

Supporting Information

Spontaneous Synthesis of a Homogeneous Thermoresponsive Polymer Network Composed of Narrow Molecular Weight Distribution Polymers

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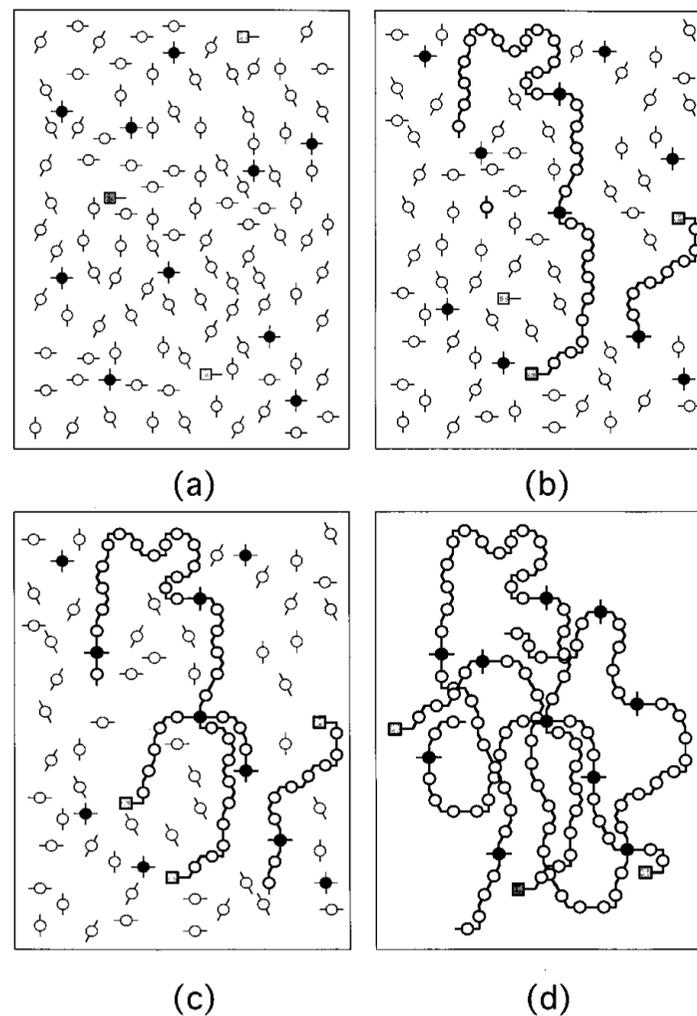
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- **Regarding gelation with various solvent compositions**

- When PETCP, NIPA, CuCl, and Me₆TREN were reacted in a solvent system with 40 vol% DMF, complete gelation of the whole system was not observed, and only a part of the solution gelled. It was mentioned in the text that the higher the composition of DMF is, the lower the initiation reaction rate and the polymerization reaction rate. This DMF composition also affects the addition reaction to the allyl group following the polymerization of NIPA, and higher compositions of DMF are considered to reduce the rate of the crosslinking reaction. From the reports thus far, improvement in reaction rate and living performance of the polymerization of NIPA is observed by adding metallic copper to this reaction system. Therefore, the synthesis of the PNIPA gel was attempted by replacing half (molar ratio) of the catalyst salt (CuCl) added with Cu(0) (Fig. S2-S4). Then, for the system to which Cu(0) was added, the whole reaction solution gelled, and a transparent PNIPA gel was obtained. Furthermore, phase separation of the solution was not confirmed until the later stage of the crosslinking reaction. The above results indicate that the reaction system in which Cu (0) is added to a mixed solvent of 40 vol% DMF has both sufficient reactivity for gelation and a good solvent property without phase separation. The solvent system with 40 vol% DMF is a good solvent for the initiator PETCP compared to the system with 25 vol% DMF. Therefore, approximately 3 times as much PETCP can be dissolved (3 mM). Therefore, by increasing the total amount of initiator, we attempted to construct a network structure with short polymer lengths between crosslinking points. As a result, we succeeded in obtaining a transparent PNIPA gel even under conditions where three times more PETCP was used. When 50 vol% DMF was used, the solution phase separated due to the heat of the reaction during the polymerization, and it became impossible for the system to exist as a uniform single phase. As seen from the solvent composition dependency of the degree of swelling of the PNIPA gel described above, the polymer network obtained shrinks with increasing temperature in the mixed solvent system containing approximately 50% DMF. Therefore, due to the heat of the polymerization reaction, PNIPA would phase separate in the system. In addition, gelation was not observed even under the condition of 75 vol% DMF. When 75 vol% DMF was used, the conversion from the monomer to the polymer is not good, as observed from the result of the synthesis using 4-branched PNIPA. Most likely, deactivation of the reactive end occurs in the latter half of the reaction. In this study, no reaction was carried out using pure DMF or water as solvent. This is because pure DMF is considerable not suitable, as the formation of Cu(0) and Cu(II) by the disproportionation reaction of CuCl is important for the rapid progress of NIPA polymerization. In the case of pure water, the disproportionation reaction of CuCl occurs, but when 4 °C was used as the polymerization temperature, the initiator, monomer and crosslinking agent precipitate, making it a poor polymerization condition.

