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Photoresponsive Hydrogel System Using Molecular Recognition of α-Cyclodextrin

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ABSTRACT: Using molecular recognition of α-cyclodextrin (α-CD), we have successfully constructed a photoresponsive hydrogel system by combination of simple components, α-CD, dodecyl (C_{12})-modified poly(acrylic acid) (p(AA/C_{12})), and a photoresponsive competitive guest, 4,4′-azodibenzoic acid (ADA). An aqueous solution of p(AA/C_{12}) exhibited a gel-like behavior because polymer chains form a network structure via hydrophobic associations of C_{12} side chains. When α-CD was added to the gel-like aqueous solution, the gel was converted to a sol mixture because hydrophobic interactions of C_{12} side chains were dissociated by the formation of inclusion complexes of α-CD with C_{12} side chains. Upon addition of ADA to a binary sol mixture of p(AA/C_{12}) and α-CD, α-CD interacted predominantly with ADA, and then hydrophobic associations of C_{12} side chains were restored, resulting in a sol-to-gel transition. When a ternary gel mixture of p(AA/C_{12}), α-CD, and ADA was irradiated with UV light, ADA was isomerized from trans to cis, and the mixture underwent a gel-to-sol transition because α-CD formed inclusion complexes more favorably with C_{12} side chains than with *cis*-ADA. When the ternary sol mixture was irradiated with visible light, ADA was isomerized from cis to trans and the mixture underwent a sol-to-gel transition. Furthermore, these gel-to-sol and sol-to-gel transitions occurred repeatedly by repetitive irradiations of UV and visible light.

Introduction

Hydrogel systems responsive to external stimuli, including temperature, pH, and light (photo), have attracted much interest of researchers because of their potentials in a broad range of fields, such as drug delivery systems, paints, coatings, and personal care goods.[1] A number of examples of temperature- and pH-responsive hydrogel systems have been reported.[2] However, there are only a few examples of successful preparation of photoresponsive hydrogel systems,[3,4] although a photoresponsive hydrogel system may be applied to environmentally benign photofunctional systems, including photonics, optical storage, and photoswitchable materials.[5] We are therefore motivated to construct photoresponsive hydrogel systems and to investigate in detail photoresponsive gel-to-sol and sol-to-gel transition behavior.

We have been studying in detail the interaction of cyclodextrins (CDs) with polymer side chains attached to water-soluble polymers[6−8] because we have been aware of the importance of polymer side chains in the macromolecular recognition in biological systems.[9] CDs are cyclic oligomers of (+)-D-glucopyranose units bound each other through α-1,4-glucoside bonding. CDs of 6, 7, and 8 glucopyranose units are called α-, *β*-, and *γ*-CDs, respectively. Since CDs interact selectively with hydrophobic compounds of a size matching their cavity size to form inclusion complexes in aqueous media, CDs have attracted much interests as biomimetic compounds, such as enzyme models.[10] Previously, we investigated the interaction of CDs with alkyl side chains attached to poly(acrylamide) backbone and found that CDs interacted more selectively with polymer-carrying alkyl guests than with low-molecular-weight ones.[6] Recently, we also studied the interaction between a polymer bearing *β*-CD moieties and a polymer bearing azobenzene moieties and found that the *β*-CD polymer interacted with the *trans*-azobenzene polymer to form a gel-like mixture, but the *β*-CD polymer did not form a gel with the *cis*-azobenzene polymer under the same conditions.[7] More recently, we have successfully constructed aqueous systems which undergo gel-to-sol and sol-to-gel transitions utilizing the formation of inclusion complexes of α-CD with dodecyl (C_{12}) side chains in C_{12}-modified poly(acrylic acid) (p(AA/C_{12}) in Chart 1).[8]

The objective of the present study is to give photoresponsiveness to the hydrogel systems. In the present paper, we describe (i) a gel-to-sol transition using the interaction of α-CD with C_{12} side chains in p(AA/C_{12}), (ii) a sol-to-gel transition by adding a competitive guest, 4,4′-azodibenzoic acid (ADA in Chart 1), to a binary mixture of p(AA/C_{12}) and α-CD, and (iii) photoresponsive gel-to-sol and sol-to-gel transitions for a ternary mixture of p(AA/C_{12}), α-CD, and ADA using photoisomerization of ADA.

