Synthesis of degradable porous polymers by means of ring-opening addition reaction of tri-aziridine and thiol-carboxylic acid compounds

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Research Article

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Abstract

Ring-opening addition reaction between a tri-aziridine, pentaerythriyol-tris[3-(1-aziridinyl)propionate] (AZOH) or 2,2-bishydroxymethylbutanol-tris[3-(1-aziridinyl)propionate] (AZ), and a thiol-carboxylic acid, thioglycolic acid (TGA) or thiolactic acid (TLA) or 3-mercaptopropionic acid (MPA), at room temperature in ethyl acetate produced porous polymers. The polymer networks were formed by the ring-opening reactions between the aziridine group of the tri-aziridine compounds with both the carboxylic acid and thiol groups of the thiol-carboxylic acids. The morphology of the porous polymers was composed by connected particles, whose averaged diameters ranged from about 2.5 to 7.5 μm. The reaction of AZOH and MPA under a high monomer concentration (40 wt%) yielded the porous polymer with co-continuous monolithic structure, whose backbone was formed by connected small particles of diameters of less than 0.2 μm. The porous polymers formed with TLA showed higher Young's modulus due to small particle size and high density. The porous polymers showed good thermal stability. All porous polymers were decomposed in methanol within 50 days at room temperature, suggesting that the polymers may be applicable as degradable materials.

Introduction

Aziridines are widely applicable chemicals not only for synthetic intermediates but also monomers due to their high reactivity originated from ring strain of the aziridine group. Aziridines can yield the corresponding polymers via ionic ring-opening polymerization [1]. Aziridine group shows high reactivity with nucleophiles accompanied by ring opening. The aziridine group reacts with carboxyl group under mild conditions [2], and the reaction has been widely applied to synthesize functionalized polymers [3–12].

We have recently reported the synthesis of network polymes by ring-opening addition reaction of a tri-aziridine compound, 2,2-bishydroxymethylbutanol-tris[3-(1-aziridinyl)propionate] (AZ), with various dicarboxylic acid in some organic solvents [13]. The polymerization reactions in ethanol yielded the porous polymers, Scheme 1 (a). The ring-opening addition reaction between the aziridine and carboxylic acid should drastically decrease the miscibility between the formed polymer network and the solvent, and effectively induced phase separation via spinodal decomposition. Morphology, mechanical properties, and absorption capacity of the resulting porous polymers were strongly affected by the molecular structure of the dicarboxylic acid used.

Herein we report the synthesis of the porous polymers by ring-opening addition reaction of tri-aziridine and the bi-functional monomers where the bifunctional monomers have -COOH and -SH groups with different nucleophilicity. The intention of the present work is to expand the scope of chemical structure of the bifunctional monomer leading to a wider variety of porous polymer structure. Incorporation of the two different connecting moieties derived from -COOH and -SH groups would be useful for functionalization of the porous polymers. We used, pentaerythriyol-tris[3-(1-aziridinyl)propionate] (AZOH) and AZ as tri-aziridines and thioglycolic acid (TGA), thiolactic acid (TLA), and 3-mercaptopropionic acid (MPA) thiol-

carboxylic acid, and the reactions were conducted in ethyl acetate (EA) [Scheme 1 (b)]. The effect of molecular structure on the morphology and mechanical properties of the resulting porous polymers was studied. Furthermore, the resulting porous polymers which absorbed methanol (MeOH) were degradable, and the absorption and degradation behavior were investigated.

Experiment

Materials

AZOH and AZ were kindly donated from Sogo Pharmaceutical Co. and Ltd. Nippon Shokubai Co., Ltd., respectively, and were used as received. TGA, TLA, and MPA (Tokyo Chemical Industry Co., Ltd) were used without further purification. High-purity grade ethyl acetate (EA) and MeOH (Kanto Chemical Co., Inc.) were used as received.

Synthesis of porous polymers

The feed molar ratio of tri-aziridine to thiol-dicarboxylic acid was 2/3 (mol/mol).

The reaction of AZOH with TGA in EA at a monomer concentration of 30 wt% is described as a representative example. AZOH (0.879 g, 2.06 mmol), EA (3.03 mL, 2.72 g), and TGA (0.214 mL, 3.09 mmol) were added to a 20 mL vial, and the mixture was stirred by a vortex mixer for several minutes to make a homogeneous solution. The reaction solution was introduced to a 10-mL ampoule and sealed. The reaction system was kept at room temperature for 24 h. The obtained porous polymer was soaked in methanol to replace the solvent and dried under at room temperature first under normal pressure for 24 h and then in vacuo for 6 h. The reaction with AZ, TLA, or MPA was conducted by the same procedure.

Analytical procedures

FT-IR spectra of the porous polymers were recorded on an FT-IR-Affinity-1S (SHIMADZU Corporation) using attenuated total reflection (ATR) method. Thirty scans were accumulated from 4000 to 500 cm^{-1}.