- **Mechanical properties of the obtained polymer gel**

- The mechanical properties of the polymer gel prepared in this study were not measured because it is currently difficult to process the sample into the required shape due to the restriction of the preparation conditions. However, Movie S1 shows a video comparing the behavior of the polymer gel obtained in this study with the mechanical compression of a polymer gel obtained by conventional radical polymerization. The polymer gel obtained by the new method proved to be strong against compression. However, since the crosslinking rate of the polymer gel obtained in this study is considerably lower than that of the polymer gel used for comparison, it is impossible to accurately compare the mechanical behavior. Since PNIPA is considered to behave as a so-called “hard polymer” having a relatively long persistent length, if a perfectly homogeneous polymer network is formed, the polymer gel is expected to be more brittle than the conventional system when subjected to such a compression test to cause large deformation.



Scheme S1. Scheme of the formation process of a polymer network obtained by conventional radical polymerization by T. Tanaka et al. in *J. Chem. Phys.* **106**, 2906-2910 (1997). (a) Initial solution of monomer (○), crosslinker (●), and initiator (■) molecules. (b) Polymerization starts. The “walker” picks up the monomer and crosslinker molecules randomly. (c) Propagation. When a growing chain intercepts an already existing one, it can either form a crosslink or disengage without forming one. (d) Result of polymerization. Some crosslinker molecules remain without having formed covalent bonds.

Table S1. Gelation using the combination of the fast living radical polymerization and the slow crosslinking reaction ([NIPA]:[I]:[CuCl]:[Me₆TREN] = 2000:1:20:20, [NIPA] = 2 M, DMF:H₂O = 25:75, temperature = 4 °C, I: initiator).

RUN	[NIPA] (M)	Temp. (°C)	[NIPA]/[I]	[TA-G]/[I]	reaction solution (after several days)
1-1	2	4	2000	1	NO gelation
1-2	2	4	2000	2	partial gelation
1-3	2	4	2000	3	gel
1-4	2	4	2000	4	gel
1-5	2	4	2000	5	gel

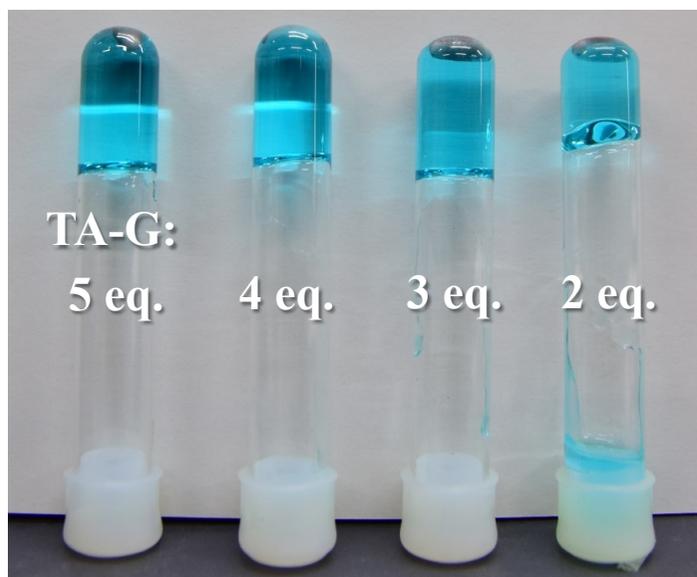


Figure S1. Gelation using the combination of the fast living radical polymerization and the slow crosslinking reaction ([NIPA]:[I]:[CuCl]:[Me₆TREN] = 2000:1:20:20, [NIPA] = 2 M, DMF:H₂O = 25:75, temperature = 4 °C, I: initiator).

