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Polymerization mechanism of nitrogen-containing heteroaromatic compound under high-pressure and high-temperature conditions

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Abstract

Hydrogenated carbon nitride is synthesized by polymerization of 1,5-naphthyridine, a nitrogen-containing heteroaromatic compound, under high-pressure and high-temperature conditions. The polymerization progressed significantly at temperatures above 573 K at 0.5 GPa and above 623 K at 1.5GPa. The reaction temperature was relatively lower than that observed for pure naphthalene suggesting the reaction temperature is considerably lowered when nitrogen atoms exist in the aromatic ring structure. The polymerization reaction largely progresses without significant change of N/C ratio. Three types of dimerization are identified; naphthylation, exact dimerization, and dimerization with hydrogenation as determined from the GC/MS analysis of soluble products. IR spectra suggest hydrogenation products were likely to be formed with sp^3 carbon and NH bonding. ^{13}C ssNMR reveals that the sp^3/sp^2 ratio is 0.14 in both the insoluble solids synthesized at 0.5 and 1.5 GPa. Not only the dimers but also soluble heavier oligomers and insoluble polymers formed through more extensive polymerization. The major reaction mechanism of 1,5-Nap was common to both the 0.5 and 1.5 GPa experiments, although the required reaction temperature increased with increasing pressure and aromatic rings preferentially remained at the higher pressure.

Introduction

Carbon nitride materials have attracted attention due to their potential applications in metal-free photocatalysis [1-2] and photodegradation [3]. Various crystalline polymorphs of C_3N_4 were reported and theoretical studies pointed out that the hardness of some C_3N_4 phases were comparable or even higher than that of diamond [4-8]. Amorphous carbon nitrides have also been synthesized by chemical vapor deposition (CVD) and physical vapor deposition (PVD) techniques [9]. To synthesize and characterize nitrogen-doped carbon materials, it is important to evaluate N/C ratios, sp^3/sp^2 ratios, and behavior of hydrogen atoms during the synthesis which are generally retained in nitrogen-doped carbon materials as essential components of their structures [10]. The application of high-pressure and high-temperature (HPHT) conditions is considered a useful technique for the synthesis of carbon nitride materials as well as CVD and PVD techniques [11]. The crystal structures and bonding of carbon nitride materials have been investigated above 100 GPa and/or above a few thousand kelvin using laser heated diamond anvil cells [12-14], although it was difficult in these studies to reveal the mechanism of the chemical reaction because controlling the heating temperature is difficult and analytical methods are limited due to the extremely small sample size in diamond anvil cell devices. Several HPHT experiments using large-volume presses, such as piston-cylinder apparatus, belt-type press, and multi-anvil press have also been performed. Various analytical methods such as X-ray diffraction (XRD)

measurements, Raman and infrared (IR) spectra, X-ray photoelectron spectroscopy (XPS), and transmission electron microscope (TEM) with electron energy loss spectroscopy (EELS) have been used to evaluate crystallinity, chemical compositions, and bonding of the reaction products [11, 15-19]. It has been reported that the N/C ratio of carbon-nitride materials decreases with increasing temperature, in the case where synthesis focused on 1,2,4-triazole ($C_2N_3H_3$) [19] and melamine ($C_3N_6H_6$) [17]. Graphitic C_3N_4 decomposed into diamond and probably N_2 above 1073-1173 K at 22-25 GPa [18]. However, details of the reaction mechanism remain unclear.

The pressure-induced polymerization mechanism of various aromatic compounds including nitrogen-containing heteroaromatic compounds have also been studied [20-25] and it was generally concluded that the decrease of the intermolecular distances with increasing pressure resulted in polymerization [26-27]. Polymerized products were obtained after compression above 20 GPa at room temperature and some products were shown to exist as an amorphous solid phase containing considerable sp^3 carbon [22-23, 25]. One-dimensional sp^3 carbon nitride nanothreads have been shown to form from slow compression/decompression of pyridine (C_5H_5N) [28-29] and aniline ($C_6H_5NH_2$) [30] to around 20 GPa as well as carbon nanothreads formed from the high pressure polymerization of benzene (C_6H_6) [31-32]. The atomic N/C ratio of the carbon nitride nanothreads was not considerably changed from that of the starting material while significant conversion from sp^2 to sp^3 bonding occurred during the reaction [28]. Diffraction measurements suggested a

polytwistane structure for the carbon nitride nanothread derived from a [4+2] Diels-Alder cycloaddition reaction [29].

Applying HPHT conditions to aromatic compounds potentially induces complex reactions because H-elimination and polycondensation can be induced by temperature, noting that it is clear that oligomerization/polymerization are likely to be induced by pressure. Oligomerization of aromatic hydrocarbons has been observed at 500–773 K at ambient pressure and at 3.5 GPa, and 773–973 K at 7 GPa [33-34]. Oligomerization with dehydrogenation and new C-C bond(s) formation between the aromatic rings were reported by using mass spectrometry of the reaction products [33]. Shock experiments on benzene, naphthalene and other PAHs showed that amorphous carbon, hydrogen/hydrocarbon gases, and oligomers were formed at shock pressures and temperatures above around 10 GPa and 800 K [35-36]. In shock experiments of naphthalene, optically dark products of amorphous carbon were predominantly observed. In addition, various methylation, phenylation, and naphthylation products were formed by radical reactions [36]. HPHT experiments revealed that polymerization of pyridine proceeds at approximately 8 GPa and 750–800 K, a reaction temperature that was distinctly lower than that of benzene polymerization [37]. However, details regarding the reaction mechanism and the specific role of nitrogen during the course of the reaction has not been resolved.

Naphthyridines ($C_8H_6N_2$) consist of two fused aromatic rings like naphthalene, but

where two of the CH groups are replaced with nitrogen atoms. There are several isomers that differ in the position of nitrogen atoms in the aromatic rings. Pressure-induced irreversible reaction of 2,3-naphthyridine (hereafter 2,3-Nap) and 1,5-naphthyridine (hereafter, 1,5-Nap) to form amorphous solids were observed at around 16-18 GPa at room temperature at pressures not remarkably different for the polymerization of naphthalene [25]. The recovered amorphous products contained a considerable amount of nitrogen bonded to both sp^3 and sp^2 carbons [25]. The temperature-induced chemical reaction of 2,3-Nap was reported at >523 K at 0.5 and 1.0 GPa, and >548 K at 1.5 GPa [38]. The reaction products were investigated by using gas chromatograph-mass spectrometry (GC/MS) and matrix-assisted laser desorption/ionization (MALDI) Time of Flight (TOF) mass spectrometry (MS), and cleavage of the aromatic ring and release of nitrogen atoms with the formation of o-xylene and o-tolunitrile were indicated. In addition, the decomposed products reacted with the remaining 2,3-Nap to form larger oligomers. The N-N bond in the aromatic ring accelerated reactions to decompose the molecule and to oligomerize at lower temperatures than those typically reported for pure aromatic hydrocarbon oligomerization reactions. In the 1,5-Nap molecule, nitrogen atoms are located in separate aromatic rings (Figure 1) and the molecule possesses a center of symmetry and belongs to the point group C_{2h} [39] in contrast to 2,3-Nap. In this study, polymerization of 1,5-Nap under HPHT conditions was experimentally investigated at temperatures between 473-623 K and at pressures of 0.5 GPa and

1.5 GPa. Complex reaction products including soluble dimers and heavier oligomers, and insoluble hydrogenated carbon nitride were identified and were evaluated analytically to reveal the details of the reaction process and nitrogen behavior during the reaction.

Experimental

1,5-naphthyridine ($C_8H_6N_2$, Tokyo Chemical Industry Co. LTD., purity >98 %) and naphthalene ($C_{10}H_8$, Sigma-Aldrich, purity >99.7%) for about 10-20 mg was used as the initial material for the HPHT experiments. A gold sample capsule with 4 mm outer diameter was cleaned with acetone or dichloromethane and heated in an oven at 450 °C for 4 h prior to encapsulating the sample to remove organic contaminants. The sample was welded shut following which the capsule was pressurized using a piston-cylinder apparatus equipped with a hydraulic press and tungsten carbide rams and compression ring. A cylinder with 4 mm inner diameter was used without a pressure medium. The sample was first compressed to the target pressure at room temperature and then heated using a band-type external heater surrounding the cylinder. The temperature was measured using a K-type thermocouple attached to the top of the cylinder. The details of the apparatus were described in a previous study [38]. The reaction time for all experiments was fixed at four hours.

The samples after the HPHT experiments were recovered from the capsules in distilled dichloromethane solvent to prevent the reaction products from escaping. The solution was initially

filtered by carbon-free glass filter to extract soluble products from insoluble products. The carbon, nitrogen and hydrogen contents of the reaction products were analyzed using an elemental analyzer (Vario EL cube; Elementar Analysensysteme GmbH) for the soluble samples after evaporating the solvent and for the insoluble samples. IR spectra of the soluble reaction product were obtained in solid-state after drying in a vacuum desiccator ensuring that the solvent and the stating material were removed. Both soluble and the insoluble products were pelletized with KBr plates and IR absorption spectra in the mid-IR region were measured. A Fourier transform IR spectrometer (FT-IR: FTIR-6100/IRT-5000; Jasco) was used equipped with a globar source, a KBr beam splitter, and a liquid nitrogen cooled mercury cadmium telluride (MCT) detector. The typical aperture size was 50 × 50 μm. The wavenumber resolution was set to 4 cm^{-1}.

For soluble products, mass spectrometry was performed using a GC/MS (JMS-K9; JEOL Co.) equipped with a 30 m × 0.25 mm I.D. capillary column, with a 0.25 μm layer of stationary phase (HP-5, Agilent Technology Co.). The GC column temperature was programmed as in our previous studies [38, 40]. A GC-flame ionization detector (GC/FID, GC-2014; Shimadzu) equipped with an HP-5 capillary column was used for quantitative analysis of the remaining 1,5-Nap and the reaction products. The GC column temperature was programmed as in the GC/MS measurements. Methyl laurate ($C_{13}H_{26}O_2$), methyl stearate ($C_{19}H_{38}O_2$), and methyl triacontanate ($C_{31}H_{62}O_2$) were used as internal standards for GC/FID and GC/MS analyses. The mass spectra

127 of the reaction products were also analyzed using a MALDI-TOF/MS instrument (Ultraflex-III
128 and Autoflex-III, Bruker), with an α-cyano-4-hydroxycinnamic acid (α-CHCA) matrix.