JNM-ECA400 (JEOL Co. Ltd, Japan) was utilized for the observation of solid-state ^{13}C-NMR spectroscopy. The applied magnetic field was 9.38977 T, which corresponds to a resonance frequency of 100.5253 MHz for ^{13}C. The ^{13}C NMR spectrum was acquired by accumulating 2200 scans, employing a combination of high-power dipolar decoupling and cross-polarization (CP) under magic angle spinning (MAS) conditions. Moreover, the Total Suppression of Sidebands (TOSS) sequence was applied to eliminate spinning sidebands. The pulse widths for ^{1}H and ^{13}C were configured at 2.06 and 2.24 μs, respectively. The CP contact time was set to 2 ms. The spectral width amounted to 40.2 kHz, and the MAS speed was maintained at 6 kHz. These measurements were conducted at room temperature.

SEM images of the porous polymers were acquired by a JEOL JSM-7610F microscope with an LEI detector at an acceleration voltage of 3.0 kV.

Density functional theory (DFT) calculations were performed at the B3LYP/6-31G(d,p) level by using Gaussian 16 software.

Mechanical properties of the porous polymers were investigated by the compression test with a Tensilon RTE-1210 (ORIENTEC Co. Ltd.). The test samples were cut to 1-cm cube and pressed at a rate of 0.5 mm/min at room temperature.

Thermogravimetric analysis (TGA) of the polymers was conducted with a Bruker AXS TG-DTA2020SA. The sample was heated from room temperature to 480 ºC at a rate of 10 ºC/min under air atmosphere.

Results and discussion

The ring-opening addition reaction of tri-aziridine (AZOH, AZ) and thiol-carboxylic acid (TGA, TLA, MPA) was conducted in EA (monomer concentration: 30 wt%) at room temperature. The reactions were promoted without catalyst and yielded the network polymers. The reactions of AZ and MPA formed cloudy gel while the other reactions successfully yielded porous polymer.

Molecular structure of the porous polymers was studied by FT-IR and CP/MAS NMR spectroscopy. Figure 1 (i) shows FT-IR spectra of AZOH, TGA, and AZOH-TGA porous polymer. An absorption peak derived from secondary amine, formed by ring opening addition of aziridine, was detected at 1578 cm^{-1}. The small peaks arising from aziridine at 3050 cm^{-1} and thiol at 2560 cm^{-1} disappeared in the spectrum of the porous polymers. The CP/MAS NMR spectrum of the AZOH-TGA porous polymer and the assignments are shown in Fig. 1 (ii). The peaks derived from β-amino ester and α-tioester indicated that the ring opening addition of aziridine occurred with both the carboxylic and thiol groups of TGA. The other porous polymers showed similar profiles in the FT-IR and CP/MAS NMR spectra.

As described above, the ring-opening addition reaction between the aziridine and carboxylic groups occurs easily under the mild conditions without catalyst due their inherently high reactivity. In connection with the present work, ring-opening addition reactions between the aziridine and the thiol groups have been reported. Leeuwen and co-workers reported a regio-selective addition of thiophenol and aliphatic aziridines derived from norephedrine without catalysts or bases [14]. Similar reactions were reported for thiophenol addition to non-activated aziridines to yield regio-selective b-amino sulfides [15, 16]. The addition of CF_3SO_3H, a strong protic acid [17], Lewis acids including $ZnCl_2$, Zn $(CF_3SO_3)_2$, $Cu(CF_3SO_3)_2$, and $Yb(CF_3SO_3)_2$ [18], boron trifluoride-diethyl etherate [19], and a organophosphine (tributylphosphine) [20], is known to accelerate the reaction.

Although the reaction between AZOH or AZ with 1,6-hexane dithiol (HDT), an alkane dithiol, was attempted to synthesize the network polymer, no reaction occurred. This result may indicate that the thiol group in thiol-carboxylic acid (TGA, TLA, MPA) is activated by the carboxylic group to facilitate the reaction. The reaction between the aziridine and thiol groups would be promoted by the interaction between the HOMO of the S atom and the LUMO of the aziridine. In order to obtain information on this aspect, molecular structures of TGA, TLA, MPA, and HDT were optimized by DFT calculations. Figure 2

shows the optimized structures with molecular orbital representation. In the structures of TGA, TLA, and MPA, the thiol group is located in the vicinity of the carbonyl group, and orbital-orbital interactions between S and C = O groups would be expected. In a sharp contrast, such interactions are absent for HDT. The higher reactivities of TGA, TLA, and MPA than HDT can thus be reasonably interpreted.

SEM images of the AZOH based porous polymers are shown in Fig. 3. The AZOH-TGA and AZOH-TLA porous polymers (monomer concentration: 30 wt%) showed the surface morphology composed by connected particles, whose average diameters were 2.7 μm or 2.6 μm, respectively. AZOH-MPA porous polymer was formed by the connected particles with larger size in comparison with those in the AZOH-TGA and AZOH-TLA porous polymers. The diameters of the particles in the AZOH-MPA porous polymer decreased with increasing in the monomer concentration in the reaction systems, as shown in Figs. 4 (c), (d), and (e). The expanded SEM image of AZOH-MPA porous polymer, prepared from the reaction solution with 40 wt% monomer concentration, cleared the porous morphology of co-continuous structure whose backbones were formed by connected small particles less than 0.2 μm in the diameter. Figure 4 shows the SEM images of AZ based porous polymers. The surface morphology of these porous polymers was like those of the corresponding porous polymers with AZOH, as shown in Fig. 3. The averaged diameter of the particles in the AZ-TGA or AZ-TLA porous polymer was 5.3 μm or 3.5 μm, respectively, which was slightly larger than that of the corresponding porous polymers with AZOH.