Table S2. Dependence of gelation on the solvent composition (DMF/H₂O). The combination of the fast living radical polymerization and the slow crosslinking reaction was used as the gelation method. ([NIPA]:[I]:[CuCl+Cu(0)]:[Me₆TREN] = 2000:1:20:20, [NIPA] = 2 M, temperature = 4 °C, I: initiator)

RUN	[NIPA] (M)	temp.	[NIPA]/[I]	[TA-G]/[I]	DMF/H ₂ O (vol/vol)	reaction solution (after several days)
1-5	2	4	2000	5	25/75	gel
2-1	2	4	2000	5	40/60	partial gelation
2-2	2	4	2000	5	50/50	(phase separation)
2-3	2	4	2000	5	75/25	NO gelation

Table S3. Gelation using the combination of the fast living radical polymerization and the slow crosslinking reaction ([NIPA]:[I]:[CuCl]:[Me₆TREN] = 2000:1:20:20, [NIPA] = 2 M, temperature = 4 °C, I: initiator).

RUN	[NIPA] (M)	temp.	[NIPA]/[I]	[CuCl]/[Cu(0)]	DMF/H ₂ O (vol/vol)	reaction solution (after several days)
2-1	2	4	2000	100/0	40/60	partial gelation
3-1	2	4	2000	50/50	40/60	gel
3-2	2	4	1000	50/50	40/60	gel
3-3	2	4	667	50/50	40/60	gel (quite soft)

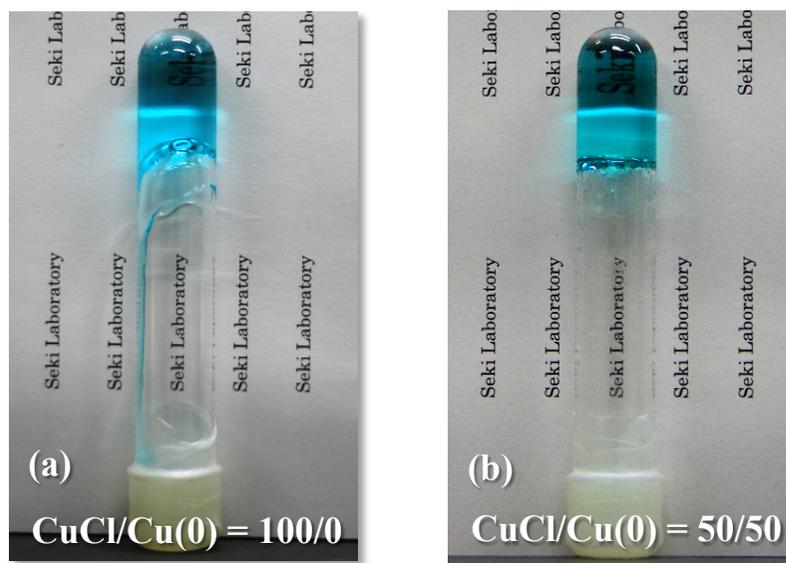


Figure S2. Appearance of the resultant gels using the method combining the fast living radical polymerization and the slow crosslinking reaction ([NIPA] = 2 M, DMF:H₂O = 75:25, temperature = 4 °C, [TA-G]/[initiator] = 5; (a) [NIPA]:[initiator]:[CuCl]:[Me₆TREN] = 2000:1:20:20; (b) [NIPA]:[initiator]:[CuCl]:[Cu(0)]:[Me₆TREN] = 2000:1:10:10:20).