Experimental Section

Materials. Poly(acrylic acid) (p(AA)) (Wako Pure Chemical Co.) was used as supplied. The average molecular weight of p(AA) was reported to be 250 000 by the supplier. α-Cyclodextrin (α-CD) (Junsei Chemical Co.) was recrystallized twice from water. 4,4′-Azodibenzoic acid (ADA) (Tokyo Kasei Kogyo Co.) was used as received. *N,N*-Dimethylformamide (DMF) was purified by distillation under reduced pressure. Milli-Q water was used for preparation of aqueous solutions. Other reagents were used as received.

A copolymer of acrylic acid and *N*-dodecylacrylamide (p(AA/C_{12})) was prepared from p(AA) and *n*-dodecylamine in the presence of *N,N′*-dicyclohexylcarbodiimide (DCC) according to the procedure of Iliopoulos et al.[11] The degree of modification was determined to be 5.2 mol % by elemental analysis and ^{1}H NMR.

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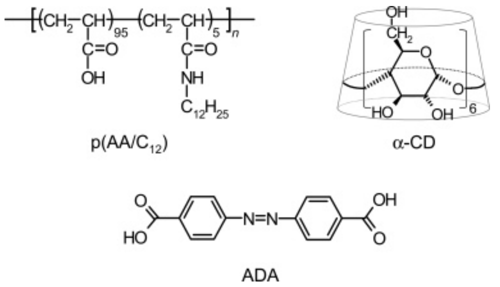
Chart 1. Structures of the Chemicals Used in This Study



Measurements. (a) Preparation of Sample Solutions. Sample polymer solutions were prepared as follows: A predetermined amount of p(AA/C_{12}) was dissolved in a carbonate buffer containing 0.05 M sodium carbonate and 0.05 M sodium bicarbonate, and the solution was heated at 60 °C for 1 day.

(b) Creep Recovery. Creep recovery measurements were performed with a RheoLogica DynAlyser 100 stress-controlled rheometer equipped with a cone and plate under an applied stress of 1.0 Pa at 25 °C by using a circulating water bath. The radius of the cone was 25 mm, and the angle between the cone and plate was 4°. For measurements under photoirradiation, a handmade glass plate equipped with UV (NSHU550B, Nichia Co.) or blue (NSPB500S, Nichia Co.) light-emitting diodes was employed.

The obtained creep compliance−time data were analyzed by using a conventional four-element model composed of the Maxwell and Kelvin−Voigt bodies in series.[12] The creep compliance as a function of time t, $J(t)$, is defined as

$$J(t) = J_0 + J_d(1 - \exp(t/\lambda)) + t/\eta \tag{1}$$

where J_0 and η are the instantaneous compliance and the steady-shear viscosity, respectively, for the Maxwell body, and J_d and λ are the delayed compliance and the relaxation time, respectively, for the Kelvin−Voigt body.

(c) UV−Vis Absorption Spectroscopy. UV−vis absorption spectra were recorded with a Shimadzu UV-2500PC spectrophotometer using a 1 cm path length quartz cuvette.

Photoisomerization of ADA. ADA was isomerized by photoirradiation using a 500 W Xe lamp (Ushio Inc.) equipped with a cutoff filter (Hoya UV34) and a band-pass filter (Hoya U340) for UV light or with a cutoff filter (Hoya Y45) for visible light. The distance between the sample cell and the lamp was fixed at 40 cm.

Results and Discussion

Gel-to-Sol Transition Using the Interaction of α-CD with p(AA/C_{12}). It is known that hydrophobes in hydrophobically modified water-soluble polymers interact intra- and intermolecularly in aqueous media.[13] Under semidilute or concentrated conditions, intermolecular associations usually dominate over intramolecular ones, leading to the formation of polymer aggregates with network structures which exhibit viscoelastic properties.[14] Creep recovery measurements indicated that 5.0 g/L p(AA) exhibited a typical behavior of Newtonian liquids and 5.0 g/L p(AA/C_{12}) showed a viscoelastic behavior (see Figure S1 in the Supporting Information). Using eq 1, η values for p(AA) and p(AA/C_{12}) were determined to be 5.8×10^{-3} and 2.0×10^{4} Pa·s, respectively, under an applied stress of 1.0 Pa.[15]