129 Solid-state ^{13}C nuclear magnetic resonance (ssNMR) spectroscopy of the insoluble products
130 were performed with a Varian-Chemagnetic Infinity 300 Nuclear Magnetic Resonance
131 spectrometer. The resonance frequency of ^{13}C was 75 MHz. The insoluble products were loaded
132 into a zirconia oxide capsule (outside diameter of φ5 mm for ^{13}C NMR) with boron nitride inserts
133 to position the small sample in the middle of the RF coil. For the ^{13}C NMR measurement, a ^{1}H-
134 ^{13}C cross polarization with magic angle spinning (CP-MAS) experiment was conducted. The
135 MAS frequencies were 12 kHz. Variable amplitude cross polarization (VACP) was used to ramp
136 up the RF power on the ^{13}C channel during the CP contact time. The ^{1}H 90º excitation pulse length
137 was 4 μs. A variable contact time (form 1 to 12 ms) CPMAS experiment was performed in order
138 to optimize signal and minimize distortion due to variation in C-H distances, the optimum ^{1}H-^{13}C
139 contact time for maximum signal for both sp^2 and sp^3 carbon was found to be 4.5 ms. In order to
140 achieve adequate signal to noise the number of acquisitions was 80,000×4times with a recycle
141 delay of 1s, thus each sample spectrum required ca. 4 days of signal acquisition. The chemical
142 shift of ^{13}C NMR spectra were calibrated by solid hexamethylbenzene that was referenced to
143 tetramethylsilane (TMS).

144 **Results**

1. P-T conditions of the chemical reaction.

The HPHT experiments with 1,5-Nap performed at 0.5 and 1.5 GPa, and at temperatures ranging from 473 to 623 K are listed in Table 1. In addition, a HPHT experiment of naphthalene at 1.5 GPa and 623 K was performed for comparison. During the HPHT experiments of 1,5-Nap at 0.5 GPa, the stroke of the piston discontinuously increased when the temperature reached around 533 K, implying melting of 1,5-Nap. In contrast, such a discontinuity was not observed during the heating at 1.5 GPa up to 623 K, suggesting 1,5-Nap remained as a solid at 1.5 GPa.

Figure 2 and table 1 show the remaining percentage of 1,5-Nap as determined by GC/FID analysis of the recovered samples. At 0.5 GPa, the percentage of recovered 1,5-Nap decreased to around 75 %, initial, after heating at 523 K and 548 K. In addition, the solution of the recovered samples changed to yellow, while the solution of starting material was transparent. These results indicate that the chemical reaction starts around that temperature to form soluble reaction products. After heating at >573 K, the remaining 1,5-Nap decreased to < 6 %, and a black insoluble product was observed in a brown solution indicating that the chemical reaction progressed significantly to form both soluble and insoluble products. 1,5-Nap is nearly absent after heating at 598 and 623 K, and insoluble solid product formed but the solution of these samples was transparent suggesting most of the soluble reaction products were now in the insoluble solid phase. At a pressure of 1.5 GPa, most of the 1,5-Nap still remained unreacted after heating at <573 K. The

163 remaining 1,5-Nap decreased to approximately 60 % after heating at 598 K and dropped further
164 to ~ 5 % after heating at 623 K with both soluble and insoluble product clearly evident. The results
165 indicate the thermal onset of chemical reaction of 1,5-Nap was above 523 K at 0.5 GPa, and above
166 548 K at 1.5 GPa, namely the required reaction temperature increases with increasing pressure.
167 In contrast, most of naphthalene was recovered after heating at 1.5 GPa at 623 K and reaction
168 products were not detected.

169 **2. The soluble products**

170 The elemental analysis of the soluble product from 1.5 GPa, 623 K showed N/C and H/C ratio
171 as 0.242 ± 0.002 and 0.762 ± 0.046, respectively which was nearly equal to that of the starting
172 material (N/C = 0.249 ± 0.001, H/C = 0.720 ± 0.054) suggesting nitrogen and hydrogen atoms
173 are very largely retained in the reaction products. FT-IR analysis reveals some IR peaks in the
174 soluble products (Figure 3a, b) that are comparable in frequency with those observed from the
175 starting material [39]. For example, the C-H bending modes at around 820, 840, 1110, 1190, 1220
176 cm^{-1}, ring stretching modes at around 1300, 1400, 1490, and 1590 cm^{-1}, C-H stretching modes at
177 around 3000-3100 cm^{-1} were obtained from the soluble products while the width of the peaks
178 became broader than those in the IR spectrum of the initial material. In contrast, a significant
179 decrease in the intensity of the skeletal deformation mode absorbance at around 1018 cm^{-1} was
180 observed. It is clear that aromatic rings remain even in the reaction products, although as they are

181 now polymerized. In addition, new peaks were detected in the spectra of the reaction products.

182 The peaks observed at 1350 and 1450 cm^{-1} are interpreted to be sp^3 C-H bending modes, and the

183 peaks at 2850, 2930, and 2960 cm^{-1} are fundamental C-H stretching modes associated with sp^3

184 carbon [41-42]. The peaks appeared at around 730 and 790 cm^{-1} are assigned to N-H wagging modes

185 and a new peak near 1620 cm^{-1} is likely a N-H bending mode. Finally, the broad peak spanning

186 3230 and 3320 cm^{-1} is likely due to fundamental N-H stretching modes [41].

187 A considerable number of dimers were detected by GC/MS and GC/FID analysis of the

188 soluble reaction products. The mass number and possible molecular structure of the reaction

189 products were estimated by the clearly identified molecular ions in all of the mass spectra. Figure

190 4a, b shows representative total ion chromatogram (TIC) at 1.5 GPa, 623 K and 0.5 GPa 573 K.

191 Four isomers of $[M]^{\bullet+}$ = 258 were detected (Figure S1a), which were likely to be formed by

192 naphthylation, defined as dimerization with dehydrogenation. Products of $[M]^{\bullet+}$ = 260 (Figure

193 S1b) were also detected, with a molecular ion mass consistent with exactly twice of that of 1,5-

194 Nap indicating those products formed by dimerization without release of any atoms, e.g.,

195 hydrogen. Several products which has $[M]^{\bullet+}$ = 262 and 264 were detected (Figure S1c and S1d,

196 respectively), which interpreted to be dimers of 1,5-Nap with hydrogeneration of 2H's and 4H's,

197 respectively. Hence, the major reaction products of dimers are classified as three types,

198 naphthylation (2M-2H), exact dimerization (2M), and hydrogenation dimerization (2M+2H,

2M+4H). Reaction products with $[M]^{\bullet+}$ = 386, 388 and 392 were also detected, which are likely trimers formed by combination of these three types of reaction. The hydrogenation of 1,5-Nap was also suggested by the presence of a product with a molecular ion $[M]^{\bullet+}$ = 134 (Figure S2a) detected in the recovered samples from >523 K, at 0.5 and 1.5 GPa (Table S1). In addition, minor peaks with $[M]^{\bullet+}$ = 236, 250 were also detected. These are interpreted to form by the partial ring opening with release of two or one carbon atom(s) from the dimer. Minor peaks with $[M]^{\bullet+}$ = 276, 278 were also detected, which could be methylation products of $[M]^{\bullet+}$ = 262, 264. Methylation might occur when the released carbon by the partial ring opening dimers reacts with simple dimers.

The approximate molar yields of the several dimers were roughly quantified using the peak area of the chromatogram relative to that of an internal standard (methyl stearate) measured by GC/FID. The response factor of 1,1'-biphenyl was used for the quantification, whose structure was regarded as being similar to that of the naphthylation dimers. Table S1, Figure 5a and 5b shows the molar yield of the representative reaction products, in which sum of four isomers of $[M]^{\bullet+}$ = 258, three isomers of $[M]^{\bullet+}$ = 260, seven isomers of $[M]^{\bullet+}$ = 262, five isomers of $[M]^{\bullet+}$ = 264, five isomers of $[M]^{\bullet+}$ = 276, 278, and one each for products $[M]^{\bullet+}$ = 236, 250 were included. The dimers were detected above 523 K at 0.5 GPa, the total molar yields increasing with increasing temperature up to 548 K. With increasing temperature above 573 K the total molar yields of dimer decreases relative to that of lower temperatures. At 1.5 GPa, the dimers were

217 detectable above 548 K and the total molar yields increase with increasing temperature up to 623
218 K. Figure 5c and 5d presents the relative ratio of the reaction products from 523-573 K at 0.5 GPa
219 and from 598, 623 K at 1.5 GPa, respectively, in which total molar yields of the dimers excess
220 1 %. At 0.5 GPa, relative concentration of $[M]^{\bullet+}$ = 258 decreased with increasing temperature,
221 while those of $[M]^{\bullet+}$ = 262, 264 increased. In contrast, the proportion of $[M]^{\bullet+}$ = 258 slightly
222 increased and $[M]^{\bullet+}$ = 264 decreased with increasing temperature to 623 K at 1.5 GPa. These
223 results suggest that hydrogenation occurs more frequently at lower pressure. Molecules with $[M]^{\bullet+}$
224 = 236, 250 and $[M]^{\bullet+}$ = 276, 278, which are products interpreted to form with ring opening, were
225 detected only 573, 598 K at 0.5 GPa, and 598, 623 K at 1.5 GPa (table S1) and the relative
226 percentage is much less than that of the products with $[M]^{\bullet+}$ = 258, 260, 262, and 264. The ring-
227 opening reaction is, therefore, considered to be a minor reaction. The proportion of sum of $[M]^{\bullet+}$
228 = 236, 250, 276, and 278 are on the order of 8 % at 0.5 GPa 573 K, where this sum is on the order
229 of 1 % at 1.5 GPa 623 K even though the remaining percentage of 1,5-Nap were similar so the
230 reaction progress was in both cases similar in rate. These results suggest that the ring-opening
231 reactions preferentially occur at lower pressure.

232 Figure 6 presents a representative MALDI-TOF/MS spectrum of the sample recovered
233 from 1.5 GPa, 573 K and the inset shows enlarged view of ions in the range of *m/z* = 250-290.
234 Intense peaks of *m/z* = 259-269 were detected, and the molar weight was comparable that of the

235 dimers of 1,5-Nap detected by the GC/MS, while some of the peaks in MALDI-TOF spectra were
236 likely $[M+H]^{\bullet+}$ ions, a common feature of MALDI-TOF/MS. In addition, peaks of m/z = 275-279
237 were detected. These peaks might be $[M+H]^{\bullet+}$ ions of methylation products of the 1,5-Nap dimers.
238 The series of clusters appear periodically approximately 130 mass units apart which was
239 comparable to the molar weight of the starting material. Molecular clusters are observed up to
240 masses in excess of *m/z* = 2000. Each cluster are reasonably interpreted to represent dimers,
241 trimers, and higher oligomers up to N=15.

242 **3. The insoluble hydrogenated carbon nitride polymer**

243 A considerable amount of insoluble hydrogenated carbon nitride polymer was obtained from the
244 recovered samples from >573 K at 0.5 GPa and >598 K at 1.5 GPa (as discussed above). The
245 elemental analysis of the insoluble products from 1.5 GPa at 623 K shows that the N/C = 0.2476
246 ± 0.0003. The N/C ratio is comparable with that observed in the starting material indicating that
247 selective release of nitrogen had scarcely occurred. H/C ratio of the insoluble products was 0.653
248 ± 0.015, which is lower than that of the initial material and the soluble products and indicates a
249 loss of ca. 13 % hydrogen. Figure 3 c, d presents the IR spectra of the insoluble materials from
250 1.5 GPa at 623 K and 0.5 GPa at 623 K, respectively. Many of the IR peaks appears at
251 wavenumbers similar to those in the soluble product (Fig. 3b) although the peak widths and
252 relative intensities are slightly different. The peak absorbance between 1100-1600 cm^{-1} is larger

than from soluble product suggesting the formation of a broad peak in this region underlying the sharper vibrational peaks. These results suggest that the soluble and insoluble products are both formed in a series of polymerization reactions, but the insoluble products are likely formed from additional polymerization reactions beyond that which formed the oligomerized soluble products. This is evident as H/C ratio of the insoluble products is lower than that of the soluble products by 13 %, implying that polymerization with dehydrogenation account for large percentage of the solid products.

