ADVANCED MATERIALS

Supporting Information

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Phase-Separation-Induced Anomalous Stiffening, Toughening, and Self-Healing of Polyacrylamide Gels

*Koshiro Sato, Tasuku Nakajima, Toshiyuki Hisamatsu, Takayuki Nonoyama, Takayuki Kurokawa, and Jian Ping Gong**

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Phase Separation-Induced Anomalous Toughening and Self-healing of Polyacrylamide Gels

Koshiro Sato, Tasuku Nakajima, Toshiyuki Hisamatsu, Takayuki Nonoyama, Takayuki Kurokawa, Jian Ping Gong*

K. Sato, T. Hisamatsu

Laboratory of Soft & Wet Matter, Graduate School of Life Science, Hokkaido University, Kita-10, Nishi-8, Kita-ku, Sapporo, Hokkaido, 060-0810, Japan

E-mail: gong@mail.sci.hokudai.ac.jp

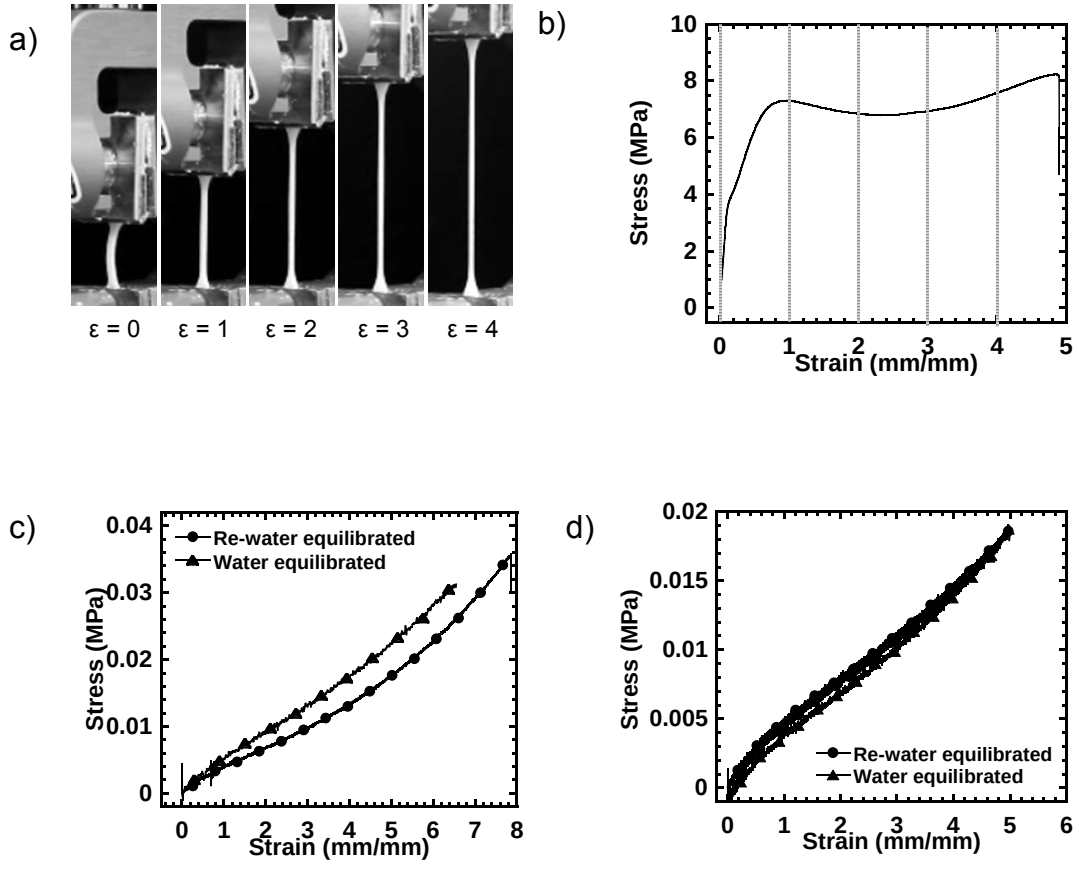
Dr. T. Nakajima, Dr. T. Nonoyama, Dr. T. Kurokawa, Prof. J. P. Gong