After our first report on the formation of inclusion complexes of CDs with hydrophobic side chains attached to poly(acrylamide) backbone,[6] some research groups have reported that the formation of inclusion complexes of CDs with hydrophobes suppresses hydrophobic associations.[16−20] As reported previously,[8] since α-CD interacts with C_{12} side chains in p(AA/C_{12}) to form inclusion complexes, hydrophobic associations of C_{12} side chains are prevented by addition of α-CD, resulting in a decrease in η of the viscoelastic aqueous solution of p(AA/C_{12}). Figure 1 shows η as a function of the concentration of α-CD ([α-CD]) for mixtures of p(AA) and α-CD and for mixtures of p(AA/C_{12}) and α-CD under an applied stress of 1.0 Pa. In the case of mixtures of p(AA) and α-CD, η is constant at ca. 6×10^{-3} Pa·s independent of [α-CD]. On the other hand, in the case of mixtures of p(AA/C_{12}) and α-CD, η is practically constant at ca. 2×10^{4} Pa·s in the region $0 \leq$ [α-CD] $<$ 5.0 g/L, but η exhibits a drastic decrease of more than 6 orders of magnitude in a relatively narrow region $5.0 \leq$ [α-CD] ≤ 10.0 g/L. This observation indicates that, in this [α-CD] region, the formation of inclusion complexes of α-CD with C_{12} side chains causes a considerable disruption of interpolymer aggregates under an applied stress of 1.0 Pa. At [α-CD] $>$ 10.0 g/L, η values for mixtures of p(AA/C_{12}) and α-CD are on the same level as those for mixtures of p(AA) and α-CD, indicating that hydrophobic associations of C_{12} side chains are suppressed by the formation of inclusion complexes. Since excess free α-CD molecules may exist at [α-CD] $>$ 10.0 g/L, [α-CD] has been fixed at 10.0 g/L for a sol-to-gel transition by adding a competitive guest to a binary mixture of α-CD and p(AA/C_{12}), as described below.

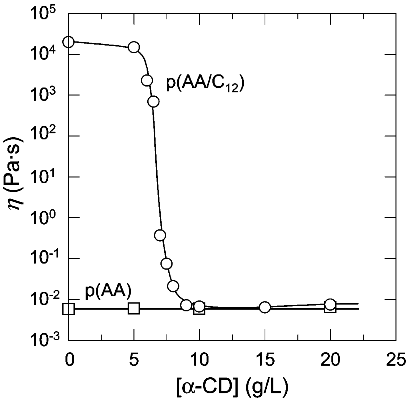


Figure 1. η as a function of [α-CD] for mixtures of p(AA) and α-CD and for mixtures of p(AA/C_{12}) and α-CD under an applied stress of 1.0 Pa. Polymer concentration = 5.0 g/L.

Sol-to-Gel Transition by Adding a Competitive Guest to a Binary Mixture of α-CD and p(AA/C_{12}). In this study, ADA has been chosen as a photoresponsive competitive guest. To investigate the complex formation behavior of α-CD with ADA, UV−vis absorption spectra were measured using ADA as received, in which most of ADA molecules take the trans form.[21] An absorption band due to the $\pi \rightarrow \pi^*$ transition of *trans*-ADA around 331 nm shifted to a longer wavelength region with increasing [α-CD] (see Figure S2a in Supporting Information). This observation is indicative of the formation of inclusion complexes of α-CD with ADA, as reported for other azobenzene derivatives.[22] Using the wavelength at absorption maximum (λ_{max}) due to *trans*-ADA, reciprocals of peak shift ($\Delta\lambda_{max}^{-1}$) were calculated and plotted against $[\alpha\text{-CD}]^{-1}$ to make the Benesi−Hildebrand plot. These plots were fitted well with a straight line, indicative of the formation of 1:1 inclusion complexes of α-CD with *trans*-ADA (see Figure S2b in Supporting Information). From the straight line,