We measured ^{13}C ssNMR spectra of the starting material and the insoluble reaction products obtained from 0.5 GPa, 623 K, and 1.5 GPa, 623 K. A spectrum of pure 1,5-Nap was acquired but suffered from very long spin-lattice (T_1) relaxation times and poor cross polarization dynamics (i.e., long T_{CH} and short $T_{1\rho}$) resulting in a frustratingly low S/N ratio. Nevertheless, three of the four magnetically inequivalent carbon nuclei are clearly observed as very sharp peaks at 124.5 (carbons 3 & 7), 137.5 (carbons 4 & 8) and 151.5 ppm (carbons 2 & 6) were detected in the ^{13}C ssNMR spectrum of pure 1,5-Nap, all of which are assignable as sp^2 carbon (Figure S3). Interestingly, we could not detect the bridgehead carbon atoms (9 & 10) predicted to be at ~ 144 ppm, this is likely due to the lack of protonation and poor ^{1}H-^{13}C cross polarization efficiency. The peak areas of the three peaks that are observed are essentially equal (given the low S/N) as expected (the 9 & 10 bridgehead carbon atoms would be expected to be equal in intensity to the

other three carbon types).

In the ^{13}C ssNMR spectra of the insoluble products, both sp^3 (major in abundance) and sp^2 carbon (minor in abundance) are detected (Figure 7). The sp^3/sp^2 ratio was determined to be 0.14 based on the peak areas in the ^{13}C ssNMR spectra; where a pressure dependence on this ratio was not observed. The sp^2 region of the ^{13}C ssNMR spectra could be adequately fit by four broad peaks at frequencies around 122, 136, 142, and 151 ppm (Figure S4a and S4c) that likely correspond to the 3 & 7, 4 & 8, 9 & 10, and 2 & 6 carbon atoms of the 1,5-Nap precursor, respectively. Variable contact time experiments show that the peak at 142 ppm has a cross polarization rate time constant (T_{CH}) of 950 µs, whereas the 122 pm peak has a T_{CH} of 540 µs; the larger value of T_{CH} for the 142 ppm peaks is consistent with the assignment of bridge head carbon that is more distant from protons. Whereas the four magnetically inequivalent carbon types in 1,5-Nap "monomer" would be expected at equal intensities, integration of the four peaks that dominate the sp^2 carbon region for the insoluble solids reveals differences in the percent contribution of certain carbons to the total sp^2 region. For example, 0.5 GPa solids, peaks at 151 and 136 ppm (likely corresponding to the 2 & 6 and 4 & 8 carbons in the 1,5-Nap "monomer") are considerably weaker than that of the 142 and 122 ppm peaks (likely corresponding to the 9 & 10, bridge head, carbons and the 3 & 7 carbons) (Table S2a). In the case of the 1.5 GPa solids, peak intensity at 136 ppm (the 4 & 8 carbon atoms) is significantly weaker than the other three

peaks (Table S2b). Such selective reductions in intensity of certain carbon peaks may signify which of the initial 1,5-Nap carbon atoms are involved in the pressure and temperature induced formation of polymeric linkages.

The peaks corresponding to sp^3 carbon (0 to 60 ppm) can be adequately fit with five and four peaks (Figure S4b, d, respectively). The relatively intense peaks at ~ 23, 30, and 38 ppm are consistent with aliphatic carbon (largely CH_3, CH_2 and CH groups, respectively) where the CH_2 groups are predominant in both samples formed at 0.5 GPa and 1.5 GPa. Higher frequency weak peaks at 45, and 54 ppm are consistent with sp^3 carbon bonded to -NH and -N, respectively [41]. These peaks are present in the sample from 1.5 GPa (Figure S4b), although, but reduced in intensity in the 0.5 GPa experimental products (Figure S4d) suggesting that nitrogen atoms are more associated with sp^2 carbon in the lower pressure solid products. A shoulder peak at 13 ppm was observed only from the spectrum from 0.5 GPa, which could be ascribed to CH_3 groups [41]. It is suggested in these two ^{13}C ssNMR spectra that methyl groups intensity is slightly enhanced in the lower pressure solid products.

Discussion

The chemical reaction of 1,5-Nap proceeds significantly above 573 K at 0.5 GPa and above 623 K at 1.5GPa and soluble reaction products revealing oligomerization are readily obtained from the samples recovered from >523 K at 0.5 GPa and >548 K at 1.5 GPa. The insoluble

307 hydrogenated carbon nitride polymer was synthesized from >573 K, at 0.5 GPa, and >598 K at
308 1.5GPa. N/C ratio of the reaction products of both soluble and insoluble products were quite
309 similar with that of 1,5-Nap, indicating that release of nitrogen atoms with chemical reaction was
310 limited with the solids forming reaction in the present temperature ranges and that the nitrogen
311 atom was contained in an aromatic ring and connected only with carbon. In contrast, nitrogen
312 atoms are selectively released from aromatic rings with the oligomerization when two nitrogen
313 atoms were localized in one aromatic ring forming a N-N bonding as in 2,3-Nap [38]. In case of 2,3-
314 Nap, the N-N covalent bond is easily dissociated under high temperature and the aromatic ring
315 was subjected to both nitrogen and carbon opening reactions.

316 The dimers of the reaction products which were detected by the GC/MS analysis of the
317 soluble products clarified into three types of dimerization products, that is naphthylation (2M-
318 2H), exact dimerization (2M), and dimerization with hydrogenation (2M+2H, 2M+4H) products.
319 In contrast, naphthalene dimers were not detected from 1.5 GPa and 623 K in this study and
320 oligomerization with naphthylation of naphthalene was reported at 773 K, 7 GPa and at 820 K,
321 ambient pressure in the previous studies [33-34]. These results indicate that reaction temperature for
322 polymerization was lowered by existence of nitrogen even though naphthylation reactions can
323 occur in both naphthalene and in 1,5-Nap. In case of oligomerization of naphthalene, dimerization
324 with release of 2H and 4H, with formation of condensation products were observed at ambient

325 pressure and high pressure [33, 43-44]. It was pointed out that the cleavage of a carbon-hydrogen bond
326 to produce a highly reactive free radical can initiate polymerization at ambient pressure [43-44]. In
327 contrast, dimerization products with release of 4H were not detected in the present study of 1,5-
328 Nap. Exact dimerization (2M), and dimerization with hydrogenation (2M+2H, 2M+4H) were
329 formed by the 1,5-Nap reaction while these products were not observed in the naphthalene
330 oligomerization [33, 43-44]. The dimerization reaction for 1,5-Nap is, therefore, somewhat different
331 than that observed in case of naphthalene oligomerization. Exact molecular structures are not
332 unambiguously revealed from the mass spectrometry, although the IR spectra (Fig 3) of the
333 soluble reaction products suggested both modest amounts of sp^3carbon and NH functional groups
334 are formed during the reaction. [2+2] and [4+2] Diels-Alder cycloaddition reactions are the likely
335 initiation pathways to form the various dimers including both dehydration and hydrogenation
336 dimers (Figure 8a). The products of $[M]^{\bullet+}$ = 262, 264 would be formed from hydrogenation of the
337 exact dimerization products. Several isomers of the dimers are found so that further studies
338 through theoretical analysis is required to confirm the details of the reaction pathway(s). In case
339 of the pressure-induced reaction of benzene, Diels-Aider reactions are clearly the pathway to form
340 various oligomers [27, 31]. For polymerized benzene, three types of low molecular weight
341 dimerization products are identified, including biphenyl (2M-2H), benzene dimers (2M), and
342 naphthalene (2M-C_2H_4) all formed by the pressure-induced oligomerization of benzene after

343 compression above 13 GPa, room temperature [45]. In contrast, for 1,5-Nap condensed dimers
344 formed with elimination of ethylene were not detected in the reaction products. Elimination of
345 ethylene is evidently limited in the present pressure and temperature ranges. In addition, a
346 hydrogenation product of a molecular ion $[M]^{\bullet+}$ = 134 suggests that hydrogenation without
347 dimerization had also progressed. In the present temperature ranges, hydrogen atoms prefer to
348 remain in the carbon nitride polymer products and even bond with nitrogen atoms. Higher
349 temperatures would be required before large-scale dehydrogenation would occur as has been
350 reported for other aromatic hydrocarbons [33]. Several products formed by ring-opening and
351 methylation were detected, although those quantities were remarkably small compared with that
352 of the three types of dimerization, thus are very minor side reactions.

353 ^{13}C ssNMR spectral analysis of the insoluble products indicate that the sp^3/sp^2 ratio is
354 small, on the order of 0.14. For the purpose of this discussion, consider a proposed "infinite" 1,5-
355 Nap insoluble polymer formed exclusively through 3,4-7,8 [2+2] cycloaddition linkages as shown
356 in Figure 8b; where the corresponding sp^3/sp^2 ratio would be 1.0. This is much higher than what
357 is measured. If 100 % dehydrogenation ($-H_2$) occurred (let's say at the respective 7,4 carbons)
358 yielding a purely "bi-naphthrydine" linked polymer (Figure 8c) the sp^3/sp^2 ratio would be zero.
359 It can be easily shown that if 50 % formation of "bi-naphthridine" linkages yields an sp^3/sp^2 ratio
360 of 0.33. The ^{13}C ssNMR data, therefore, reveal that the polymer contains both the cycloaddition

361 linkages (Figure 8b) and bi-naphthyridine linkages (Figure 8c) which form by elimination of
362 hydrogen from the decomposition of the cycloaddition linkages in the polymer. Given that the
363 sp^3/sp^2 ratio of the insoluble polymer is measured at 0.14 suggests that around 75 % of the polymer
364 linkages are bi-naphthyridine linkages. The H/C ratio of the insoluble product is 0.65, which is
365 significantly higher than the H/C ratio calculated when the polymer consists of 75 % of the bi-
366 naphthyridine linkages (where H/C would be predicted to be 0.558). The high H/C ratio suggests
367 that CH_2/CH_3 and NH functional groups are also contained in the polymer as is indicated in the
368 IR spectra (Figure 3c, d) and the ^{13}C ssNMR spectra (Figure 7). It is interesting to note that the
369 sp^3/sp^2 ratio of the carbon nitride nanothreads was previously reported to be around 3.5 [28] and in
370 the case of polymer formed from benzene the sp^3/sp^2 ratio is nearly 4.0 (where all of the sp^3 carbon
371 is CH)[31], which is much higher than that in the insoluble material (sp^3/sp^2 = 0.14) characterized
372 in this study (where the sp^3 carbon for the 1,5-Nap polymer is predominantly CH_2) [31].