The morphology of these porous polymers should be formed by polymerization induced phase separation via spinodal decomposition (SD). A phase separation model of the present reaction systems via SD is illustrated in Scheme 2. The co-continuous monolithic structure is formed at early stage of the phase separation. The progress of the phase separation transfers the morphology from the co-continuous monolithic structure to the particles due to the interfacial tension of the droplets, and their size increase with progress of the phase separation. The half-fused particles were fixed at the transition stage from the co-continuous structure (early stage of SD) to the isolate particles (late stage of SD). The connected particles with small diameters, as shown in Fig. 3 (f), are formed at this transition stage. High monomer concentration (40 wt%) of AZOH-MPA system should preferentially accelerate the polymerization (fixation) rate in the phase separation, which yielded the porous polymer with the co-continuous structure, as illustrated in Scheme 2 (i). The size of the particles should be depended on the phase separation morphology at the fixation period. In the case of the AZOH based porous polymers obtained from the reaction systems with 30 wt% of the monomer concentration, Figs. 3 (a), (b), and (d), the AZOH-MPA porous polymer showed larger averaged particle size, as shown in Fig. 3 (d). One explanation of the result is that the lower crosslinking density derived from longer molecular length of MPA would decelerate the polymerization (fixation). As the result, the relative phase separation rate would increase in the reaction, and the phase separation at the later stage composed by larger particle size should be formed, as illustrated in Scheme 2 (iii).

Mechanical properties of the porous polymers were investigated by compression test. Figure 5 shows stress-strain curves of AZOH-TGA, AZOH-TLA, and AZOH-MPA porous polymers prepared in the reaction systems with the monomer concentration of 30 wt%. The results are summarized in Table 1. The order of

the Young's modulus of the porous polymers is as follows: AZOH-TLA > AZOH-TGA > AZOH-MPA. The similar tendency was observed in AZ based porous polymers. Both the small particle size and high bulk density should increase the Young's modulus of the porous polymers with TLA. Another possibility to explain the results would be derived from molecular structure of the thiol-carboxylic acid used. Existence of a methyl group in TLA hinders rotation of C-C linkage between the thiol and carboxylic acid and would induce rigidity in the network, which should heighten the Young's modulus. The AZ-TLA and AZ-TGA porous polymers showed lower Young's modulus in comparison with those of the corresponding AZOH based porous polymers despite the higher bulk density. The larger particle size in the AZ based porous polymers should decrease the Young's modulus. The Young's modulus of the AZOH-MPA porous polymer increased with increasing of the monomer concentration in the reaction systems due to the decrease of the particle size and increase of the bulk density.

Table 1
Structure and mechanical properties of the tri-aziridine and thiol-carboxylic acid porous polymers

Run	Aziridine	Thiol-carboxylic acid	Monomer conc. [a] [wt%]	Particle size [μm]	Bulk density [g/cm^3]	Young's modulus [kPa]	T_{d5} [°C]	T_{d50} [°C]
1	AZOH	TGA	30	2.7	0.318	226	163	373
2	AZOH	TLA	30	2.6	0.375	685	174	375
3	AZOH	MPA	20	7.4	0.205	51.4		
4	AZOH	MPA	30	6.2	0.348	75.4	184	348
5	AZOH	MPA	40	< 0.2	0.579	414		
6	AZ	TGA	30	5.3	0.388	96.3	162	342
7	AZ	TLA	30	3.5	0.457	136	168	347

[a] Monomer concentration in the reaction solution.

Thermal stability of the porous polymers was investigated by TGA (Fig. S1). Weight loss of all the porous polymers gradually began at round 160 °C (5 wt% weight loss was attained at the temperatures ranged from about 160 °C to 180 °C). The weight loss promoted more than 200 °C, and 50 wt% weight loss was attained at the temperatures ranged from about 350 °C to 375 °C. These phenomena should be derived from thermal-oxidative degradation of ester groups originated from tri-aziridine and thiol-carboxylic acid compounds.