Laboratory of Soft & Wet Matter, Faculty of Advanced Life Science, Hokkaido University, Kita-10, Nishi-8, Kita-ku, Sapporo, Hokkaido, 060-0810, Japan

Estimation of solvent fraction in the gels by using NMR: Solvent (DMF-water mixture) in the p-PAAm gels was extracted by immersing small pieces of the gels in methanol-d_4 (CD_3OD) for 6 hours in Ar atmosphere at 25°C. ^{1}H NMR spectra of the extracted solvents were recorded on 400 MHz NMR α400 (JEOL Ltd.) at room temperature. The C_{DMF} in the gels was calculated from number ratio of DMF to water estimated from the peak areas. We used the peaks at 7.97 ppm and 4.87 ppm for CH of DMF and H_2O respectively for calculation of number ratio.[S1] The amount of absorbed water vapor in the preparation process is estimated by the ratio of integral of water peak to one of methanol (proton exchanged, 3.34 ppm). In

each test, absorbed water is calculated from the peak of methanol and subtracted from total integral value of water. The number ratio of DMF to water is converted to weight ratio by the value of molecular weight of the chemicals.

Supporting Figure S1. (a, b) Appearance of a 80p-PAAm gel in tensile deformation and its stress-strain curve. The pictures of the sample during deformation were captured from a movie of the tensile test. The sample never showed clear necking behavior until its fracture despite having the yielding point. (c) Stress-strain curve of water-equilibrated PAAm and re-water- equilibrated 80p-PAAm for comparison of mechanical properties. (d) Loading and unloading tensile test of water-equilibrated PAAm and re-water-equilibrated 80p-PAAm. For clarity, only 1-10% of the data are shown in plots. (e) Loading and unloading tensile test of a 40o-PAAm. Such highly shrunken samples show high value of W_{extf} (~10^{1} MJ m^{-3}) due to large ε_f, however, the hysteresis loss U_{hys} is small (~10^{-1} MJ m^{-3}) unlike tough phase separated gels.



e)

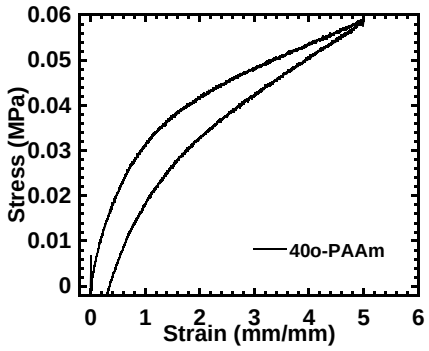

0.06
0.05
0.04
0.03
0.02
0.01
0
Stress (MPa)
0
1
2
3
4
5
6
Strain (mm/mm)
40o-PAAm

Figure S2. Pure shear test of p-PAAm gels. (a) Geometry of notched sample for pure shear test. (b) Experimental photo image of the pure shear test. For both the unnotched sample (left) and notched sample (right), the upper clamp was pulled upward at constant velocity of 100 mm min^{-1} from their initial distance (L_0 = 8mm) between the two clamps, while the lower clamp was fixed. The force-stretch length curves of the samples were recorded. (c) Force-stretch length curves of the unnotched (solid line) and notched (broken line) samples of p-PAAm. The grey area is the work $W(L_c)$ done by the applied force to the unnotched sample at the critical stretching distance L_c that the notched sample start to propagate the crack. L_c was determined by video monitoring. The method is adopted from the literature.[18, 22]