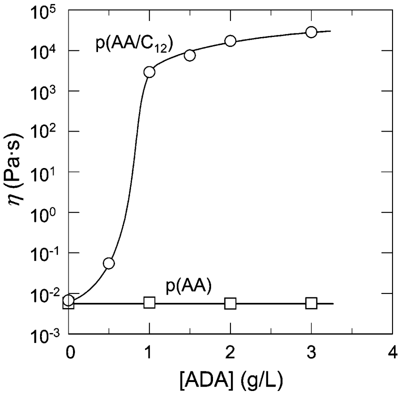


Figure 2. η as a function of [ADA] for mixtures of p(AA), α-CD, and ADA and for mixtures of p(AA/C_{12}), α-CD, and ADA under the applied stresses of 1.0 Pa. Polymer concentration = 5.0 g/L, [α-CD] = 10.0 g/L.

the association constant for α-CD and *trans*-ADA ($K_{CD/t-ADA}$) was determined to be 1.0×10^4 M^{-1}.[23]

Since $K_{CD/t-ADA}$ (1.0×10^4 M^{-1}) is ca. 4 times as high as the association constant for the formation of 1:1 inclusion complexes of α-CD with C_{12} side chains in p(AA/C_{12}) (2.3×10^3 M^{-1}),[8] α-CD may interact more favorably with ADA than with C_{12} side chains in ternary mixtures of p(AA/C_{12}), α-CD, and ADA. If this is the case, addition of ADA should induce dissociation of inclusion complexes of α-CD with C_{12} side chains to restore hydrophobic associations of C_{12} side chains, resulting in a recovery of η. Figure 2 shows η as a function of the concentration of ADA ([ADA]) for ternary mixtures of p(AA), α-CD, and ADA and for ternary mixtures of p(AA/C_{12}), α-CD, and ADA. In the case of ternary mixtures of p(AA), α-CD, and ADA, η is constant at ca. 6×10^{-3} Pa·s independent of [ADA]. On the other hand, in the case of ternary mixtures of p(AA/C_{12}), α-CD, and ADA, as [ADA] is increased, η increases remarkably in the region $0 \leq$ [ADA] ≤ 1.0 g/L and then levels off at ca. 2×10^4 Pa·s when [ADA] > 2.0 g/L. At [ADA] > 2.0 g/L, η values for ternary mixtures of p(AA/C_{12}), α-CD, and ADA are as large as that for α-CD-free p(AA/C_{12}), indicating that α-CD interacts mainly with ADA and hydrophobic associations of C_{12} side chains are considerably recovered.

Photoresponsive Gel-to-Sol and Sol-to-Gel Transitions for a Ternary Mixture of α-CD, p(AA/C_{12}), and ADA Using Photoisomerization of ADA. It is well-known that azobenzene derivatives undergo trans–cis photoisomerization.[24] ADA also underwent photoisomerization from the trans to cis forms and from the cis to trans forms upon irradiation with UV (ca. 355 nm) and visible light (> 440 nm), respectively (see Figure S3 in Supporting Information). The interaction of α-CD with *cis*-ADA was also investigated in the photostationary quasi-cis state by absorption spectroscopy. In the quasi-cis state, the absorption band at ca. 430 nm due to the $n \rightarrow \pi^*$ transition of the *cis*-ADA exhibits no significant spectral change upon addition of varying concentrations of α-CD (see Figure S4 in Supporting Information). This observation indicates that α-CD does not interact or interacts very weakly with *cis*-ADA, consistent with the report on the interaction of α-CD with azobenzene.[22]

When ADA takes the trans form in ternary mixtures of p(AA/C_{12}), α-CD, and ADA, α-CD interacts more favorably with ADA than C_{12} side chains in p(AA/C_{12}). On the other hand, when ADA takes the cis form, α-CD interacts less favorably with ADA than C_{12} side chains. Therefore, association and dissociation of C_{12} side chains may be controlled by photoisomerization of ADA, leading to photoresponsive gel-to-sol and sol-to-gel transitions. Figure 3 shows photographs for a ternary mixture of 5.0 g/L p(AA/C_{12}), 10.0 g/L α-CD, and 2.0 g/L ADA under irradiation with visible and UV light. Under irradiation with visible light (>430 nm), the ternary mixture exhibits a gel-like behavior as shown in Figure 3a. When the gel-like ternary mixture is irradiated with UV light (ca. 355 nm), the mixture is gradually converted to a sol, as shown in Figure 3b. When the sol ternary mixture is irradiated with visible light, the mixture is gradually converted back to the gel-like mixture. It should be noted here that this photoresponsive ternary mixture remains homogeneous upon gel-to-sol and sol-to-gel transitions.