The porous polymers absorbed various organic solvents. The porous polymers which absorbed methanol (MeOH) were gradually getting smaller. The weight of the porous polymers immersed in MeOH was traced (Fig. 6). The weight of the porous polymers increased by absorption of MeOH and reached the maximum values within a few days. After that, the weight of the porous polymer rapidly decreased, and

all the porous polymers completely degraded within 50 days. The porous polymers obtained from the addition reaction of AZ and dicarboxylic acid were not degraded in MeOH [13]. The degradability of the present porous polymers should be derived from a-thioester group and d b-thioester groups in the polymer network, which were formed by the ring opening reaction between aziridine and thiol group of the thiol-carboxylic acid compounds [21–23]. The degradation rate of the AZOH based porous polymers is as follows: MPA > TLA > TGA. The high degradability of the AZOH-MPA porous polymer should be derived from lower crosslinking density in the polymer network owing to larger methylene length in MPA. Difference in the degradability between a-thioester group, derived from TGA or TLA, and b-thioester, derived from MPA, would be another possibility to explain the degradation rates. The AZ based porous polymers showed higher degradation rates in comparison with the corresponding AZOH based porous polymers. The affinity between the AZOH and MeOH might be higher than that of AZ and MeOH due to the OH group in AZOH. However, the degradation rates of the porous polymers showed opposite order to the affinity. One explanation of the results may be that smaller particles' size, which provides larger surface area, in the AZOH based porous polymer accelerates the degradation. Lower bulk density, which means larger space, of the AZOH based porous polymer also would increase the degradation rates.

Molecular structure of the degradation products, after evaporation of MeOH following drying under the reduced pressure, of the porous polymers was studied by ^{1}H NMR spectroscopy. The degradants were low viscous liquid and were easily soluble in $CDCl_3$. The signals derived from methyl ester, thioester, and methylene adjacent to hydroxy group were detected in the NMR spectra (Fig. S2), suggesting that the degradation products contain alcohol compounds including (ii) in Fig. S2. These results indicate that the thioester groups in the polymer network were degraded by a transesterification reaction with MeOH under the ambient conditions. Degradation products having two or more -OH functions may possibly be used as monomers for the synthesis of polyurethanes and polyesters, which implies that the materials prepared in this work may be regarded as recyclable polymers.

Conclusions

The ring-opening addition reaction of tri-aziridine (AZOH, AZ) and thiol-carboxylic acid (TGA, TLA, MPA) in EA successfully yielded the porous polymers. Both the thiol and carboxylic acid groups in thiol-carboxylic acid compounds reacted with aziridine groups via ring-opening addition. DFT calculation of the thiol-carboxylic acid revealed that the thiol group was located near the carbonyl group and the orbitals of the S atoms were larger than those of the connecting C atoms. The statement of the thiol group should make it possible to react with the aziridine group. The porous polymers showed the morphology with connected particles in the order of micrometer, which were fixed at the later stage of the phase separation via spinodal decomposition. The increase of the monomer concentration relative rate of the polymerization and fixed the porous structure at the early stage of the phase separation with co-continuous monolithic structure. The porous polymers with the small particle size and high bulk density showed high Young's modulus.

As mentioned above, the ring opening addition reactions of tri-aziridine and thiol-carboxylic acid compounds is one of the facile methods to synthesize the porous polymers. The notable features of the present porous polymers are thermal stability and solvent degradability. Applications of the present porous polymers, especially for the bio-medical fields, are under consideration now, and the results will be reported elsewhere.

Declarations

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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Conflicts of interest/Competing interests

The authors declare that they have no competing interests.

Availability of data and material

All data generated or analyzed during this study are included in this published article and its supplementary information files.

Code availability

Not applicable.

Authors' contributions

Conceptualization, N.N. and T.N.; analysis, N.N., M.J., K.I., Y.I., T.T. and M.Y.; investigation, N.N. and T.N.; analysis, N.N., M.J., K.I., Y.I., T.T. and M.Y.; writing—original draft preparation, N.N.; writing—review and editing, T.T., M.Y. and T.N.; supervision, N.N. and T.N.; project administration, N.N.; funding acquisition, N.N. All authors have read and agreed to the published version of the manuscript.

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Schemes

Schemes 1 and 2 are available in the Supplementary Files section.