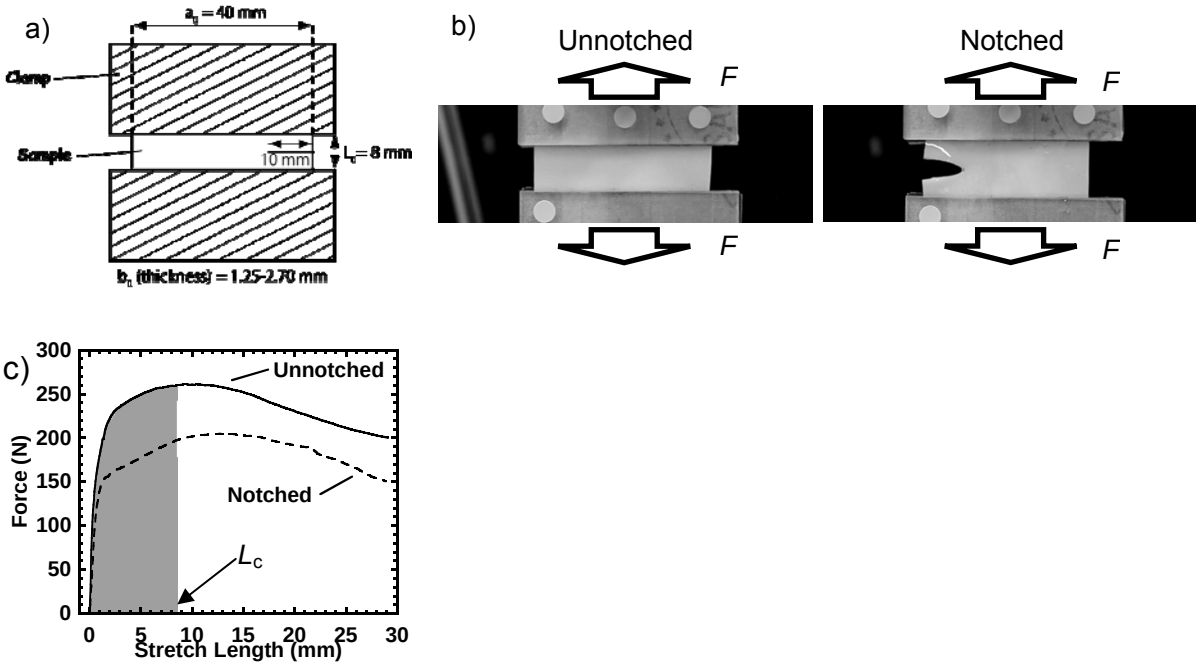


Figure S3 (a) Temperature versus C_{DMF} phase diagram of appearance of p-PAAm gels. "Tr", "Op", "St" are the transparent, opaque, and semi-transparent region respectively. (b, c) Temperature-sweep of dynamic mechanical test performed at constant shear strain amplitude of 0.1% and frequency of 10 Hz. (b) Storage modulus *G'* (closed symbols) and loss modulus *G"*(open symbols). (c) Loss tangent tan δ. Open symbols in (c) represent the data of turbid samples. For clarity, only 25% of data are shown in (b) and (c).