These gel-to-sol and sol-to-gel transitions were investigated by creep recovery. Figure 4 shows changes in η for a ternary mixture of 5.0 g/L p(AA/C_{12}), 10.0 g/L α-CD, and 1.0 g/L ADA upon repetitive irradiations of UV and visible light. Before irradiation with light, the ternary mixture exhibits a higher η (ca. 3×10^3 Pa·s). After irradiation with UV light, the mixture exhibits a lower η (ca. 2×10^{-2} Pa·s), and after succeeding irradiation with visible light, it exhibits a higher η (ca. 2×10^3 Pa·s) again. The photoisomerization of ADA in this ternary mixture was also investigated by ^{1}H NMR spectroscopy. Figure 5 shows NMR spectra for the ternary mixture before irradiation with light (a), after irradiation with UV light (b), and after succeeding irradiation with visible light (c), corresponding to the first three plots in Figure 4. In Figure 5, broad resonance bands at 7.8, 8.1, 8.2, and 8.4 ppm are ascribable to phenyl protons in *trans*-ADA and relatively sharp bands at 7.0 and 7.8 ppm to phenyl protons in *cis*-ADA. From ratios of area intensities in these spectra (Figure 5, a, b, and c), fractions of *trans*-ADA were determined to be ca. 0.95, 0.11, and 0.85, respectively. These data demonstrate that these gel-to-sol and sol-to-gel transitions occur repeatedly upon photoisomerizations of ADA from the trans to cis forms and from the cis to trans forms, respectively.

Conclusion

A photoresponsive hydrogel system has been successfully constructed by combination of simple components, α-CD, p(AA/C_{12}), and ADA. Photoresponsive gel-to-sol and sol-to-gel transition properties of this system were studied by rheometry and NMR measurements. An aqueous solution of 5.0 g/L p(AA/C_{12}) exhibited a gel-like behavior because polymer chains form a network structure via hydrophobic associations of C_{12} side chains. As α-CD was added to the gel-like aqueous solution, η exhibited a drastic decrease of more than 6 orders of magnitude in the region $5.0 \leq$ [α-CD] ≤ 10.0 g/L, indicative of a gel-to-sol transition. This is because hydrophobic interactions of C_{12} side chains are dissociated by the formation of inclusion complex of α-CD with C_{12} side chain. When ADA was added to a binary sol mixture of 5.0 g/L p(AA/C_{12}) and 10.0 g/L α-CD, η increased remarkably in the region $0 \leq$ [ADA] $\leq$ 1.0 g/L and then reached a level as high as that for α-CD-free p(AA/C_{12}), indicative of a sol-to-gel transition. This is because, in the ternary mixtures, α-CD interacts more favorably with *trans*-ADA and hydrophobic associations among C_{12} side chains are considerably