Figures

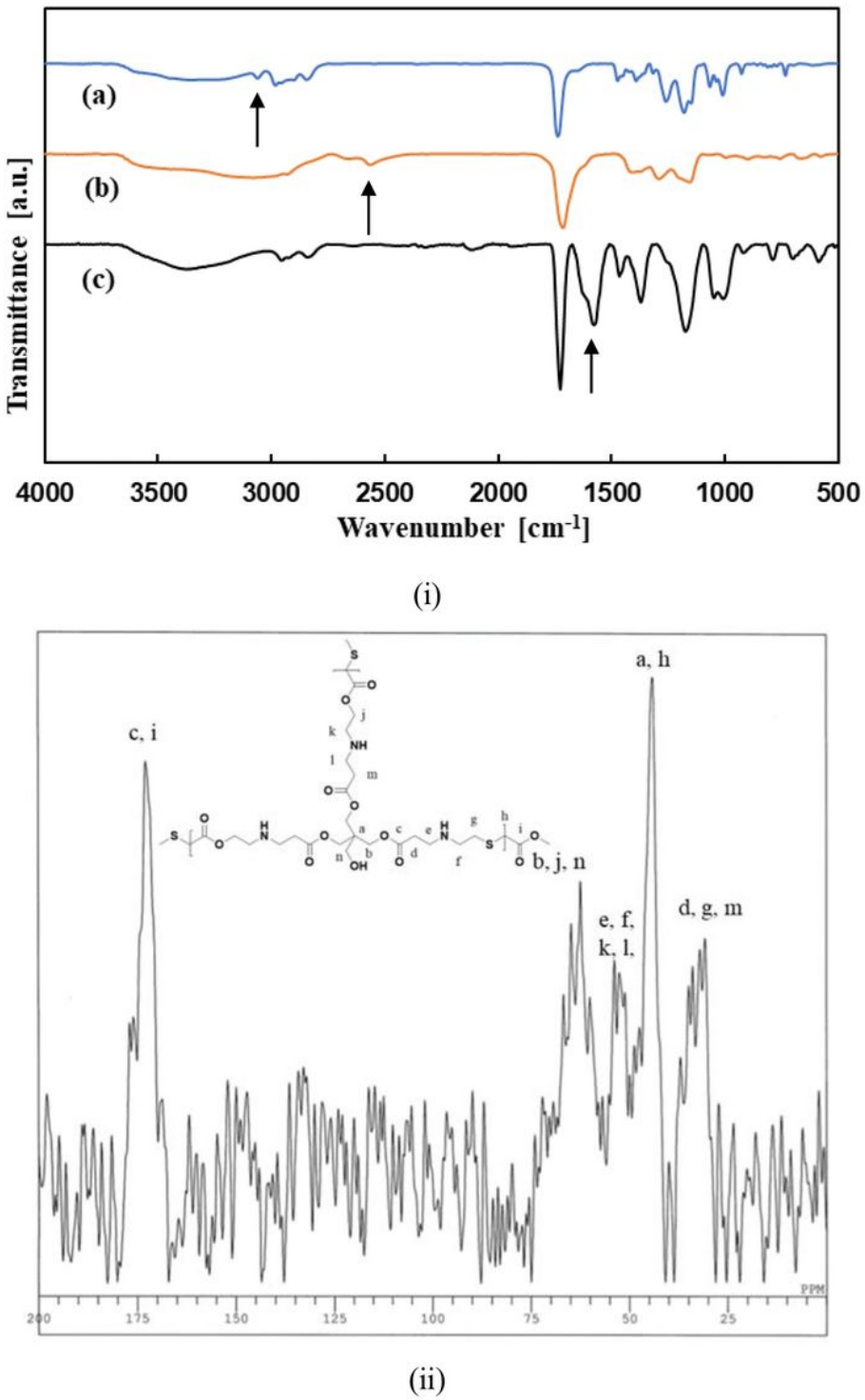

Figure 1

(i) FT-IR spectra of (a) AZOH, (b) TGA, and (c) AZOH-TGA porous polymer, and (ii) ^{13}C CP/MAS NMR spectrum of AZOH-TGA porous polymer, monomer concentration: 30 wt% (run 1).

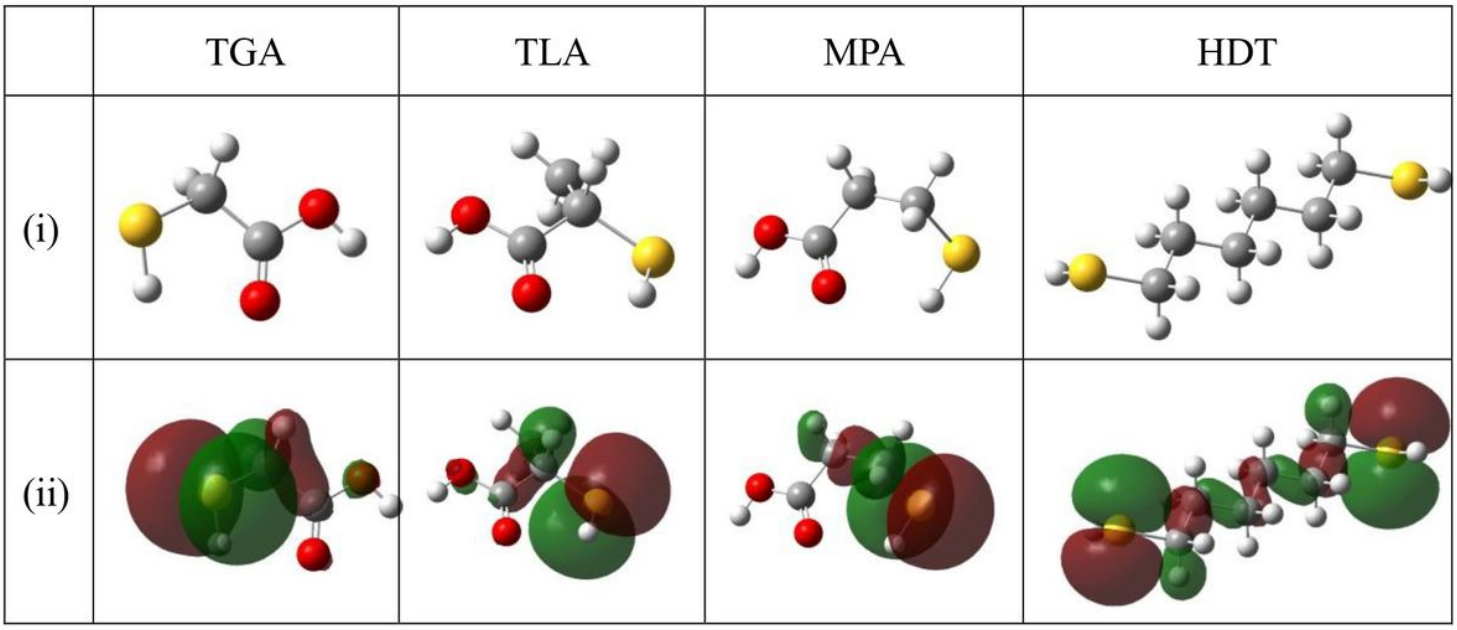

Figure 2

Molecular structures (i) without and (ii) with orbitals of TGA, TLA, MPA, and HDT optimized by DFT calculation. C is gray, O is red, S is yellow, and H is white.

