%; N, 6.69%. Found: C, 68.5%; H, 9.22%; N, 6.30%.

2.3. Synthesis of

N,N,O-triallyl-L-phenylalanine (A3F)

To a solution of L-phenylalanine (1.65 g, 10.0 mmol) in DMSO (30 mL), pulverized sodium hydroxide (2.64 g, 66.0 mol) was added, and the resulting mixture was stirred for 10 min. Allyl bromide (3.99 g, 33.0 mol) was dropwise added over a period of 30 min at room temperature. After the addition, the mixture was stirred for 24 h at room temperature and filtered. Dilute hydrochloric acid was added to the filtrate, and then extracted with ethyl acetate. The organic layer was washed with water three times, dried over sodium sulfate and concentrated in vacuo to produce A3F as a brown liquid (2.62 g) in 92% yield. ^{13}C -NMR (400 MHz, CDCl_3 , δ , ppm): 35.96 (C-9), 53.54 (C-4), 64.05 (C-7), 64.95 (C-1), 117.07 (C-6), 118.22 (C-3), 126.45 (C-13), 128.05 (C-12), 129.32 (C-11), 132.10 (C-2), 136.19 (C-5), 138.83 (C-10), 172.16 (C-8). Anal. calcd. for $\text{C}_{18}\text{H}_{23}\text{O}_2\text{N}$: C, 75.76%; H, 8.12%; N, 4.91%. Found: C, 75.4%; H, 8.09%; N, 4.91%.

2.4. Thiol-ene photopolymerization of A3A and pS4P

A mixture of A3A (0.209 g, 1.00 mmol), pS4P (0.366 g, 0.750 mmol), IRGACURE[®] 2959 (17 mg, 0.076 mmol) and acetone (2 mL) was stirred for

30 min to form a homogeneous solution. The solution was poured on a glass culture dish with a diameter of 40 mm and was dried at 60°C for 3 h. The obtained mixture was photo-irradiated for 30 s $\times$ 60 times at 1 min intervals to yield a photo-cured A3A/pS4P with the allyl/SH ratio of 1/1 (pc-A3A-pS4P) film with wrinkles. A SPOT-CURE SP-7 (250 W light source, wavelength 240–440 nm, Ushio Inc., Yokohama, Japan) device equipped with a uniform-radiation optical unit was used for UV curing (irradiation distance 200 mm, irradiation intensity 72 mW/cm²).

2.5. Thiol-ene thermal polymerizations

A typical procedure is as follows: A mixture of A3A (2.233 g, 10.67 mmol), pS4P (3.909 g, 8.00 mmol), AIBN (57 mg, 0.35 mmol) and acetone (5 mL) was stirred for 30 min to form a homogeneous solution. The solution was poured on a poly(methylpentene) culture dish with a diameter of 85 mm and was dried at room temperature for 3 h. The obtained mixture was cured at 80°C for 24 h and furthermore at 120°C for 48 h to yield a thermally cured A3A/pS4P with the allyl/SH ratio of 1/1 (A3A-pS4P) film (thickness: ca. 1.0 mm).

In a manner similar to the preparation of A3A-pS4P except using A3F (2.282 g, 8.00 mmol), pS4P (3.269 g, 6.00 mmol), AIBN (56 mg, 0.34 mmol) and acetone (4 mL), a thermally cured A3F/pS4P with the allyl/SH ratio of 1/1 (A3F-pS4P) film (thickness: ca. 1.0 mm) were prepared. Thermally cured A3A/S4P and A3F/S4P with the allyl/SH ratio of 1/1 (A3A-S4P and A3F-S4P) were similarly prepared by using S4P instead of pS4P.