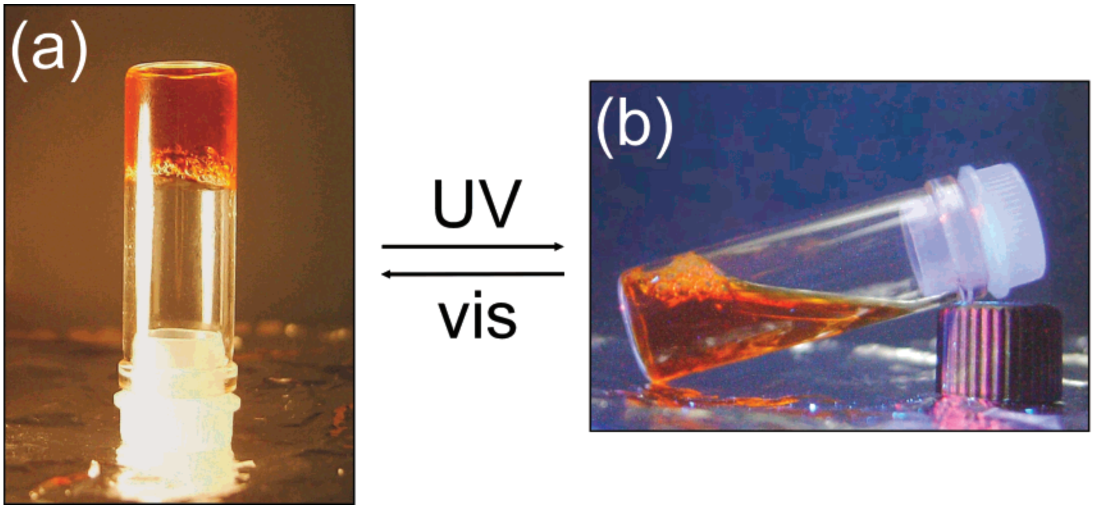


Figure 3. Photographs for a ternary mixture of 5.0 g/L p(AA/C_{12}), 10.0 g/L α-CD, and 2.0 g/L ADA under photoirradiation with visible (a) and UV light (b).

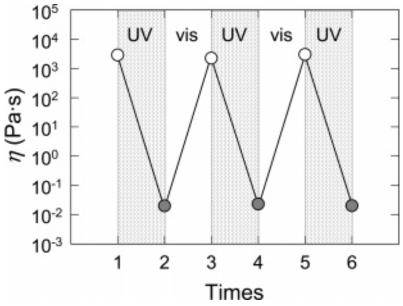


Figure 4. Change in η for a ternary mixture of 5.0 g/L p(AA/C_{12}), 10.0 g/L α-CD, and 1.0 g/L ADA under repetitive irradiations with UV (closed) and visible light (open).

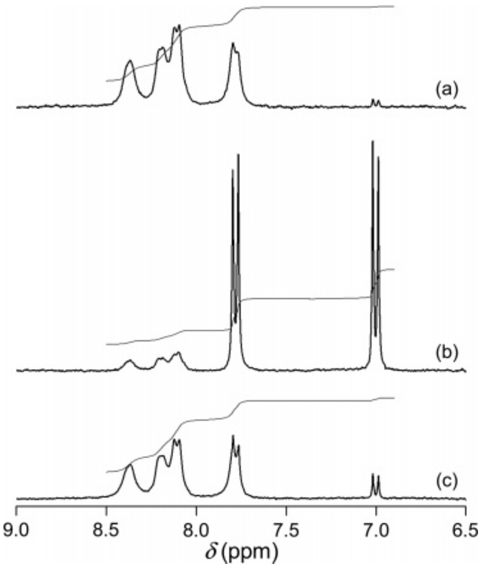


Figure 5. ^{1}H NMR spectra of a ternary mixture of 5.0 g/L p(AA/C_{12}), 10.0 g/L α-CD, and 1.0 g/L ADA; before irradiation with light (a), after irradiation with UV light (b), and after succeeding irradiation with visible light (c).

restored. When a ternary gel mixture of 5.0 g/L p(AA/C_{12}), 10.0 g/L α-CD, and 1.0 or 2.0 g/L ADA was irradiated with UV light, the mixture underwent a gel-to-sol transition. When the ternary sol mixture was irradiated with visible light, the mixture underwent a sol-to-gel transition. Creep recovery and ^{1}H NMR data demonstrated that these gel-to-sol and sol-to-gel transitions occurred repeatedly upon photoisomerizations of ADA from the trans to cis forms and from the cis to trans forms.

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Supporting Information Available: Creep compliance−time plots for p(AA) and p(AA/C_{12}), UV−vis absorption spectra of ADA and Benesi−Hildebrand plot for inclusion complexes of α-CD with ADA, time evolution of UV−vis absorption spectra for ADA, and UV−vis absorption spectra of ADA in the quasi-cis state. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) Fitting data in Figure 1 using eq 1, characteristic values for 5.0 g/L p(AA) and p(AA/C_{12}) were determined as follows: For p(AA), $J_0 = 0$ Pa^{-1}, $J_d = 0$ Pa^{-1}, and $\eta = 5.8 \times 10^{-3}$ Pa·s: for p(AA/C_{12}), $J_0 = 4.4 \times 10^{-2}$ Pa^{-1}, $J_d = 1.3 \times 10^{-2}$ Pa^{-1}, $\lambda = 5.4 \times 10^1$ s, and $\eta = 2.0 \times 10^4$ Pa·s.

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