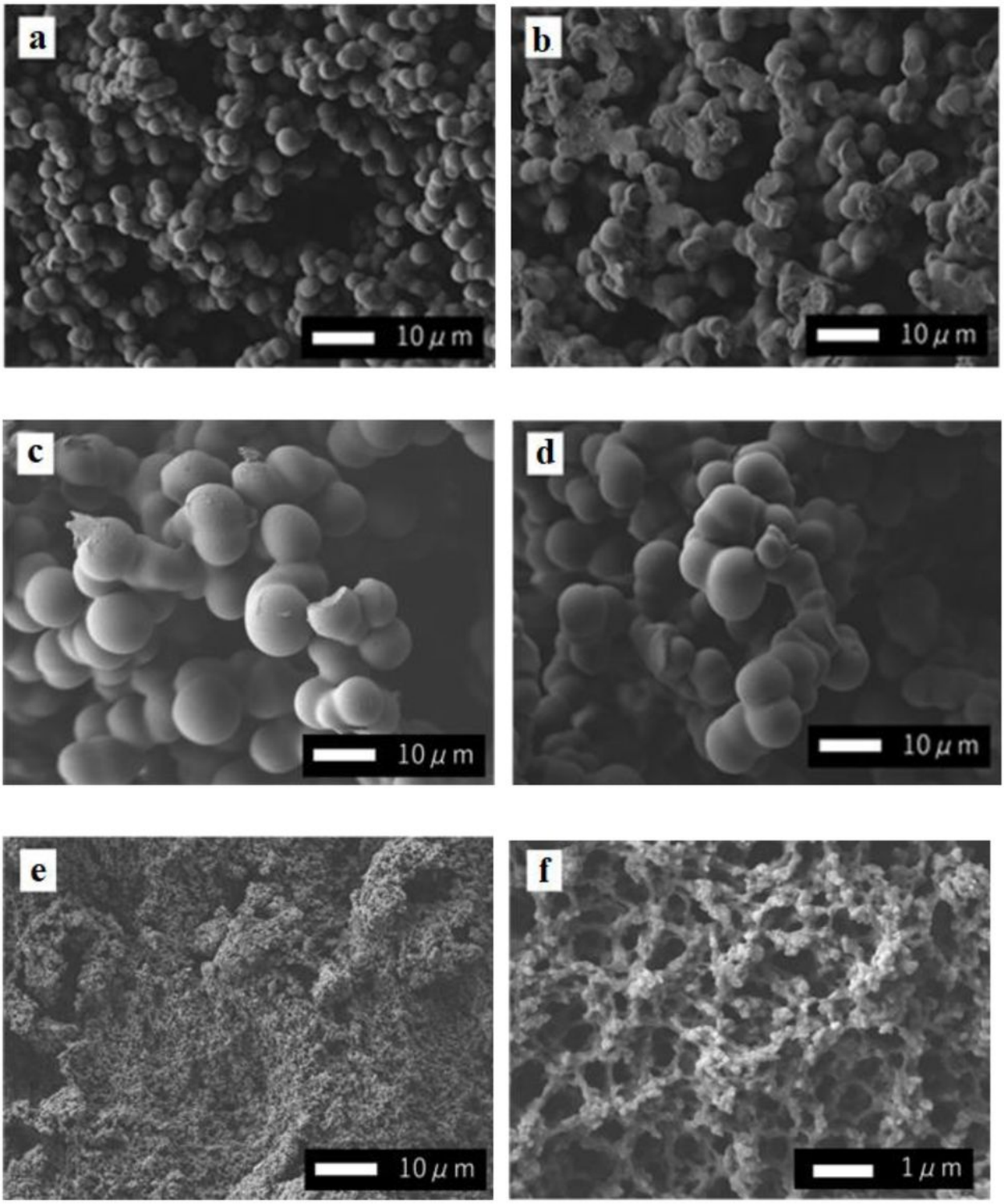

Figure 3

SEM images of (a) AZOH-TGA and (b) AZOH-TLA porous polymers, monomer concentration in the reaction solution: 30 wt%, AZOH-MPA porous polymer, monomer concentration in the reaction solution: (c) 20 wt%, (d) 30 wt%, and (e), (f) 40 wt%.