2.6. Measurements

Proton and carbon nuclear magnetic resonance (^1H - and ^{13}C -NMR) spectra were recorded on a Bruker AV-400 (400 MHz) (Madison, WI, USA) using CDCl_3 as a solvent. Fourier transform infrared (FTIR) spectra were recorded on a Shimadzu FT-IR 8100 (Kyoto, Japan) by the attenuated total reflectance (ATR) method. Elemental analyses were performed on a SUMIGRAPH NCH-22F elemental microanalyzer (Sumika Chemical Analysis Service, Ltd., Ehime, Japan). Degree of swelling (D_s) was measured by dipping a thermally cured film (length 10 mm, width 10 mm, thickness 1.0 mm) in deionized water, acetone or DMF at room temperature for 48 h according to Equation (1):

$$D_s [\%] = 100 \frac{w_1 - w_0}{w_0} \quad (1)$$

where w_0 is the initial weight of the cured film and w_1 is the weight of the swollen film after dipping. The differential scanning calorimetry (DSC) measurements were performed on a Perkin-Elmer Diamond DSC (Waltham, MA, USA) in a nitrogen atmosphere. The samples were heated from -100 to 200°C at a heating rate of $20^\circ\text{C}\cdot\text{min}^{-1}$ to determine the glass transition temperature (T_g). The 5% weight loss temperature (T_5) was measured on a Shimadzu TGA-50 thermogravimetric analyzer at a heating rate of $20^\circ\text{C}\cdot\text{min}^{-1}$ in a nitrogen atmosphere. Tensile testing of the rectangular plates (length 50 mm,

width 10 mm, thickness 1.0 mm) was performed at room temperature using a Shimadzu Autograph AG-1 based on the standard method for testing the tensile properties of plastics (JIS K7161:1994, ISO527-1). The span length was 25 mm, and the testing speed was $10\text{ mm}\cdot\text{min}^{-1}$. Five specimens were tested for each set of samples, and the mean value and standard deviation were calculated.

3. Results and discussion

3.1. Synthesis and characterization of A3A and A3F

Triallylated amino acids, A3A and A3F whose all *N*- and *C*-terminal active hydrogens are substituted by allyl groups were conveniently synthesized by

Figure 3. ^1H -NMR spectra of (a) A3A and (b) A3F in CDCl_3 . The ^1H -signals displayed in red and blue are related *O*-allyl and *N*-allyl groups, respectively.

Figure 4. ^{13}C -NMR spectra of (a) A3A and (b) A3F in CDCl_3 . The ^1H -signals displayed in red and blue are related *O*-allyl and *N*-allyl groups, respectively.

reactions of L-alanine and L-phenylalanine with allyl bromide in the presence of excess pulverized sodium hydroxide in DMSO, respectively (Figure 1). Figure 3a shows ^1H -NMR spectrum of A3A in CDCl_3 . The methyl and methine ^1H signals of alanine residue of A3A were observed at δ 3.65 (m, 1H, H-7) and 1.30 ppm (d, 3H, H-9), respectively. The ^1H signals of *N,N*-diallyl groups were observed at δ 5.81 (m, 2H, H-5), 5.21 (m, 2H, H-6a), 5.11 (m, 2H, H-6b) and 3.30, 3.19 ppm (m, 4H, H-4), respectively. The proton signals of *O*-allyl group were observed at δ 5.95 (m, 1H, H-2), 5.35 (m, 1H, H-3a), 5.27 (m, 1H, H-3b) and 4.60 ppm (m, 2H, H-1). Figure 3b shows ^1H -NMR spectrum of A3F in CDCl_3 . The phenyl, methine and benzyl methylene ^1H signals of phenylalanine residue of A3F were observed at δ 7.26 (m, 2H, H-12), 7.18 (m, 3H, H-11,13), 3.75 (m, 1H, H-7) and 3.09, 2.90 ppm (m, 2H, H-9), respectively. The ^1H signals of *N,N*-diallyl groups were observed at δ 5.69 (m, 2H, H-5),

5.16 (m, 2H, H-6a), 5.06 (m, 2H, H-6b) and 3.39, 3.11 ppm (m, 4H, H-4), respectively. The proton signals of *O*-allyl group were observed at δ 5.82 (m, 1H, H-2), 5.26 (m, 1H, H-3a), 5.20 (m, 1H, H-3b) and 4.52 ppm (m, 2H, H-1). The fact that *N*- CH_2 protons (H-4 of A3A or A3F) were observed as complex signals indicates that the two methylene protons are magnetically non-equivalent probably due to steric hindrance around the *N*-methylene groups. Figure 4 shows ^{13}C -NMR spectra of A3A and A3F in CDCl_3 . As are shown in the figure, all the carbons of A3A and A3F were reasonably assigned. The assignment of ^1H and ^{13}C -signals of A3A and A3F shown in Figure 3 and Figure 4 was confirmed by H–H correlated spectroscopy (COSY), C–H COSY and the heteronuclear multiple bond correlation (HMBC) spectroscopy.