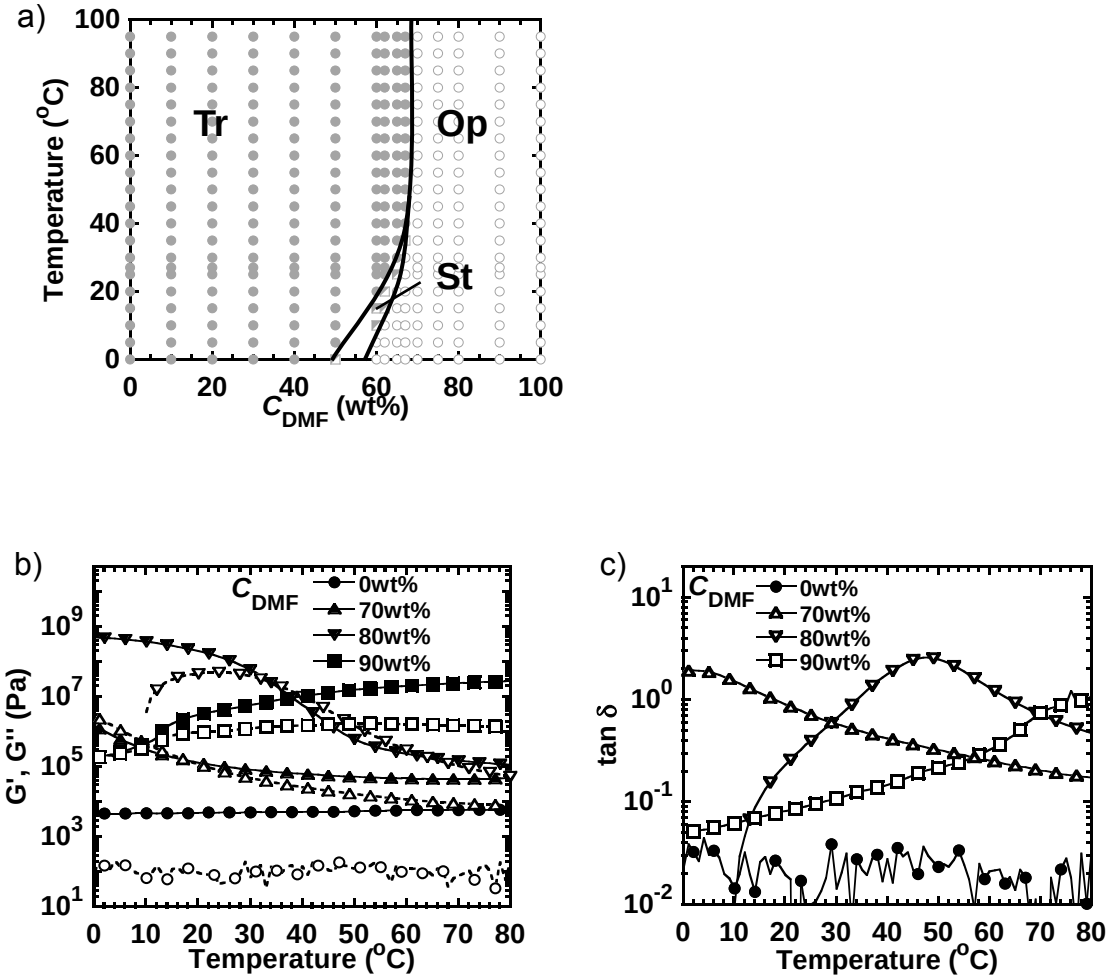
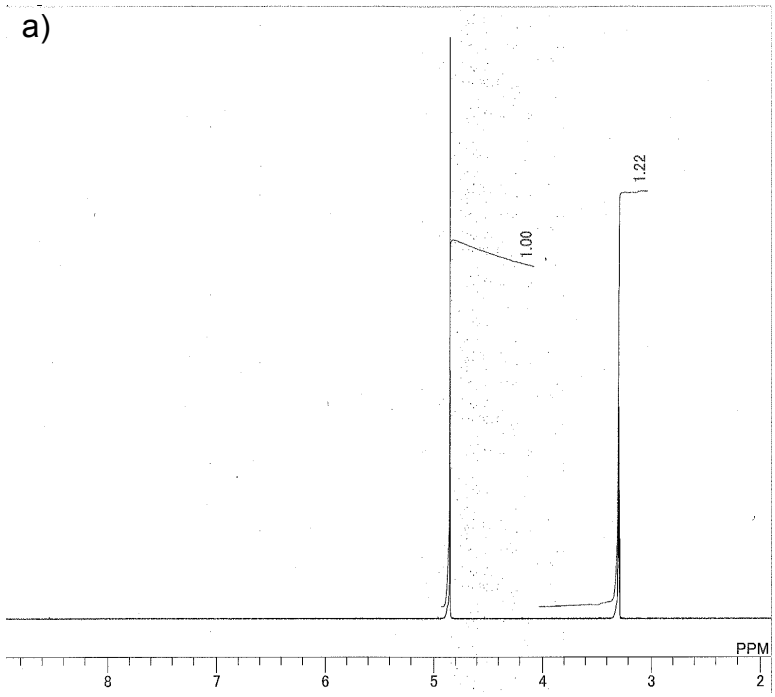