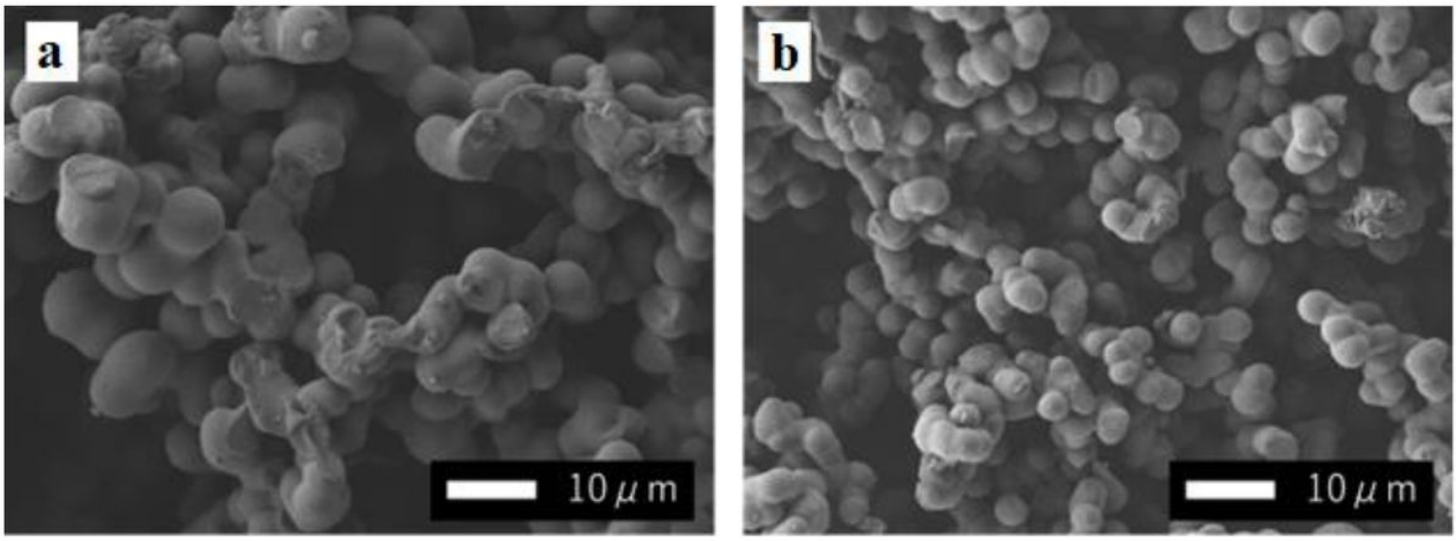

Figure 4

SEM images of (a) AZ-TGA and (b) AZ-TLA porous polymers, monomer concentration in the reaction solution: 30 wt%.