It is important for checking the progress of thiol-ene reaction of A3A and A3F to assign the IR absorption bands related to the allyl groups. Figure 5 shows

Figure 5. FT-IR spectra of (a) L-alanine and A3A and (b) L-phenylalanine and A3F. The wavenumbers displayed in red and blue are related to allyl and phenyl groups, respectively.

FT-IR spectra of A3A and A3F compared with those of L-alanine and L-phenylalanine. In the FT-IR spectrum of A3F, the bands characteristic to benzene ring were observed at 1605, 1497 and 746 cm^{-1} , which are ascribed to aromatic C=C stretching vibration and aromatic =C–H out-of-plane bending vibration, respectively. As the bands which are common in the spectra of A3A and A3F, the bands due to olefinic and/or aromatic C–H stretching vibrations and aliphatic C–H stretching vibration were observed at 3082–3028 cm^{-1} and 2982–2810 cm^{-1} , respectively. Also, the bands due to C=O and C–O (C–N) stretching vibrations were observed at 1730 and 1151 cm^{-1} , respectively. Furthermore, the bands ascribed to allyl C=C stretching ($\nu_{\text{C}=\text{C}}$) and =C–H out-of-plane bending ($\delta_{\text{C}=\text{H}}$) vibrations were observed at 1641 cm^{-1} and 993 (987), 916 (918) cm^{-1} , respectively. These bands characteristic to allyl group were used for the confirmation of progress of thiol-ene reaction of A3A and A3F with

the proviso that a weak absorption band is also observed at 916 cm^{-1} for L-alanine.

3.2. FT-IR analysis for the thiol-ene polymerization of A3A and A3F

Thiol-ene photopolymerization of A3A and pS4P at the allyl/thiol ratio of 1/1 in the presence of a photoinitiator (Irgacure[®] 184) produced a crosslinked yellow film (pc-A3A-pS4P) with many wrinkles, as is obvious from Figure 6. Although other photoinitiators (Irgacure[®] 819, Irgacure[®] 2959 and camphorquinone) were examined, we could not get a flat film. Furthermore, photo-irradiation of a mixture of A3F/pS4P in the presence of a photoinitiator produced a viscous liquid whose surface portion only is hardened. There is a possibility that the sterically hindered diallylamino groups of A3A and A3F have a lower reactivity than the allyl ester group at room temperature. Next, thiol-ene thermal polymerizations were examined. When A3A and A3F were

thermally cured with pS4P in the presence of AIBN at 80–120°C, flat and flexible films (A3A-pS4P and

Figure 6. Photographs of pc-A3A-pS4P, A3A-pS4P and A3F-pS4P films

A3F-pS4P) with a brown color were obtained (Figure 6). Also, we could get similar flat films by the thiol-ene thermal polymerizations of A3A and A3F with S4P. Also, we confirmed that A3A or A3F by itself cannot be thermally cured in the presence of AIBN at the same curing condition.

Figure 7 shows FT-IR spectra of pc-A3A-pS4P, A3A-pS4P and A3A-S4P compared with those of A3A, pS4P and S4P. The absorption bands related to allyl $\nu_{C=C}$ (1641 cm^{-1}) and δ_{C-H} ($993, 916\text{ cm}^{-1}$) vibrations were non-existent for pc-A3A-pS4P,

Figure 7. FT-IR spectra of pc-A3A-pS4P, A3A-pS4P and A3A-S4P compared with those of A3A, pS4P and S4P

Figure 8. FT-IR spectra of A3F-pS4P and A3F-S4P compared with those of A3F, pS4P and S4P

A3A-pS4P and A3A-S4P. Furthermore, an absorption band due to stretching vibration of S–H group ($\nu_{\text{S-H}}$) at 2567 cm^{-1} which was observed in a longitudinally enlarged spectrum at the wavelength region from 2500 to 2700 cm^{-1} for pS4P or S4P was non-existent for all the cured resins. These results indicate that thiol-ene reaction between allyl and thiol groups almost completely progressed. Although pc-A3A-pS4P was a heterogeneous film with many wrinkles, the thiol-ene photopolymerization considerably proceeded. In a similar manner, smooth progress of thiol-ene thermal polymerizations of A3F with pS4P and S4P was also confirmed, as is obvious from Figure 8. However, the fact that A3F did not produce a fully crosslinked film by thiol-ene photopolymerization suggests that the phenyl group of A3F hinders the photopolymerization at room temperature. Thermal and mechanical properties of the homogeneous film of thermally cured A3A or A3F with pS4P or S4P were investigated in the next section.

