# Notes

## Stumuli-Responsive Organogel Based on Poly(*N*-propargylamide)

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#### Introduction

The reversible volume change of gels upon external stimuli was shown, for the first time, by Tanaka et al.<sup>1</sup> After this discovery, much effort has been made on the synthesis and application of the stimuli-responsive gels, especially those of hydrogels, in view of their scientific and technological importance.<sup>2</sup> A wide variety of external stimuli are available for the volume change of gels, including temperature, pH, solvent composition, and so on. Creation of organogel that undergoes quick volume change in isotropic organic solvents would greatly expand the potentiality of responsive gels.<sup>3</sup> The helix– coil transition is promising as a means to cause quick volume change of gels by external stimuli.

Poly(*N*-propargylamides) can be prepared in a stereoregular form (cis-transoidal) using Rh catalysts.<sup>4</sup> They construct intramolecular hydrogen bonds between the amide groups, which induce a helical conformation. The most characteristic points of the poly(*N*-propargylamide) helix is that, like  $\alpha$ -helical polypeptides, the transition from a disordered to a helical state involves negatively large enthalpy and entropy changes.<sup>4b</sup> Thus, changing the temperature and/or adding polar solvents that can hydrogen-bond significantly affect the enthalpy and entropy terms, which influence the equilibrium between the helical and disordered states. Such a conformational change should be accompanied by a change in hydrodynamic volume, which would trigger the volume change of the gels.<sup>6</sup>

Here we show a new unique responsive organogel that displays quick response to change in temperature or solvent composition based on hydrogen bonding, which is accompanied by volume change in organic isotropic solvents. More specifically, the synthesis of poly(*N*propargylamides)-based copolymer gels poly(**1**) and their stimuli-responsive properties are reported (Scheme 1).

#### **Experimental Section**

Materials. The solvents were distilled by usual methods prior to use. Propargyl alcohol (Wako), adipic acid (Wako),

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*p*-toluenesulfonic acid monohydrate (Wako), [(nbd)RhCl]<sub>2</sub> (Aldrich), and triethylamine (Wako) were used without further purification. Monomers 1a-c were prepared according to the literature.<sup>4b</sup>

**Synthesis of Monomer 2.** A benzene solution (80 mL) of adipic acid (2 g, 16.9 mmol), propargyl alcohol (3.3 g, 59.2 mmol), and *p*-toluenesulfonic acid monohydrate (1.6 g, 8.5 mmol) was refluxed for 2 h. The reaction mixture was washed with saturated aqueous NaHCO<sub>3</sub> and brine, dried over MgSO<sub>4</sub>, and concentrated. Monomer **2** was isolated (2.6 g, 13.3 mmol, 79%) by flash column chromatography on silica gel (hexane/AcOEt, 10/1, v/v).

**Polymerization Procedures.** A THF solution of the monomers ( $[M]_{total} = 1.0 \text{ M}$ ) was added to a THF solution of [(nbd)RhCl]<sub>2</sub>-Et<sub>3</sub>N ([monomer]/[cat]/[Et<sub>3</sub>N] = 100/1/0.1) under dry nitrogen, and the solution was kept at 30 °C for 1 h. The resulting gel was stirred in methanol and CHCl<sub>3</sub> for 5 h and then dried under reduced pressure.

**Measurements.** NMR spectra were recorded on a JEOL EX-400 spectrometer. IR and UV-vis spectra were obtained with Shimadzu FTIR-8100 and JASCO V-500 spectrophotometers. Optical rotations were measured with a JASCO 600 spectropolarimeter. CD spectra were recorded on a JASCO V-530 spectropolarimeter.

#### **Results and Discussion**

The gels were prepared with a combined catalyst,  $[(nbd)RhCl]_2$  and  $Et_3N$ , using *N*-propargyl-3-methylbutanamide (1a) as a monomer (Scheme 1). Attempts to prepare gels using bifunctional N-propargylamides gave unsuccessful results. Specifically, the amide-based cross-linkers prepared were poorly soluble in polymerization solvents, and even the soluble ones inefficiently provided insoluble gels. Thus, a bifunctional propargyl ester, dipropargyl adipate (2), was employed as a crosslinker, which led to good yields of insoluble gels.<sup>7</sup> We also prepared a gel based on poly(N-propargylpropanamide) [poly(1b)] for comparison since poly(1b) adopts a disordered conformation at room temperature irrespective of the solvent.<sup>4b</sup> The IR spectra of the resultant gels showed no absorption due to the C-C triple-bond vibration that was observed for the monomers. Thus, both of the triple bonds in the cross-linker participate in the polymerization.

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**Figure 1.** (a) Temperature dependence of the relative intensity of molar ellipticity ( $\bigcirc$ ) and absorbance ( $\blacktriangle$ ) of poly(**1a**-*co*-**1c**) at 400 nm in CHCl<sub>3</sub>. (b) Solvent-composition dependence of the relative intensity of molar ellipticity ( $\bigcirc$ ) and absorbance ( $\bigstar$ ) of poly(**1a**-*co*-**1c**) at 400 nm in mixed solvents of CHCl<sub>3</sub> and methanol.