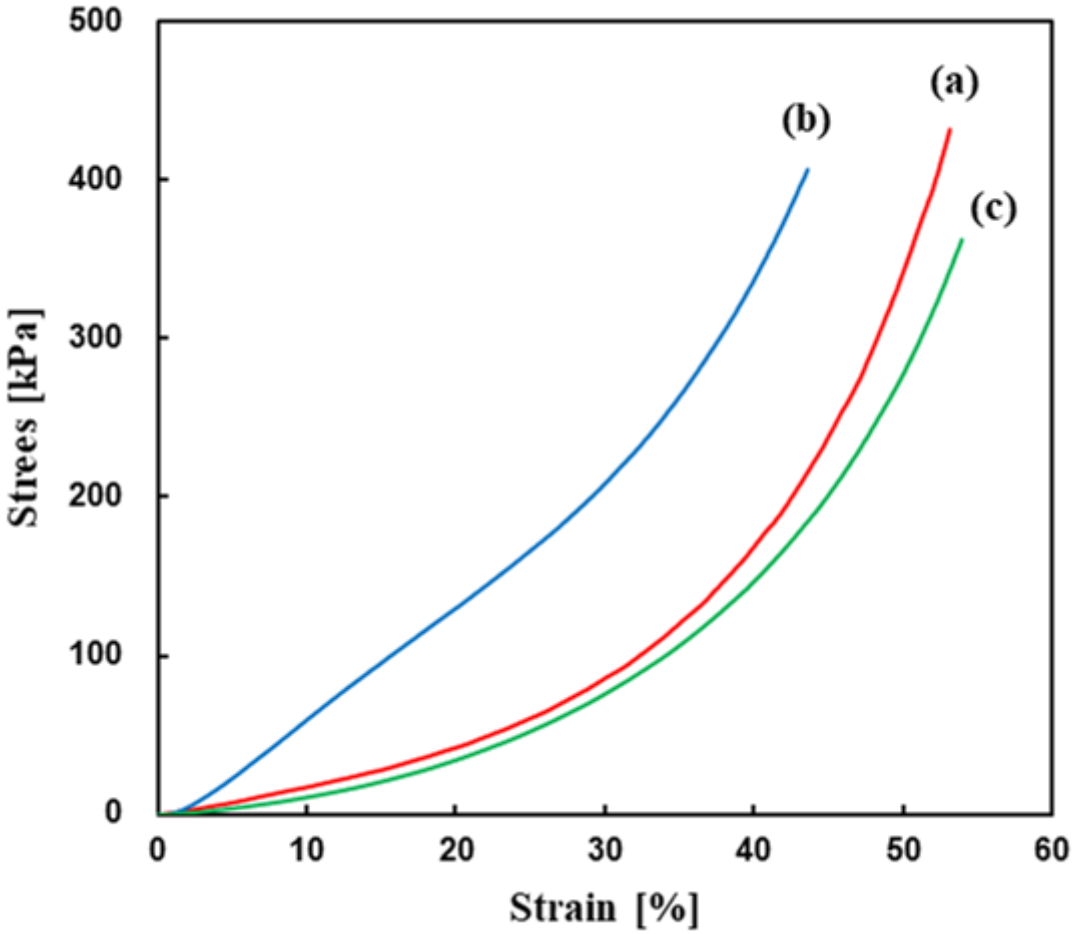

Figure 5

Stress-strain curves of (a) AZOH-TGA, (b) AZOH-TLA, and (c) AZOH-MPA porous polymers, monomer concentration in the reaction solution: 30 wt%,

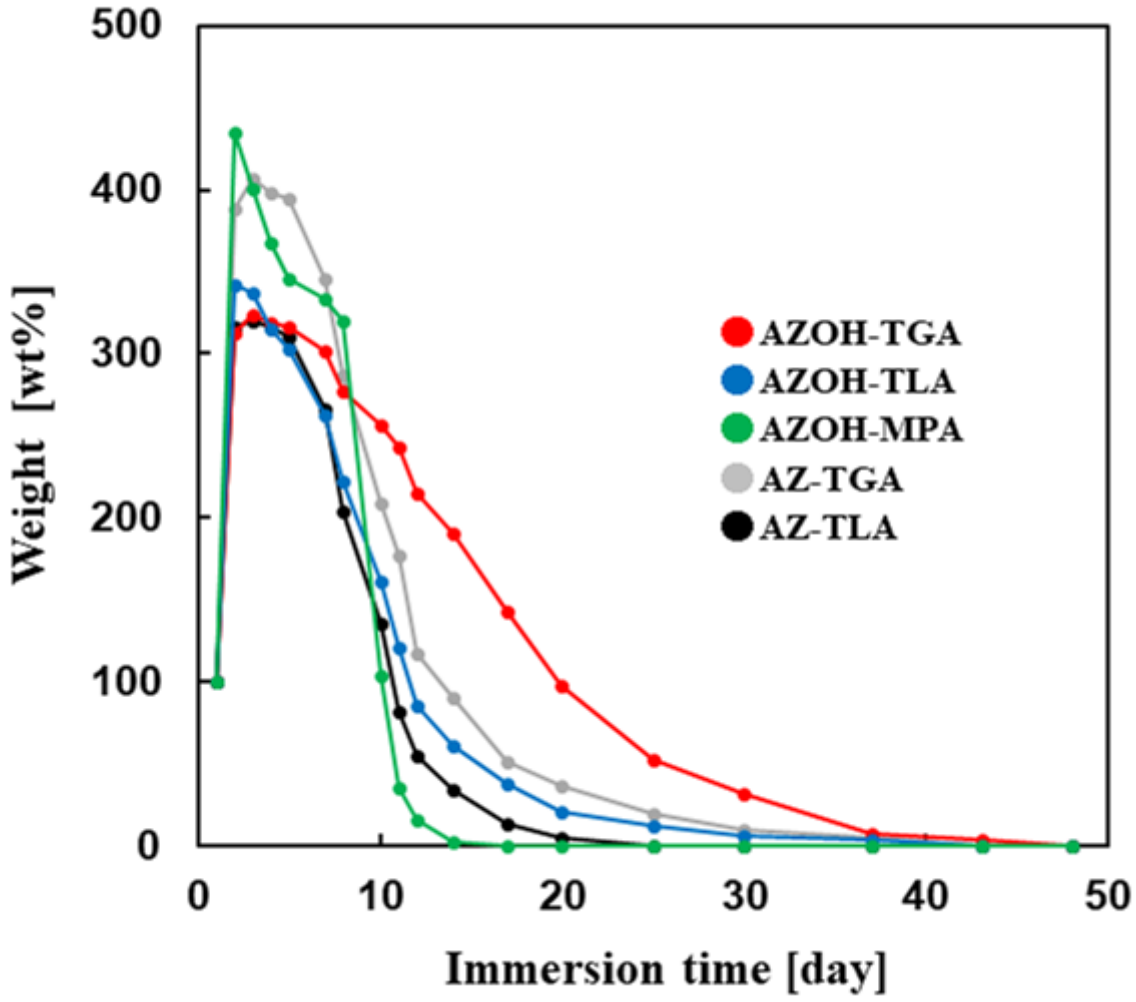

Figure 6

Time evolution of weight change of AZOH-TGA (red), AZOH-TLA (blue, AZOH-MPA (green), AZ-TGA (gray), and AZ-TLA (black) porous polymers (monomer concentration in the preparation solution: 30 wt%) immersed in MeOH.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- Scheme1and2.docx
- Text3AZThiocarboxylicacidJPRSI.doc