373 Evidence of polymerization through naphthylation, exact dimerization, and
374 hydrogenation was observed in the recovered samples of both 0.5 and 1.5 GPa. The sp^3/sp^2 ratio
375 as determined through ^{13}C ssNMR of the insoluble products obtained after heating at 0.5 GPa,
376 and 1.5 GPa was nearly the same at 0.14. These results indicate that the major polymerization
377 mechanism(s) is similar at 0.5 GPa and 1.5 GPa, even though the reaction progresses in the liquid
378 phase at 1,5-Nap at 0.5 GPa, and in the solid phase at 1.5 GPa. However, several indications of

pressure dependency on the polymerization are suggested. For example, the reaction threshold temperature was changed from 573 K at 0.5 GPa to 623 K at 1.5 GPa. The reaction threshold temperature of benzene is discontinuously changed with the phase state of the starting monomer, especially between liquid and solid phases [46]. In the case of some aromatic compounds, the onset temperatures of the chemical transformation from solid monomers to polymers decrease or are nearly constant with increasing pressure [30, 46-49]. The change of the reaction threshold temperature of 1,5-Nap between 0.5 GPa and 1.5 GPa would be related with the phase state of the stating monomer. Further *in-situ* experiments on structure and phase state relation of 1,5-Nap are necessary for understanding the effect of pressure on the reaction temperature. Quantitative analysis of the dimers suggested that the hydrogenation reactions preferentially progresses at lower pressure. The reaction products related with the ring-opening are also preferentially detected in the lower pressure experiments. Clear differences in the relative abundance of different sp^2 carbon types are observed via ^{13}C ssNMR as a function of pressure and may indicate differences in the types of monomer linkages. Formation of a minor amount of methyl groups observed via ^{13}C NMR at ~ 13 ppm is indicated in the insoluble products from 0.5 GPa, while methyl groups were not detected (or are minimal) in the insoluble solid material formed at 1.5 GPa. These results imply that ring-opening reactions preferentially occur at lower pressure namely, aromatic rings preferentially remained intact at higher pressure. Further experiments over a wider

range of pressures would be necessary to verify this possibility.

Conclusions

The self-condensation reaction of 1,5-Nap has been investigated at pressures of 0.5 and 1.5 GPa and temperatures ranging from 473 up to 623 K using a piston-cylinder-type high-pressure apparatus. The amount of recovery of unreacted 1,5-Nap significantly decreased in experiments run above 573 K at 0.5 GPa and above 623 K at 1.5GPa. Soluble reaction products were detected from >523K at 0.5 GPa and >548 K at 1.5 GPa, where the products of reaction include dimers, trimers and larger oligomers. Above 573 K at 0.5 GPa and above 598 K at 1.5 GPa, a black insoluble hydrogenated carbon nitride phase was obtained. IR spectra of both soluble and insoluble products suggested that the both products formed by a series of polymerization reactions. The present results indicated that polymerization progressed while maintaining N/C ratio of the 1,5-Nap reaction products in contrast that observed previously in 2,3-Nap, an isomer of 1,5-Nap where extensive N loss is observed [25]. Amongst the soluble products, three major types of the dimerization products were detected, these are products formed from naphthylation, exact dimerization, and dimerization with hydrogenation. Polymerization with naphthylation was also observed with pyrolysis of naphthalene [33, 43], even though the reaction temperature of 1,5-Nap was significantly lower than that observed in the aromatic hydrocarbon [33-34]. The presence of nitrogen atoms in the ring structure significantly lowered the temperature of the polymerization.

415 Polymerization with hydrogenation was observed with the reaction of 1,5-Nap, where such
416 reactions has not been reported in pure aromatic hydrocarbons pyrolysis experiments [33, 43].
417 Whereas [2+2] and [4+2] Diels-Alder cycloaddition reactions are the likely initiation point to
418 polymerization, subsequent dehydrogenation and hydrogenation reactions produces both
419 dehydrogenated and hydrogenated dimers, the methine (CH) rich cyclo-addition products
420 decompose to form predominantly bi-naphthyridine linkages eliminating H_2, thus the sp^3/sp^2
421 ratios and methine carbon content for the 1,5 Nap polymers are very low as compared with other
422 pressure induced aromatic polymerizations. The major reaction mechanism of 1,5-Nap was
423 similar at pressures of 0.5 and 1.5 GPa, although aromatic rings preferentially remained at the
424 higher pressure.
425

426 **Supplemental Information**

427 See the supplemental information
428 Representative mass spectra of the soluble reaction products from the GC/MS analysis, ^{13}C
429 ssNMR spectra of 1,5-Nap, fitting results of the ssNMR spectra from the insoluble products
430 (spectra and a table), and a table for molar yield of the representative dimers.
431

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565 **Figure captions**

566 **Figure 1** Molecular structure of 1,5-naphthyridine (1,5-Nap).

567 **Figure 2** Temperature dependence of the residual ratio of 1,5-Nap at 0.5 GPa and 1.5 GPa (red

568 and blue symbols, respectively), and that of naphthalene at 1.5 GPa 623 K (a black symbol).

569 **Figure 3** Representative IR spectra of (a) starting material, (b) soluble products from 1.5 GPa,

570 623 K, (c) insoluble products from 1.5 GPa, 623 K, (d) insoluble products from 0.5 GPa, 623 K.

571 Black dotted lines: The peaks observed in starting material. Red dotted lines: newly appeared in

572 the reaction products. Str: stretching mode, Bend.: bending mode, Wag.: wagging mode, Def.:

573 skeletal deformation mode

574 **Figure 4** Representative TIC of GC/MS measurements after heating at (a) 623 K 1.5 GPa and (b)

575 573 K, 0.5 GPa. Numbers appeared with peaks represent the *m/z* of molecular ion peak. I.S. (1)

576 and I.S. (2) are the methyl stearate and methyl triacontanoate, respectively used as internal

577 standards. Mass spectra of (a)~(f) are shown in figure S1.

578 **Figure 5** Molar yield of the reaction products (a) 0.5 GPa, (b) 1.5GPa. Residual ratio of 1,5-Nap

579 is indicated above each bar. Relative molar yield of the reaction products for heating at (c) 0.5

580 GPa, (d) 1.5GPa.

581 **Figure 6** MALDI-TOF/MS spectra of the recovered sample from 1.5 GPa, 573 K. The inset

582 represents an enlarged view of the spectrum of 2 mers region at *m/z* = 250-290.

583 **Figure 7** ^{13}C CPMAS ssNMR of the insoluble products from 0.5 GPa, 623 K and 1.5 GPa, 623

584 K.

585 **Figure 8** (a) Possible dimerization pathways with [2+2] and [4+2] cycloaddition reactions. m.w.:

586 molecular weight. Possible linkages of the insoluble polymer with (b) [2+2] cycloaddition linkage,

587 (c) bi-naphthyridine linkage.

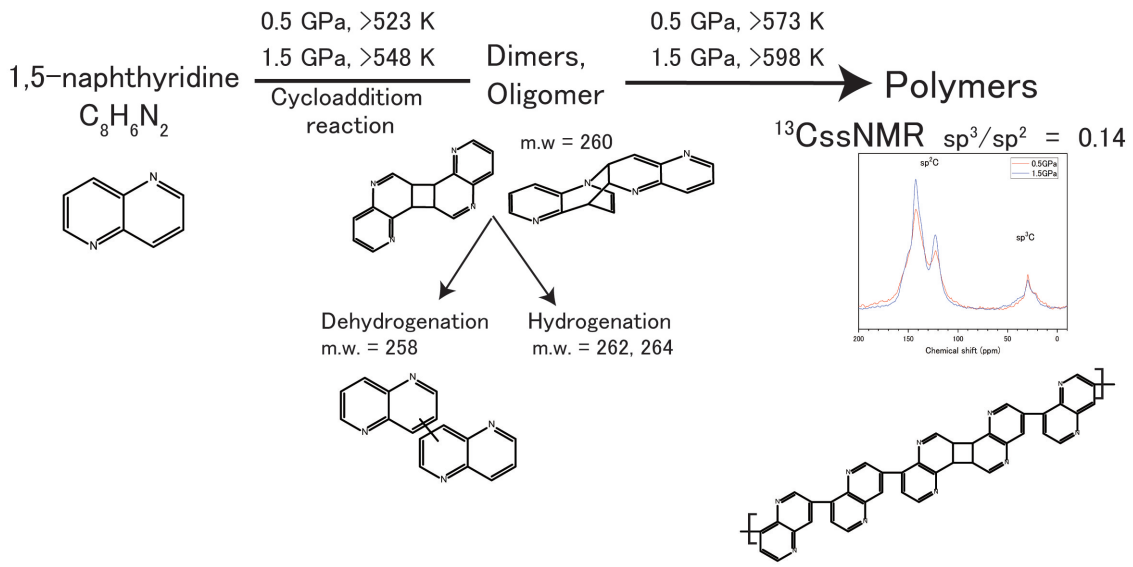
588

Table 1 Experimental conditions of the present study.

no.	Staring material	Pressure (GPa)	Temperature (K)	Remaining 1,5-Nap (%)	Soluble products	Insoluble products
1	1,5-Nap	0.5	473	92.2	-	-
2	1,5-Nap	0.5	523	75.5	+	-
3	1,5-Nap	0.5	548	78.7	+	-
4	1,5-Nap	0.5	573	4.3	+	+
5	1,5-Nap	0.5	598	0.4	±	+
6	1,5-Nap	0.5	623	0.3	±	+
7	1,5-Nap	1.5	473	94.2	-	-
8	1,5-Nap	1.5	523	99.1	-	-
9	1,5-Nap	1.5	548	96.4	+	±
10	1,5-Nap	1.5	573	94.9	+	±
11	1,5-Nap	1.5	598	58.6	+	+
12	1,5-Nap	1.5	623	5.4	+	+
13	Nap	1.5	623	94.1	-	-

1,5-Nap: 1,5-naphthyridine, Nap: naphthalene, +: detected, - not detected, ±: trace amount

TOC Graphic


1,5-naphthyridine
C8H6N2
0.5 GPa, >523 K
1.5 GPa, >548 K
Cycloadditiom reaction
Dimers, Oligomer
m.w = 260
0.5 GPa, >573 K
1.5 GPa, >598 K
Polymers
13CssNMR sp3/sp2 = 0.14
sp2C
sp3C
0.5GPa
1.5GPa
Chemical shift (ppm)
Dehydrogenation
m.w. = 258
Hydrogenation
m.w. = 262, 264