Figure S4 (a) ^{1}H NMR spectrum of pure methanol-d_4 (CD_3OD). Amount of the water vapor absorption is estimated by the peak area ratio of water (4.87 ppm) and proton-exchanged methanol (3.34 ppm). In this time, the area ratio is 1.00: 1.22. From this data, we roughly estimated the concentration of absorbed water in methanol-d_4. (b) ^{1}H NMR spectrum of the extraction from water-swollen PAAm gel. Only the peaks of water and methanol were observed. (c) ^{1}H NMR spectrum of the extraction from 50p-PAAm gel. The peak area ratio of DMF (CH, 7.97 ppm), water and methanol were 1.00, 10.01, 1.13 respectively. Number ratio of DMF molecules to water ones is 1.00: (10.01-1.13/1.22)/2 = 1.00: 4.54, and the weight ratio is 1.00: 1.12. Thus, the internal C_{DMF} is 47.2wt%. (d) NMR spectrum of extraction from 70p-PAAm. The peak area ratio of DMF, water and methanol were 1.00, 8.11, 1.53 respectively. Number ratio of DMF molecules to water ones is 1.00: (8.11-1.53/1.22)/2 = 1.00: 4.54, and the weight ratio is 1.00: 1.12. Thus, the internal C_{DMF} is 54.1wt%. (e) NMR spectrum of extraction from 80p-PAAm. The peak area ratio of DMF, water and methanol were 1.00, 9.38, 3.21 respectively. Number ratio of DMF molecules to water ones is 1.00: (9.38-3.21/1.22)/2 = 1.00: 3.37, and the weight ratio is 1.00: 0.83. Thus, the internal C_{DMF} is 54.6wt%. (e) ^{1}H NMR spectrum of extraction from 100p-PAAm. The peak area ratio of DMF, water and methanol were 1.00, 2.95, 1.20 respectively. Number ratio of DMF molecules to water ones is 1.00: (2.951.20/1.22)/2 = 1.00: 0.98, and the weight ratio is 1.00: 0.24. Thus, the internal C_{DMF} is 80.5wt%.

Table S1 DMF weight percentage in the DMF-water mixtrue in bath solution and in gels.