3.3. Properties of thermally cured films

Table 1 summarizes the values of D_s for all the thermally cured films dipped in acetone, DMF or water for 48 h. As A3A, A3F, pS4P and S4P are soluble in DMF and acetone, the fact that all the films swelled in the solvents indicates the formation of polymer network. However, the solvents after swelling tests were slightly colored yellow only for A3A-S4P and A3F-S4P in acetone and DMF, suggesting that incompletely crosslinked polymers are slightly formed for the S4P-based cured resins. It is inferred that some side-reactions disturbing the crosslinking reaction occurred because of a lower reactivity of secondary thiol groups of S4P than that of primary thiol groups of pS4P, considering that thiol and allyl groups were almost completely consumed for A3A-S4P and A3F-S4P as is obvious from the FT-IR analysis. If the crosslinking density of S4P-based cured resin is lower than that of pS4P-based cured resin, the D_s of the former resin would be higher than

Table 1. D_s values [%] of A3A-pS4P, A3A-S4P, A3F-pS4P and A3F-S4P films dipped in acetone, DMF or water at room temperature for 48 h

Sample	Acetone	DMF	Water
A3A-pS4P	30.8	109.2	2.0
A3A-S4P	33.0	109.0	1.9
A3F-pS4P	25.7	138.9	1.5
A3F-S4P	21.1	119.5	3.2

Figure 9. DSC curves of A3A-pS4P, A3A-S4P, A3F-pS4P and A3F-S4P

that of the latter. However, the D_s values of S4P-based cured resins in acetone or DMF were not always larger than those for the corresponding pS4P-based cured resin. This result may be caused by some elution of incompletely crosslinked polymers. The order of a higher D_s value by a difference of dipped solvent was DMF > acetone > water, indicating that the hydrophilicity of the formed polymer network is not so large in agreement with a hydrophobic character of other parts of the polymer network than amino acid residues.

Figure 9 shows the DSC charts of all the thermally cured resins. Every cured resin showed only a T_g at a temperature region from 13 to 39°C , suggesting that the cured resin is amorphous polymer. The T_g s of A3F-pS4P and A3F-S4P (38.7 and 29.5°C) were higher than those of A3A-pS4P and A3A-S4P (24.6 and 13.4°C), attributable to the fact that the former networks have bulky benzyl groups leading to suppression of thermal motion of the polymer chain. Also, T_g s of A3A-pS4P and A3F-pS4P (24.6 and 38.7°C) were higher than those of A3A-S4P and A3F-S4P (13.4 and 29.5°C), respectively. The possibility that S4P-based cured resin has a lower crosslinking density than pS4P-based resin does is also supported from this DSC result.

Figure 10 shows TGA curves of all the cured resins. The T_5 s of A3F-pS4P and A3F-S4P (282.0 and 266.2°C) were higher than those of A3A-pS4P and A3A-S4P (258.1 and 257.6°C), respectively. This result is attributable to a higher thermal stability of phenylalanine than alanine residue. Also, T_5 s of A3A-pS4P and A3F-pS4P (258.1 and 282.0°C) were a little higher than those of A3A-S4P and A3F-S4P (257.6 and 266.2°C), respectively. Furthermore, the char yields at ca. 500°C for A3A-pS4P and A3F-pS4P were higher than those for A3A-S4P and A3F-

Figure 10. TGA curves of A3A-pS4P, A3A-S4P, A3F-pS4P and A3F-S4P

S4P. These results may be caused by a little higher crosslinking density of the polymer network from pS4P than that from S4P, considering that the crosslinkage prevents the formation of volatile low-molecular-weight fragments even if some bonds of the main chain were cleaved. The T_5 s of A3A-S4P and A3F-S4P were comparable to those of polymer networks prepared by the thiol-ene photopolymerizations of S4P and allyl-etherified trehaloses with degrees of allylation of ca. 6 and 8 (251.4 and 289.4°C), respectively, indicating that the amino acid moiety has a similar thermal stability to the saccharide moiety [43]. However the T_5 s were lower than that (343.9°C) of the polymer network prepared by the thiol-ene photopolymerization of S4P and allyl-etherified eugenol (AEG) [44], indicating that the amino acid moiety has lower thermal stability than eugenol moiety.