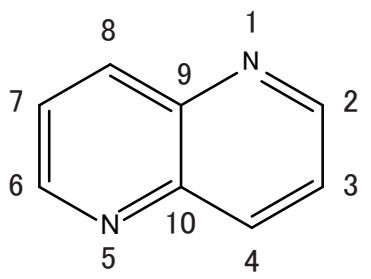


Figure 1

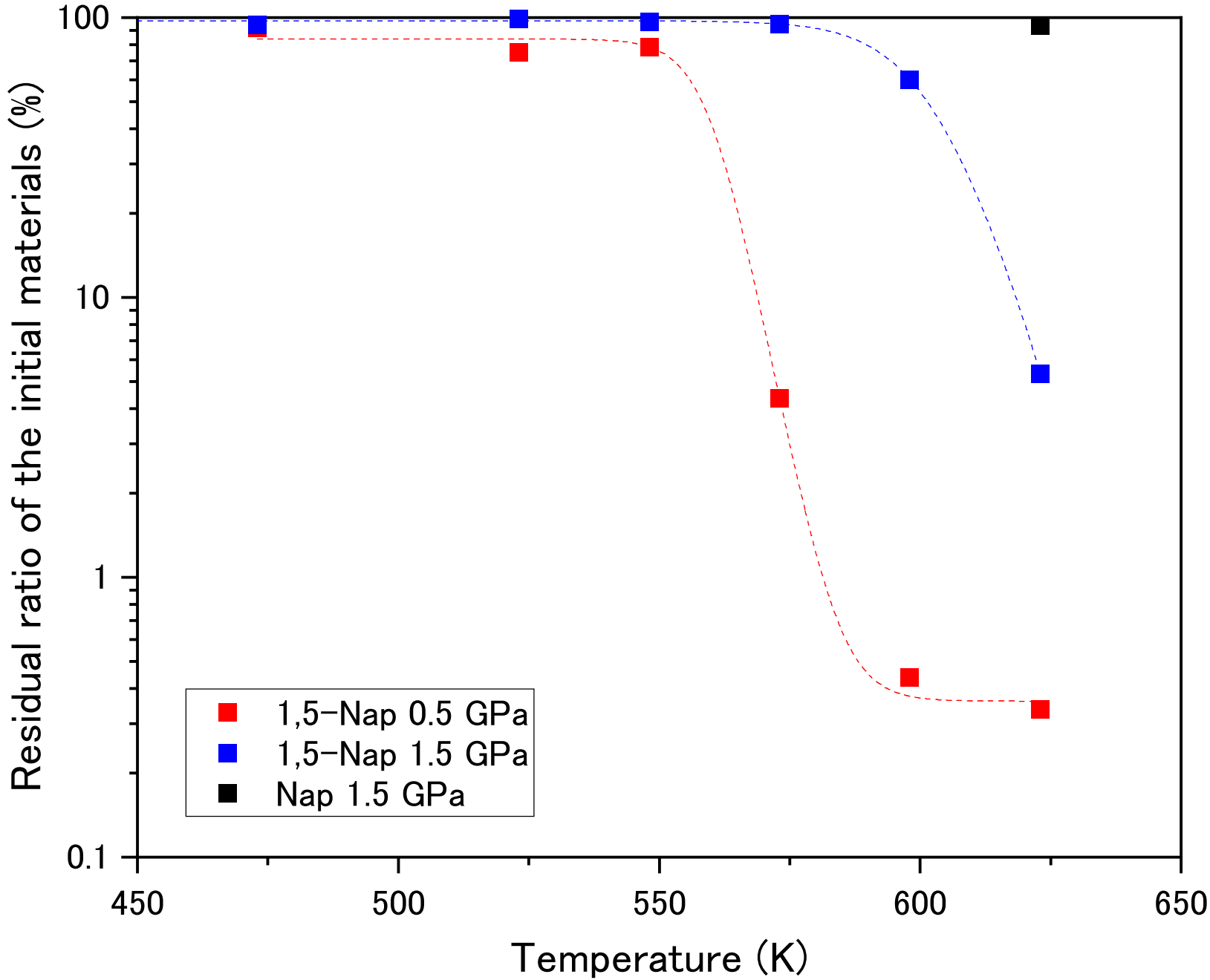

100
10
1
0.1
450
500
550
600
650
Residual ratio of the initial materials (%)
Temperature (K)
1,5-Nap 0.5 GPa
1,5-Nap 1.5 GPa
Nap 1.5 GPa

Figure 2

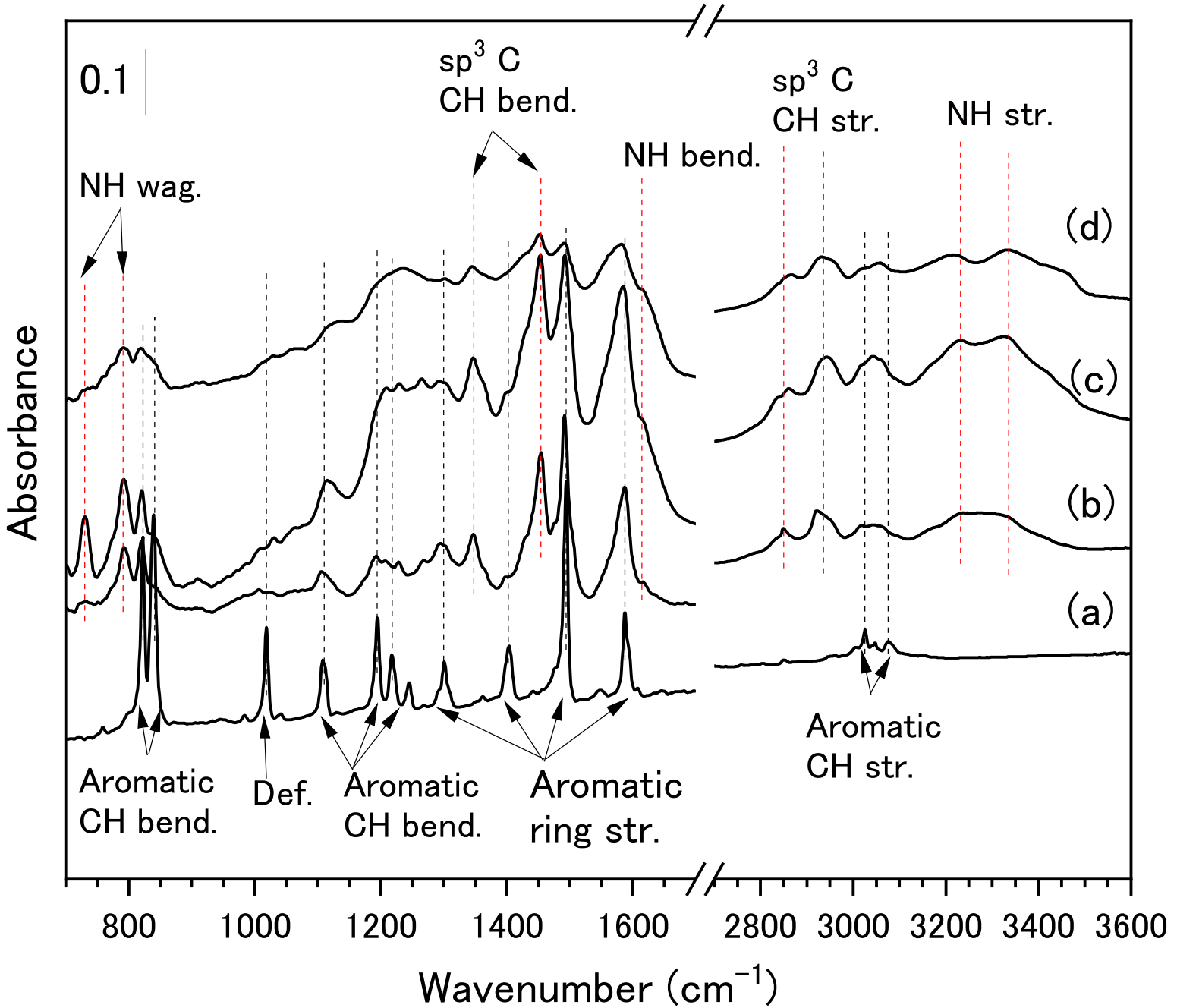

0.1
sp3 C
CH bend.
sp3 C
CH str.
NH str.
NH bend.
NH wag.
(d)
(c)
(b)
(a)
Absorbance
Aromatic
CH bend.
Def.
Aromatic
CH bend.
Aromatic
ring str.
Aromatic
CH str.
800
1000
1200
1400
1600
2800
3000
3200
3400
3600
Wavenumber (cm−1)

Figure 3

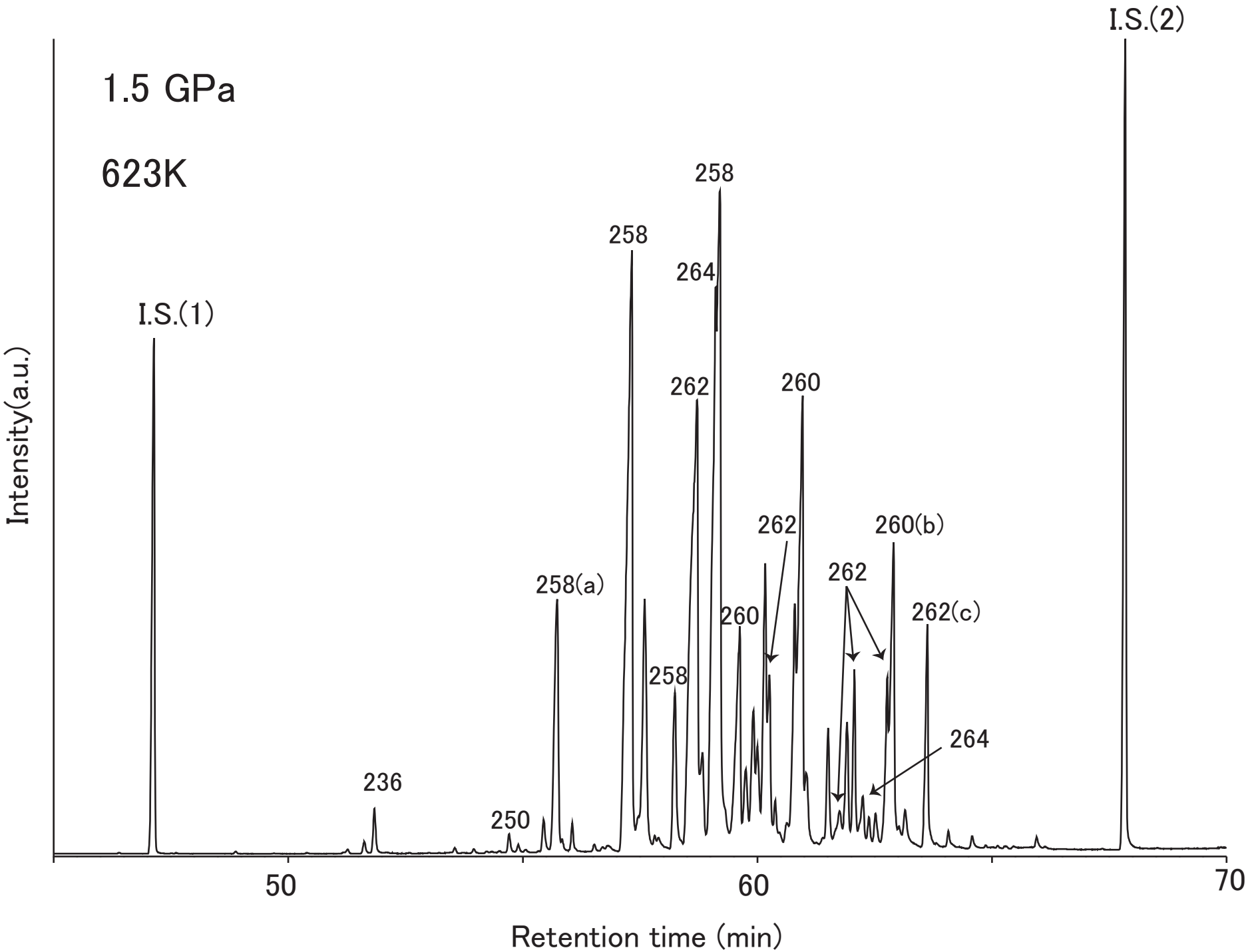

1.5 GPa
623K
I.S.(1)
I.S.(2)
236
250
258(a)
258
258
264
258
262
260
260
262
262
260(b)
262(c)
264
Intensity(a.u.)
50
60
70
Retention time (min)