The stimuli-induced conformational change of the polymer backbone was first investigated in detail by monitoring the CD and UV spectra of a copolymer of 1a with a small amount of 1c. The large persistence length of the helical domain allows poly(1a) to exist in the helical conformation with an excess of one-handed screw sense by incorporating a small amount of a chiral segment.<sup>4b</sup> Thus, both poly(1a) and poly(1a-co-1c) possess the helical conformation, but the former has identical population of the right- and left-handed helices, while the screw sense of the latter copolymer is biased as with the homopolymer from **1c**. Therefore, the copolymer displays intense Cotton effects in the absorption range of the main chain.<sup>7</sup> Since the copolymer prepared has only a very small amount of the chiral unit (7 mol %), it is expected to show almost identical behavior as with the homopolymer in terms of the thermally and solvent-induced conformational changes. Figure 1a shows the temperature dependence of the relative magnitude of the Cotton effects at 400 nm for poly(**1a**-co-**1c**) in CHCl<sub>3</sub>. The Cotton effect, centering around 400 nm, gradually decreased in intensity on heating, and the copolymer showed no CD bands at 56 °C.<sup>7</sup> The lack of the CD signal at 56 °C is not due to the equally populated right- and left-handed helices but is due to the absence of the helical conformation, which was confirmed by the UV-vis spectra.7 The helical backbone of poly(N-propargylamides) absorbs light at around 400 nm, while the disordered one displays electric absorption at 320 nm.4b Thus, the UV-vis spectrum is a good indicator for the conformation. With increasing temperature, the absorption at 400 nm gradually decreased in intensity and almost completely disappeared at 56 °C (Figure 1a). A new band appeared around 320 nm with increasing temperature.<sup>7</sup> The plots of the relative intensities of the CD and UV signals at 400 nm against temperature gave identical curves as shown in Figure 1a. Therefore, lack of the CD band of the copolymer originates from the thermally induced



**Figure 2.** (a) Temperature dependence of the relative volume of the gel based on poly(1a) in CHCl<sub>3</sub>. (b) Solvent-composition dependence of the relative volume of the gels based on ( $\bigcirc$ ) poly(1a) and ( $\triangle$ ) poly(1b) and ( $\square$ ) that of the relative swelling degree of poly(1a)-based gel in mixed solvents of CHCl<sub>3</sub> and methanol.

deformation into a randomly coiled state. The conformational change induced by the change of solvent composition was also monitored in detail using the CD and UV-vis spectra. Figure 1b plots the relative intensity of the CD and UV bands at 400 nm for the copolymer in mixed solvents of CHCl<sub>3</sub> and methanol. The magnitude of both UV and CD bands that originate from the helical conformation steeply decreased upon adding methanol, and no CD effects were observed when the methanol content exceeded 5 vol %. This means that the conformational change is completed when the methanol content reaches 5 vol %.

The temperature dependence of the volume of a cylindrical poly(1a)-based gel is illustrated in Figure 2a. The cylindrical gel (1a/2 = 97.5/2.5 in feed) with the length and diameter of 7.1 and 2.2 mm, respectively, started to shrink at approximately 35 °C, and the gel volume leveled off at 50 °C. The temperature dependence of the gel volume not strictly but roughly agreed with that of the polymer conformation (Figure 1a). Emphasis should be placed on the very rapid volume change process of the gel; the temperature jump experiment from 35.2 to 37.5 °C for this relatively large cylindrical gel indicated that the relaxation time was only 8.9 min. This is in contrast to the rather slow volume change process of the conventional responsive hydrogels based on poly(acrylic acids) and poly(acrylamides).

The volume change also occurred upon the change in solvent composition. Figure 2b plots the relative volume of the poly(**1a**)-based gel vs the solvent composition between CHCl<sub>3</sub> and methanol. The gel steeply shrank with increasing methanol composition, meaning that the continuous volume change took place. The shrinkage stopped when the methanol content reached 5 vol %, which is identical behavior to that observed in the conformational change of poly(**1a**-*co*-**1c**) (Figure 1b). The solvent-composition dependence of the swelling degree also gave an identical curve as demonstrated in Figure 2b; the initial swelling degree (26.4) decreased with

increasing methanol content and became constant (14-17) when the methanol content exceeded 5 vol %. In contrast, the volume of the gel based on poly(**1b**) (**1b/2** = 97.5/2.5 in feed) remained almost unchanged under the same conditions as illustrated in Figure 2b. Because poly(**1b**) exists in a randomly coiled state even in CHCl<sub>3</sub> at room temperature,<sup>4b</sup> it is concluded that the helix-coil transition results in the volume change. Further, it was confirmed that this transition is completely reversible. The solvent-induced volume change also very quickly proceeded. Specifically, the relaxation time of volume expansion upon switching the solvent from methanol to CHCl<sub>3</sub> was only 43 min for a cylindrical gel with the length and diameter at the swollen state of 7.1 and 2.2 mm, respectively.

#### Conclusion

We have demonstrated the first example for a novel stimuli-responsive organogel that senses external stimuli and undergoes very quick volume change in isotropic organic solvents. It has been evidenced that the volume change is driven by the conformational change of the framework between the helical and disordered structures. We also observed that the volume change occurred more rapidly when the solvent was changed from CHCl<sub>3</sub> to methanol and that this event could be monitored by the naked eye. Because this process took place quite rapidly, we could not obtain quantitative data for the relaxation time. We believe that such very quick response of the poly(N-propargylamide)-based gel in

isotropic organic solvents would allow us to expand the utility of stimuli-responsive polymer networks as chemical valves, gentle actuators, and so forth.

**Supporting Information Available:** Results for the preparation of the gel and the variable temperature CD and UV spectra of poly(**1a**-*co*-**1c**) in CHCl<sub>3</sub>. This material is available free of charge via the Internet at http://pubs.acs.org.

#### **References and Notes**

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