Figure 11 shows typical stress-strain curves by a tensile mode for A3A-pS4P, A3A-S4P, A3F-pS4P and A3F-S4P. It is obvious that a maximal stress of A3F-based cured resin is much higher than that of A3A-based cured resin, and that a strain at break of

Figure 11. Stress-strain curves of A3A-pS4P, A3A-S4P, A3F-pS4P and A3F-S4P

Table 2. Tensile properties of A3A-pS4P, A3A-S4P, A3F-pS4P and A3F-S4P

Sample	Tensile strength [MPa]	Tensile modulus [MPa]	Elongation at break [%]
A3A-pS4P	2.14±0.67	7.39±1.42	25.2±6.0
A3A-S4P	1.02±0.51	3.90±1.00	27.6±6.6
A3F-pS4P	9.48±2.02	406±129	15.9±8.6
A3F-S4P	3.02±0.66	66.5±55.8	71.8±9.1

S4P-based cured resin is higher than that of pS4P-based cured resin. Table 2 summarizes tensile strength, modulus and elongation at break of the cured resins. Tensile strengths and moduli of A3F-pS4P and A3F-S4P were much higher than those of A3A-pS4P and A3A-S4P, respectively. Especially, the former had much higher tensile moduli than the latter, attributable to the fact that the former network is in glassy state at room temperature, while the latter is in rubbery state, as is obvious from their T_g s. Also, tensile strengths and moduli of A3A-pS4P and A3F-pS4P were higher than those of A3A-S4P and A3F-S4P, respectively. Reversely, the latter displayed higher elongation at break than the former, suggesting that S4P-based polymer network has a lower crosslinking density than pS4P-based polymer network does. Consequently, A3F-pS4P exhibited the highest tensile strength and modulus (9.48 and 406 MPa), whose values were much higher than those of the already reported AEG-pS4P (0.98 and 23.9 MPa) [44]. The difference in the mechanical properties should be caused by the fact that the allyl functionality of A3F (3) is higher than that of AEG (2), leading to a higher crosslinking density.

4. Conclusions

Both *C*- and *N*-terminal allylated amino acid derivatives, A3A and A3F were conveniently synthesized by one-pot reactions of L-alanine and L-phenylalanine with allyl bromide in the presence of sodium hydroxide, respectively. Thiol-ene thermal polymerization of A3A or A3F with pS4P or S4P at allyl/SH 1/1 produced a homogeneous and flat film (A3A-pS4P, A3A-S4P, A3F-S4P or A3F-S3I), while the corresponding photo-curing did not give a successful result. Although all the thermally cured films swelled in acetone, DMF and water, some elution of incompletely crosslinked polymers was observed for the S4P-based cured resins. A higher order of D_s for each cured film was DMF > acetone > water. The T_g s (38.7 and 29.5°C) of A3F-pS4P and A3F-S4P were

higher than those (24.6 and 13.4°C) of A3A-pS4P and A3A-S4P, respectively. The T_g s (282.0 and 266.2°C) of A3F-pS4P and A3F-S4P were higher than those (258.1 and 257.6°C) of A3A-pS4P and A3A-S4P, respectively. A3F- and pS4P-based cured resins exhibited much higher tensile strengths and moduli than A3A- and S4P-based cured resins, respectively. A3F-pS4P displayed the highest T_g (282.0°C), tensile strength (9.5 MPa) and modulus (406 MPa) among all the cured resins. Biodegradability and biocompatibility of these materials are currently under consideration. The methodology in this study is expected to be applied to the preparation of various amino acid-incorporated polymer networks which are applicable to biomaterials.

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