Figure 4a

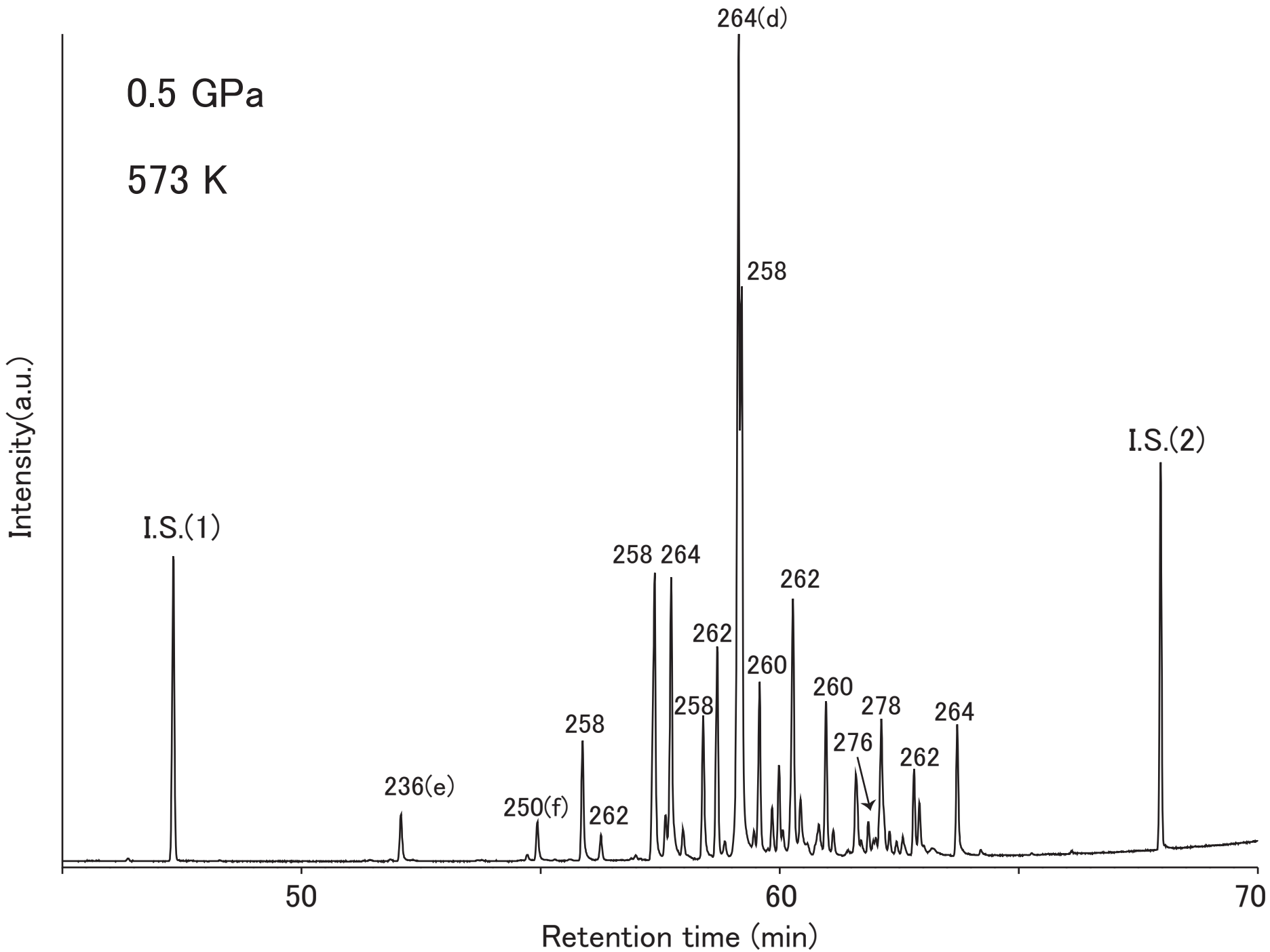

0.5 GPa
573 K
264(d)
258
I.S.(2)
I.S.(1)
258 264
262
262
260
260
258
278
264
258
276
262
236(e)
250(f)
262
Intensity(a.u.)
50
60
70
Retention time (min)

Figure 4b

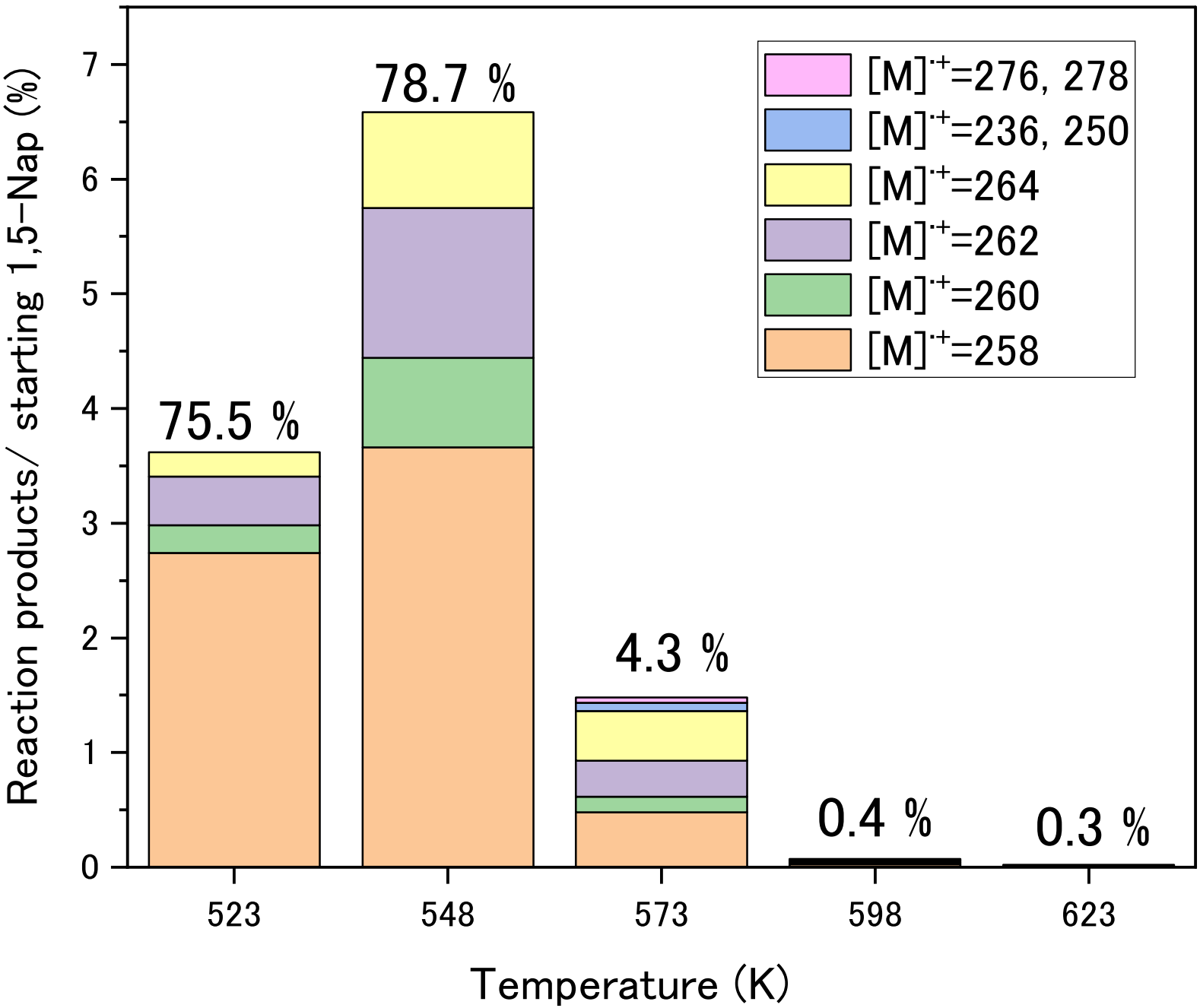

Reaction products/ starting 1,5-Nap (%)
0
1
2
3
4
5
6
7
75.5 %
78.7 %
4.3 %
0.4 %
0.3 %
[M]$^{\cdot+}$=276, 278
[M]$^{\cdot+}$=236, 250
[M]$^{\cdot+}$=264
[M]$^{\cdot+}$=262
[M]$^{\cdot+}$=260
[M]$^{\cdot+}$=258
523
548
573
598
623
Temperature (K)