Sample	C_{DMF} (wt%) in bath	C_{DMF} (wt%) in gel
50p-PAAm gel	50	47.2
70p-PAAm gel	70	54.1
80p-PAAm gel	80	54.6
100p-PAAm gel	100	80.5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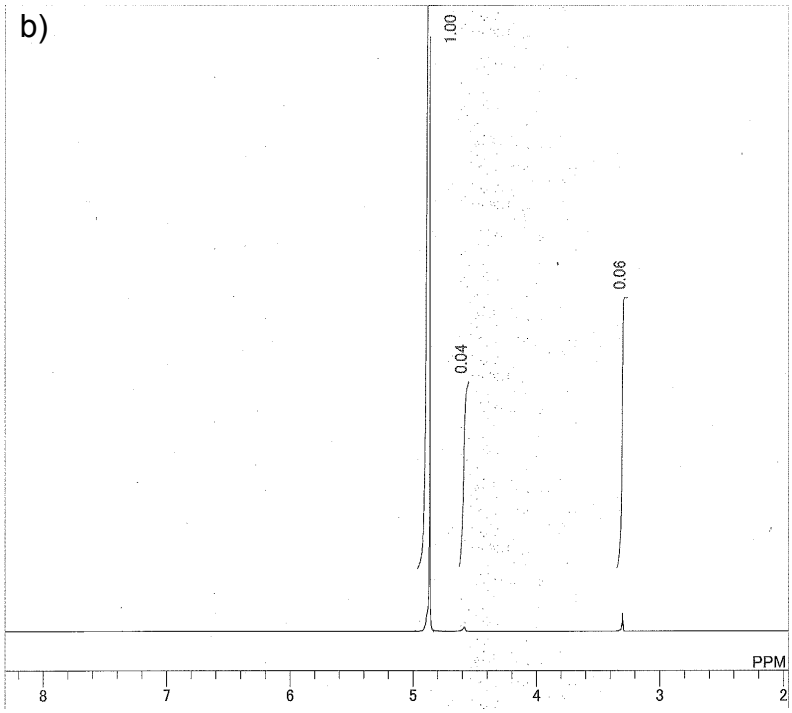
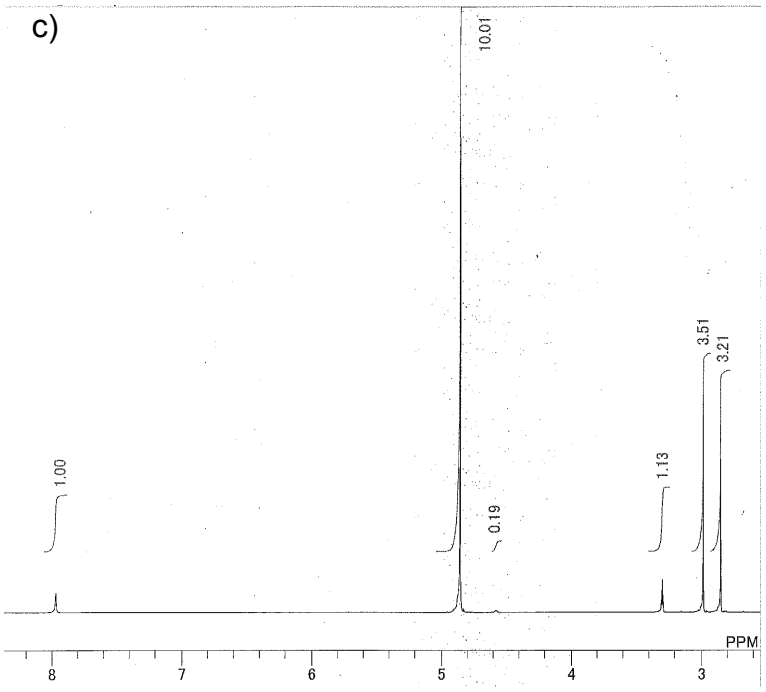
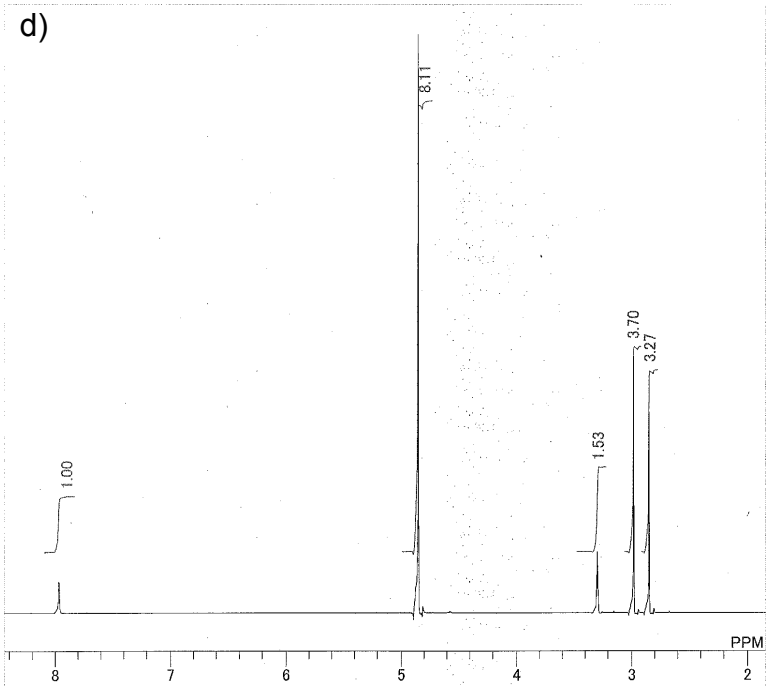