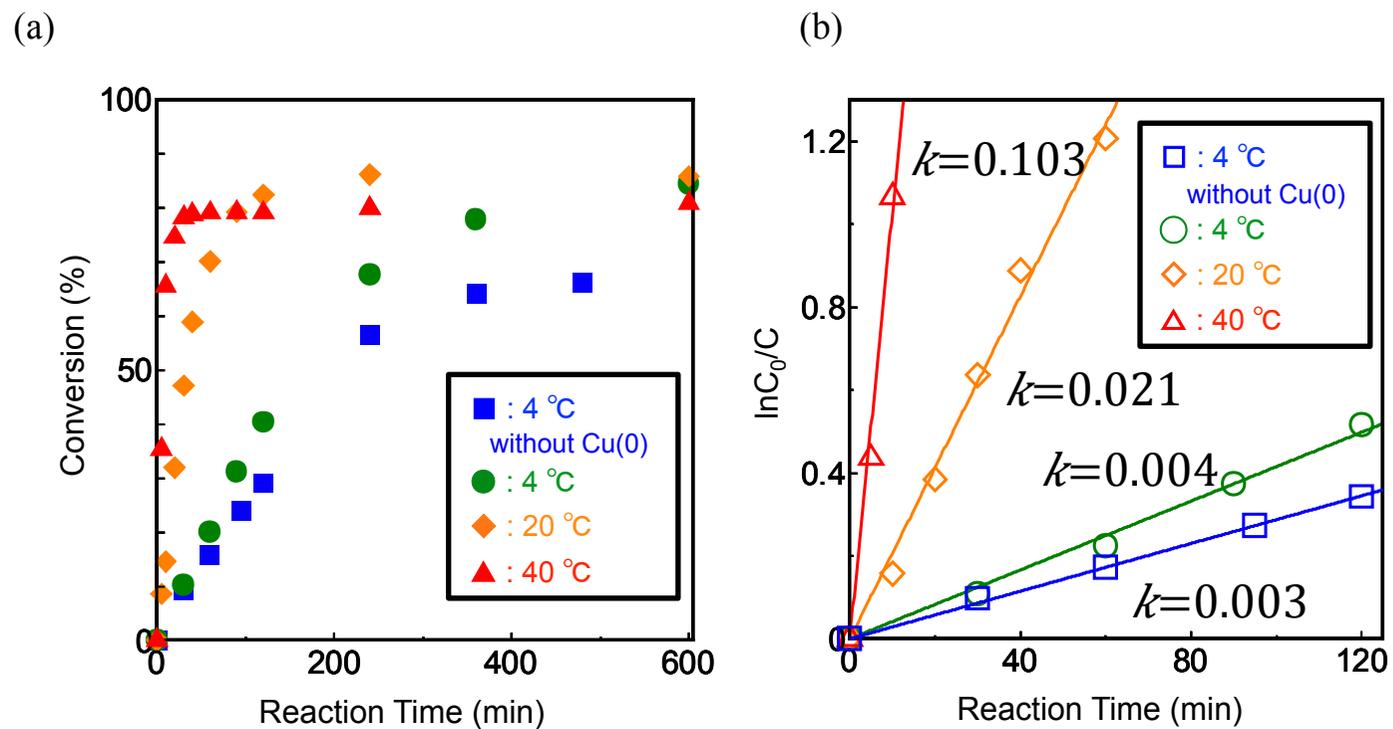


Figure S3. (a) Consumption of NIPA measured by ¹H-NMR. (b) First-order kinetics plot for the polymerization of NIPA in DMF/H₂O (50/50 vol/vol). ([NIPA] = 2 M, [NIPA] / [initiator] = 2000, blue symbol = [NIPA]: [CuCl]: [Cu(0)]: [Me₆TREN] = 100: 1: 0: 1, the other symbol = [NIPA]: [CuCl]: [Cu(0)]: [Me₆TREN] = 100: 0.5: 0.5: 1)