Figure 5a

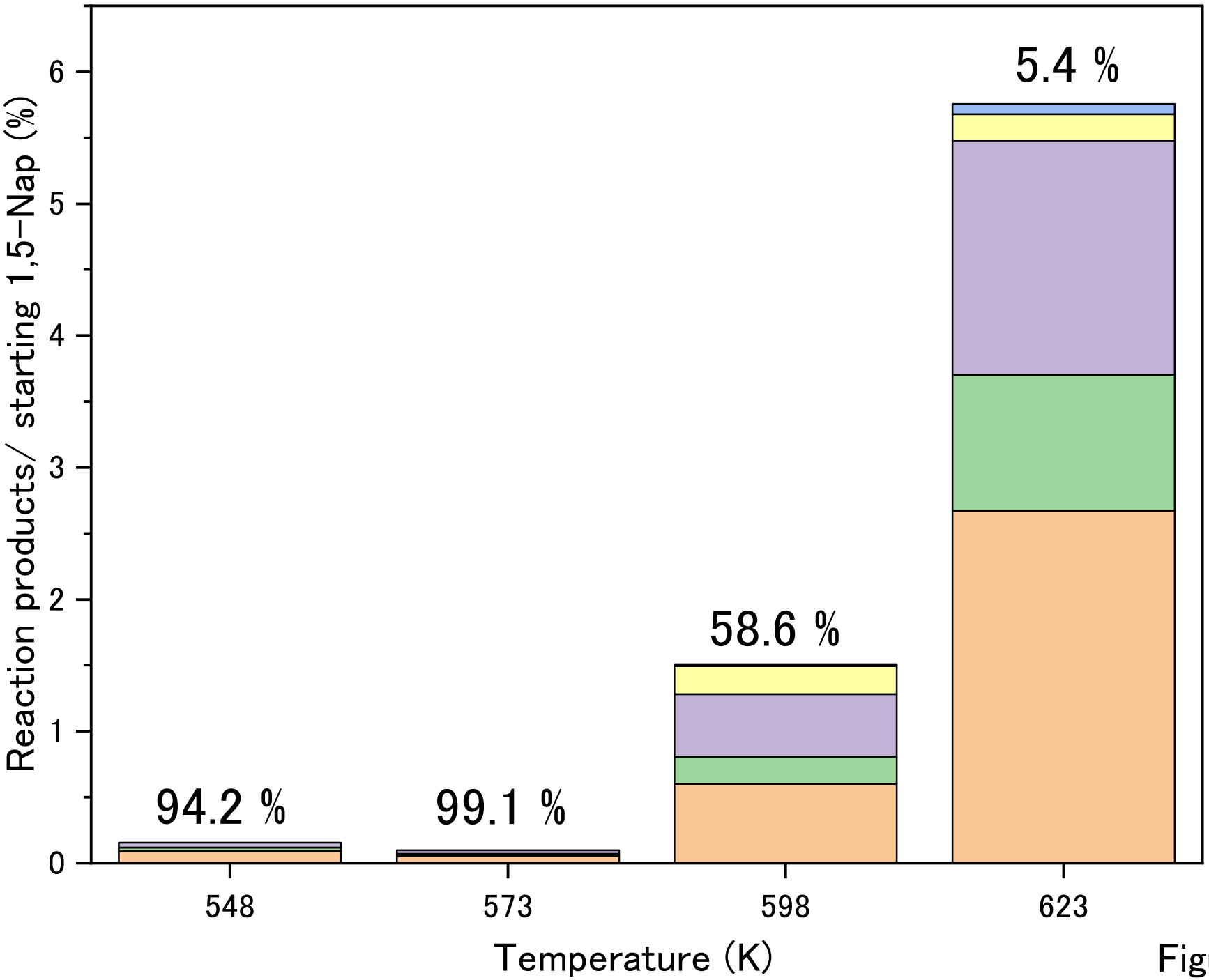

Reaction products/ starting 1,5-Nap (%)
0
1
2
3
4
5
6
94.2 %
99.1 %
58.6 %
5.4 %
548
573
598
623
Temperature (K)

Figure 5b

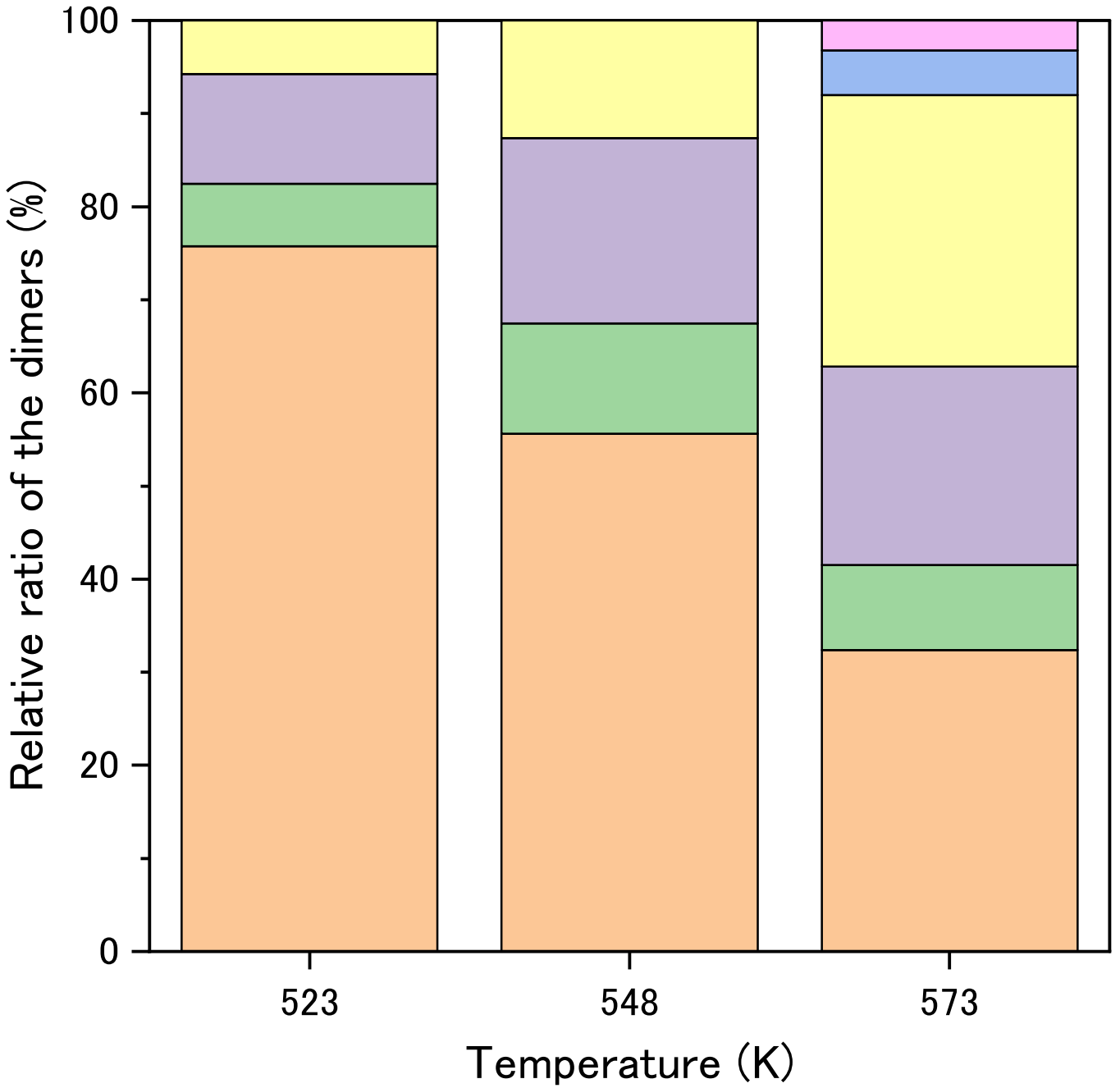

100
80
60
40
20
0
Relative ratio of the dimers (%)
523
548
573
Temperature (K)

Figure 5c

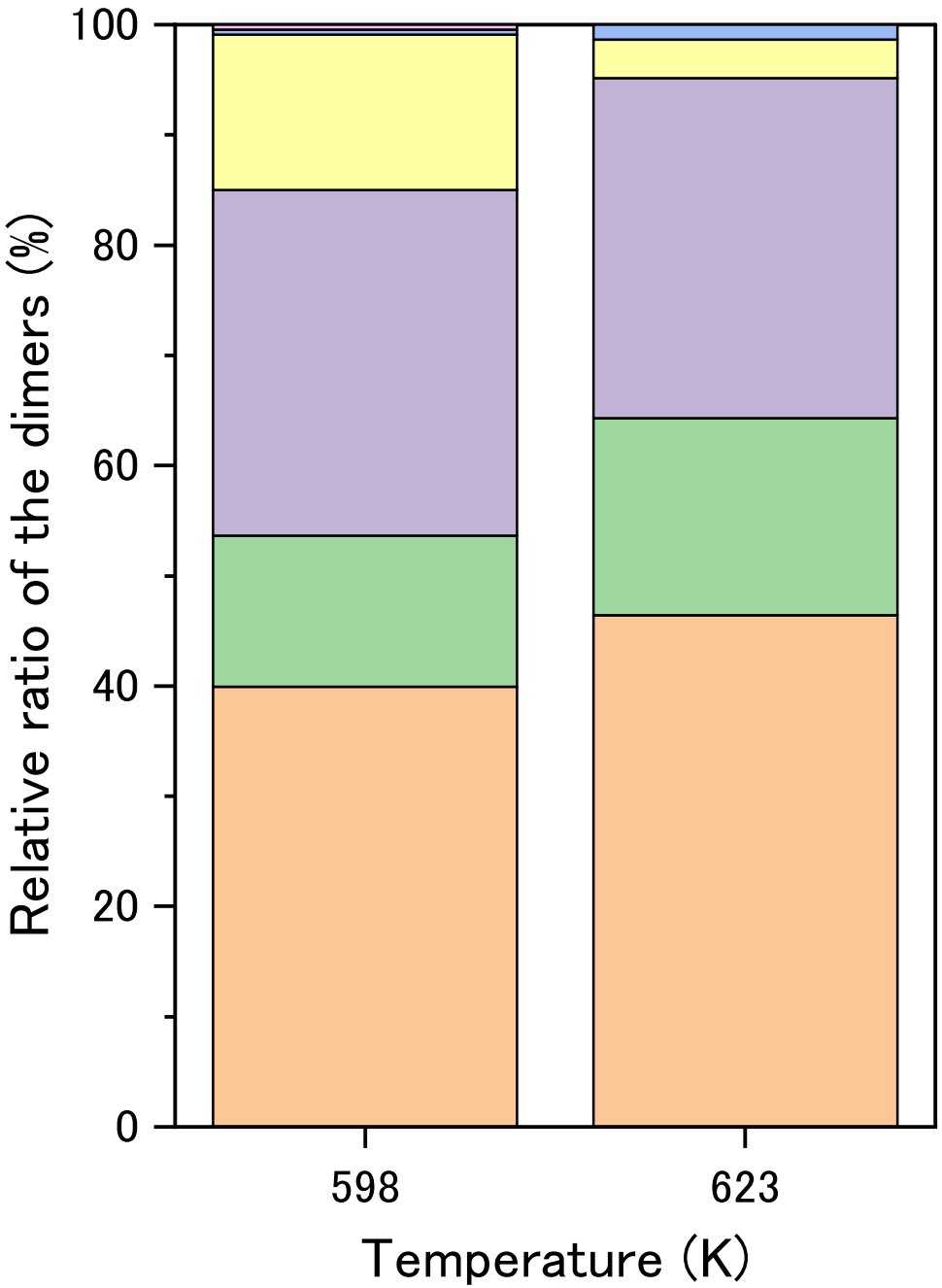

100
80
60
40
20
0
Relative ratio of the dimers (%)
598
623
Temperature (K)