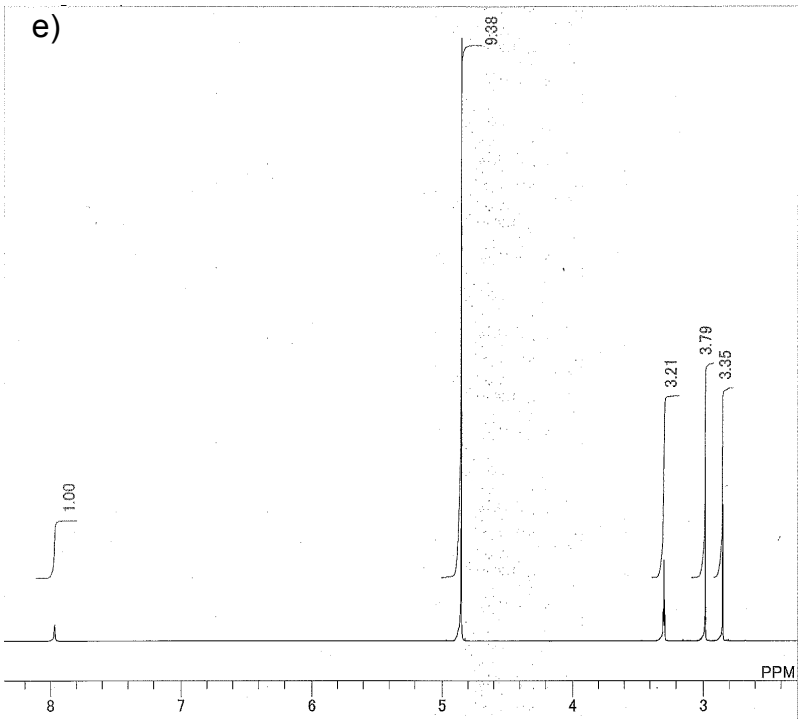
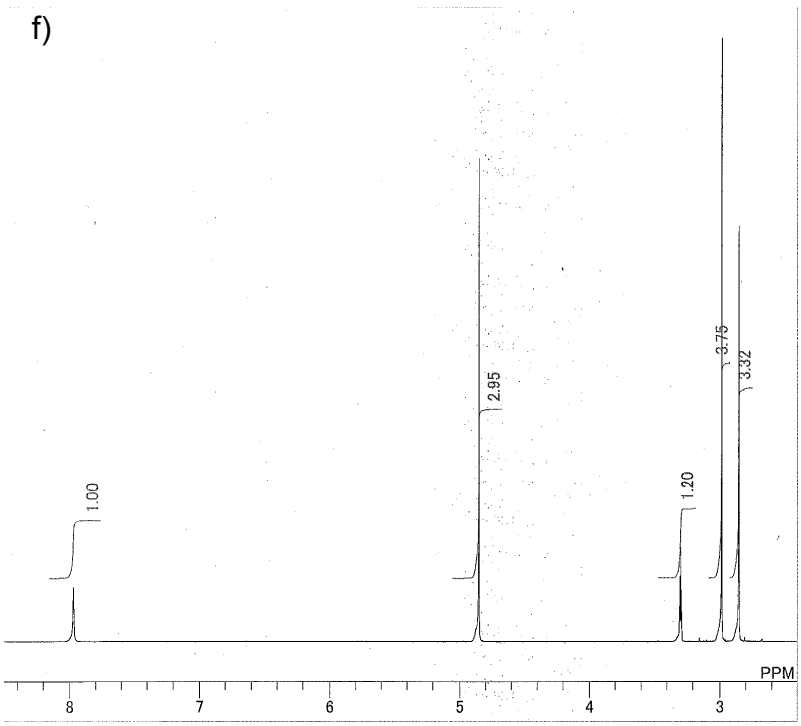
1.00
1.22
PPM
8
7
6
5
4
3
2


b)
1.00
0.04
0.06
PPM
8
7
6
5
4
3
2


c)
10.01
3.51
3.21
1.13
1.00
0.19
PPM
8
7
6
5
4
3


d)
8.11
3.70
3.27
1.53
1.00
PPM
8
7
6
5
4
3
2





[S1] H. E. Gottlieb, V. Kotlyar, A, Nudelman, *J. Org. Chem.* **1997**, *62*, 7512