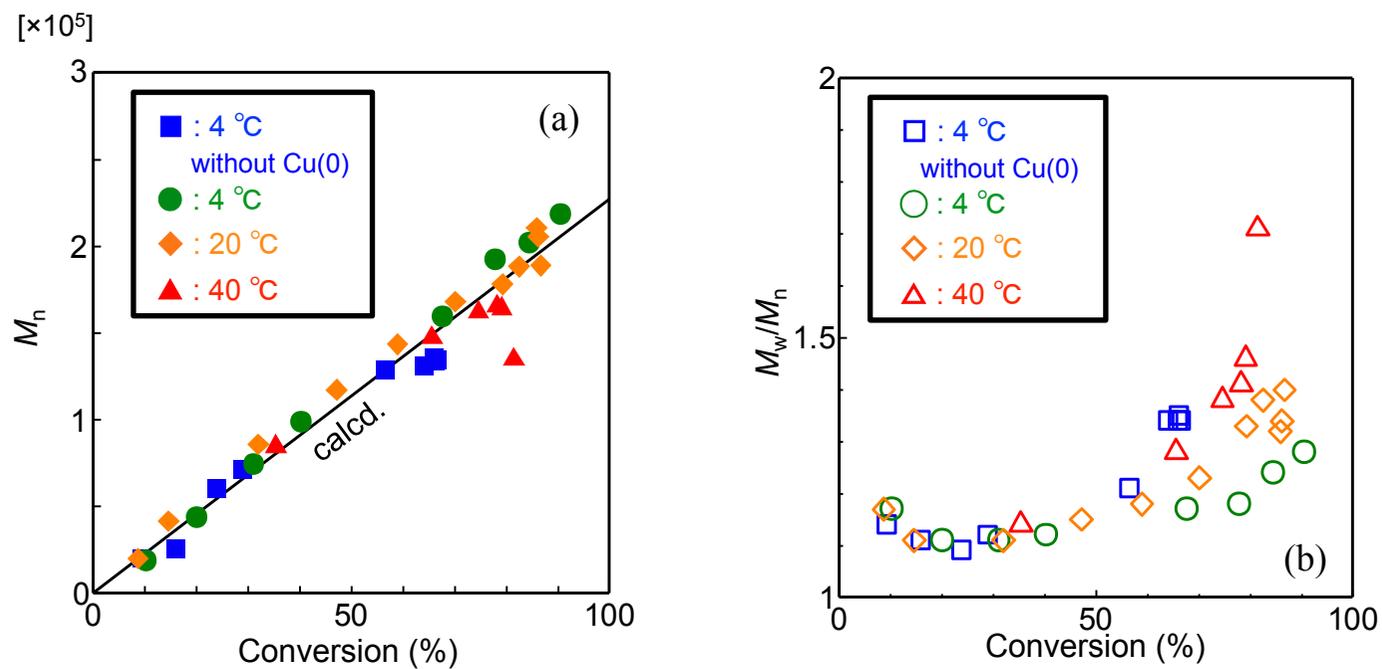


Figure S4. (a) Dependence of molecular weight (full symbols) and polydispersity (open symbols) on the conversion of NIPA (polymerization in DMF/H₂O (50/50 vol/vol), [NIPA] = 2 M, [NIPA] / [initiator] = 2000, blue symbol = [NIPA]: [CuCl]: [Cu(0)]: [Me₆TREN] = 100: 1: 0: 1, the other symbol = [NIPA]: [CuCl]: [Cu(0)]: [Me₆TREN] = 100: 0.5: 0.5: 1). The calculated line represents the theoretical molecular weights expected on the basis of the [NIPA]/[initiator] ratio.

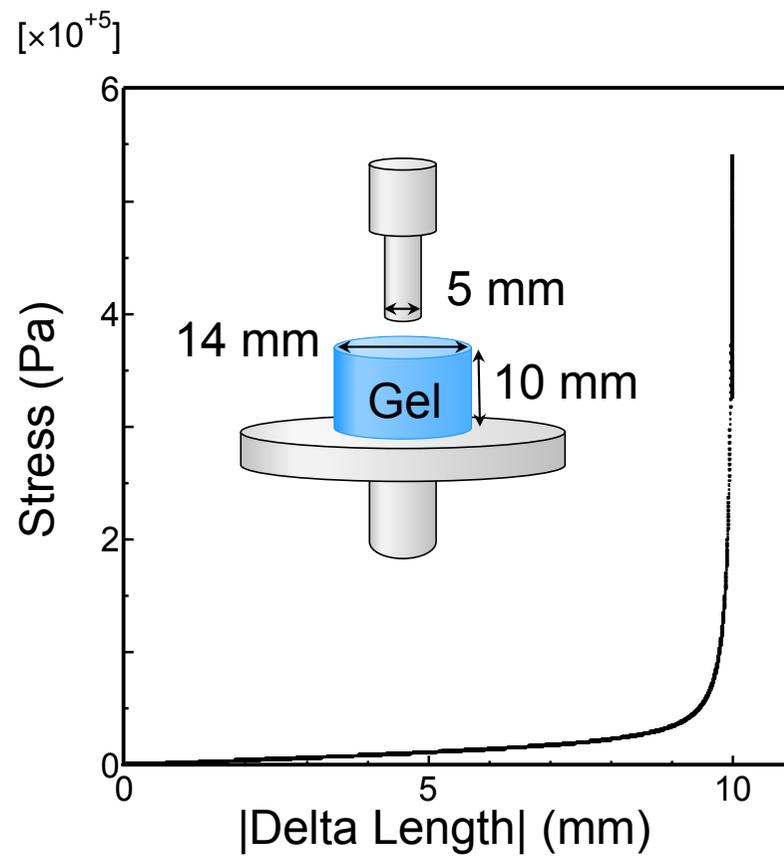


Figure S5. Result of mechanical strength measurement by indentation test of disk-shaped polymer gel. Our polymer gel does not destroy even at 5×10^5 Pa which is the limit value of our laboratory equipment (RSA-G2 solid analyzer, TA Instruments).

Movie S1. A video comparing the behavior of the polymer gel obtained in this study with the mechanical compression of a polymer gel obtained by conventional radical polymerization.