Figure 5d

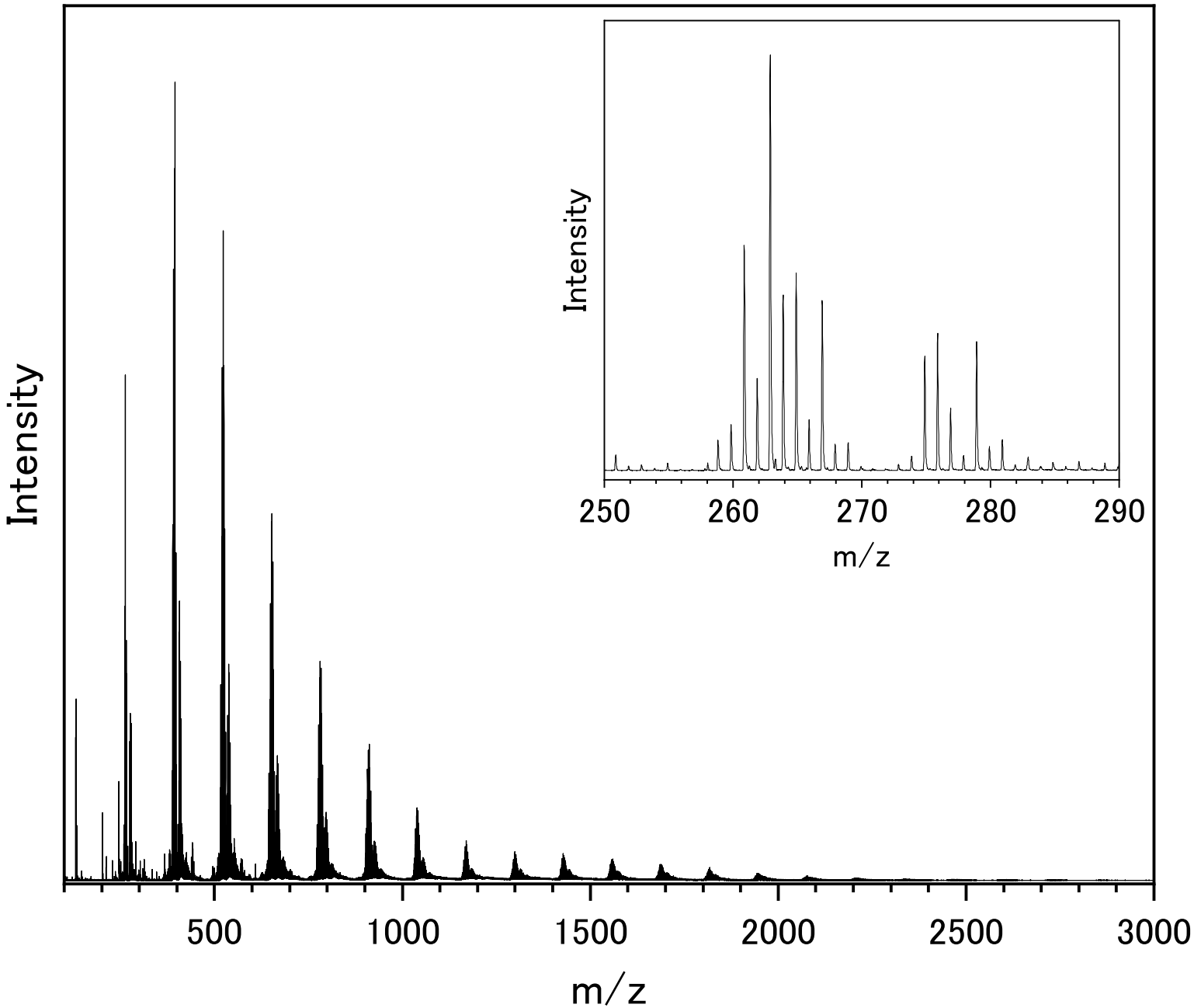

Intensity
500
1000
1500
2000
2500
3000
m/z
Intensity
250
260
270
280
290
m/z

Figure 6

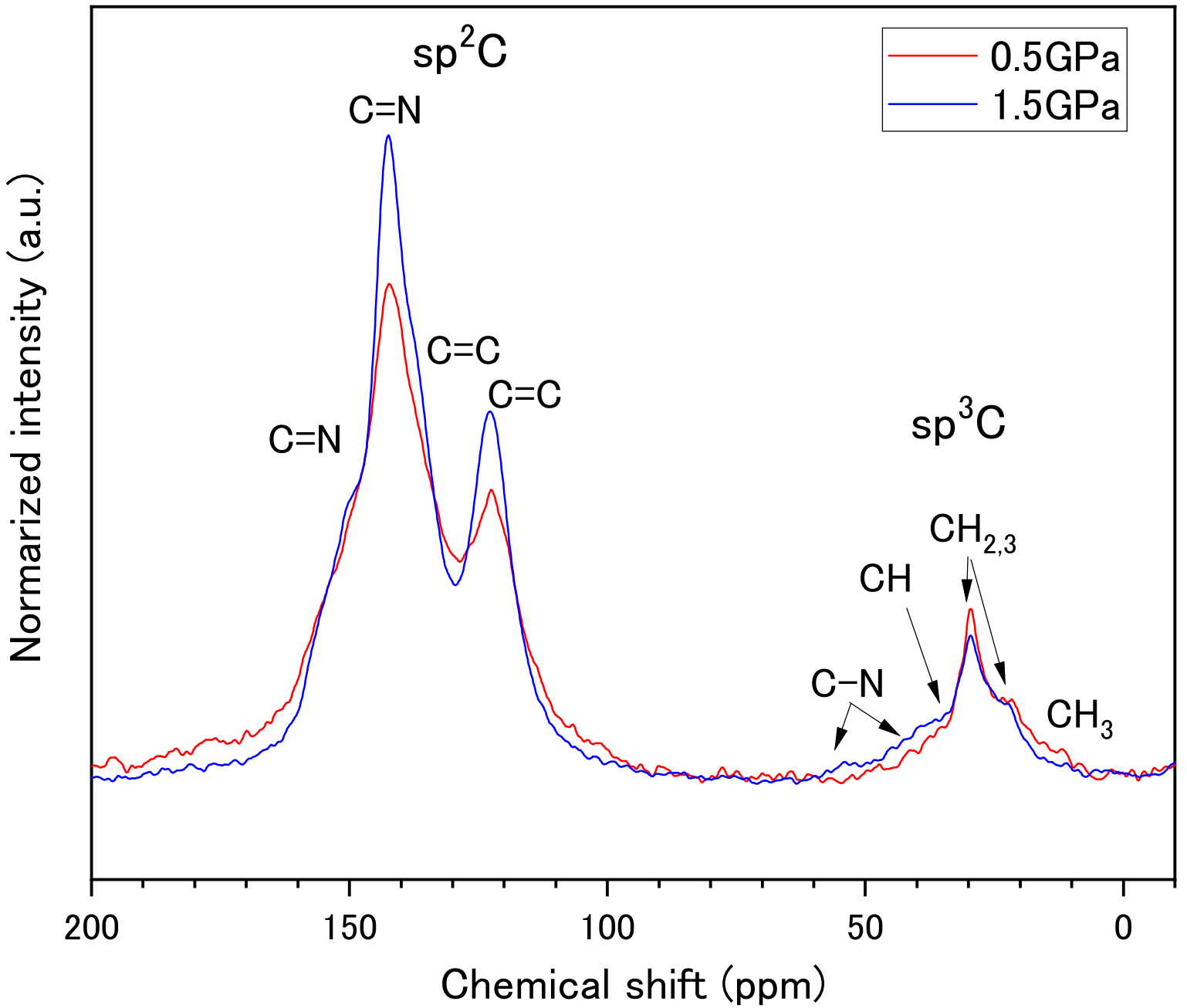

sp2C
C=N
C=N
C=C
C=C
sp3C
CH2,3
CH
C−N
CH3
0.5GPa
1.5GPa
Normarized intensity (a.u.)
200
150
100
50
0
Chemical shift (ppm)

Figure 7

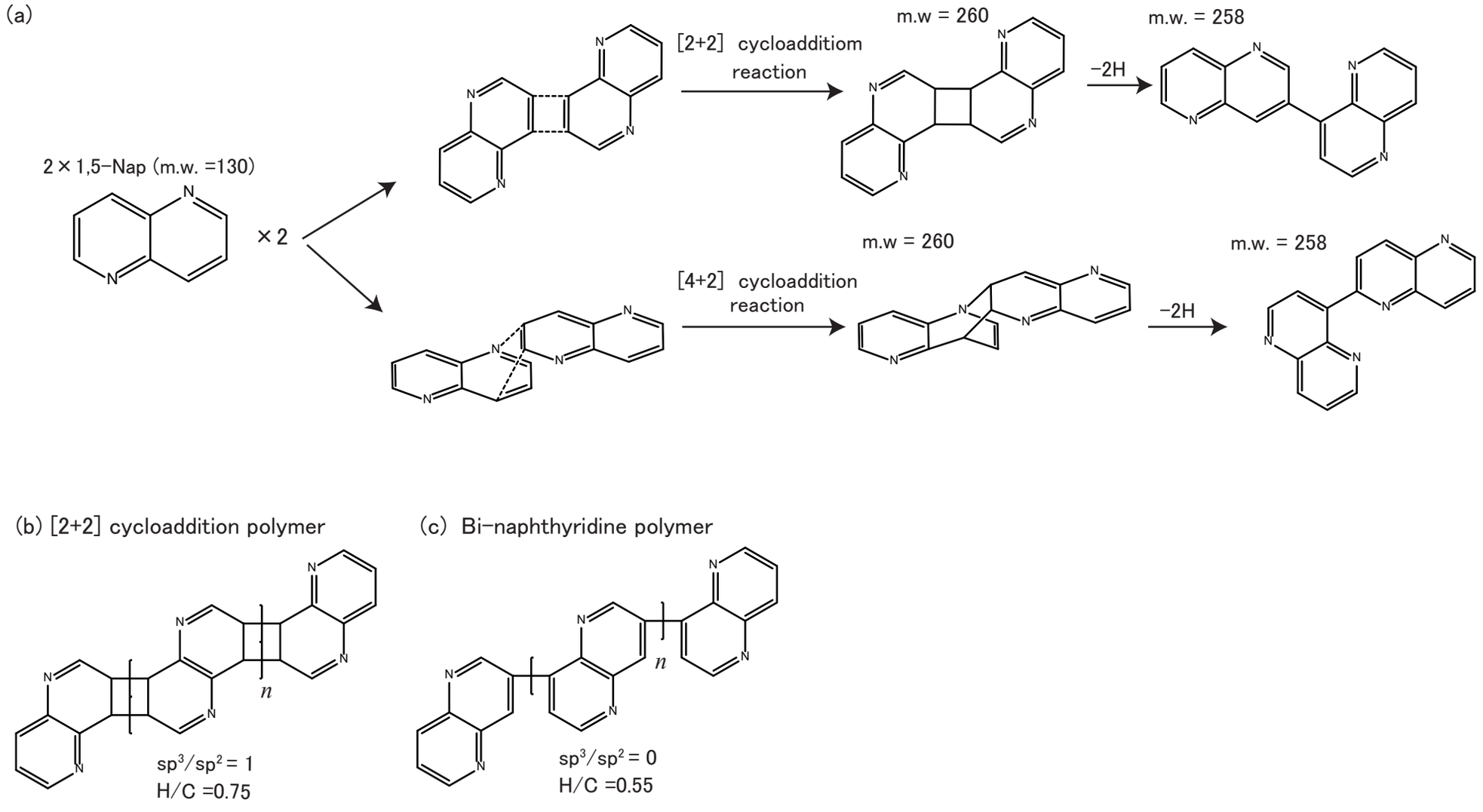

(a)
2 × 1,5-Nap (m.w. =130)
× 2
[2+2] cycloadditiom reaction
m.w = 260
−2H
m.w. = 258
[4+2] cycloaddition reaction
m.w = 260
−2H
m.w. = 258
(b) [2+2] cycloaddition polymer
n
sp3/sp2 = 1
H/C =0.75
(c) Bi-naphthyridine polymer
n
sp3/sp2 = 0
H/C =0.55

Figure 8