1. Effect of HAc Catalyst Concentration

The condensation reaction of acylhydrazine and aldehyde groups to yield acylhydrazone bonds proceeds by a stepwise mechanism involving the formation of an intermediate hemiaminal.\(^1\) At the low pH condition, hemiaminal formation is the rate-determining step.\(^2\) Acid catalysis can facilitate the formation process significantly.\(^1,3\) Therefore, the content of catalyst plays an important role in determining the reaction rate.

The effect of HAc volume fraction (4.8 - 16.7 v%) on the gelation kinetics was investigated by dynamic time sweep tests. Here the gelator concentration was fixed at 10.4 wt%. The elastic modulus ($G'$) and viscous modulus ($G''$) as a function of time are shown in Figure S1a. The increasing behavior of $G'$ and $G''$ with time are similar for different samples. At the beginning of the reaction, the system shows a liquid-like characteristic as $G'$ is far less than $G''$. As the time progresses, $G''$ increases gradually and $G'$ shows a sharp increase in the vicinity of the gel point and crosses over $G''$. Then the sample shows a solid-like characteristic, and $G'$ is larger than $G''$ and finally approaches a plateau which is defined as
the equilibrium modulus ($G_e$). As a polycondensation reaction with an average functionality larger than two, branched polymers are firstly formed by condensation of A$_2$ and B$_3$ in pre-gel regime. $G''$ increases with the molecular weight of branched polymers. When a network spanning the whole system appears, the system reaches the gel point with $G'$ increasing remarkably. In the post-gel regime, $G'$ increases until the stable network is completely formed.

The time at $G'$ and $G''$ cross-over is defined as the apparent critical gelation time ($t_{gel}$)$^4$ (Here the cross-over time of $G'$ and $G''$ plus the interval time of 5 minutes is defined as the apparent $t_{gel}$) and the inverse of the apparent $t_{gel}$ ($1/t_{gel}$) reflects the average reaction rate in the pre-gel state. It is clear that the apparent $t_{gel}$ decreases with increasing HAc volume fraction. Figure S1a also illustrates that the $G'$ plateau increases with increasing HAc volume fraction. $G_e$ can be easily obtained by performing a dynamic frequency sweep on well-gelated samples. The frequency spectra of $G'$ and $G''$ are shown in Figure S1b. The $G'$ of all gels are independent of frequency ($\omega$), validating that the stable gel has been formed. $G_e$ is plotted as a function of HAc volume fraction in Figure S1c, which shows that $G_e$ first increases but levels off when the HAc volume fraction is larger than 13.0 v%. Accordingly, the HAc volume fraction is fixed at 13.0 v% for the remaining experiments in this work.

As shown in Scheme 1, the reaction of acylhydrazine and aldehyde forms acylhydrazone bonds and the by-product of water which can be absorbed by the acid catalyst (HAc). The decreasing of free water makes the equilibrium shift to the right direction. In our system, molar concentration of HAc is much higher than that of A$_2$. It is expected that water was completely absorbed. Therefore, when the equilibrium constant is fixed, the final conversion will approach 100%, and $G'$ reaches $G_e$ eventually.
**Figure S1.** (a) Plots of storage $G'$ (solid symbol) and loss $G''$ (open symbol) modulus against time for different HAc volume fractions (4.8 v%, 9.1 v%, 13.0 v%, 16.7 v%). The samples with 13.0 v% and 16.7 v% HAc are highlighted in the inset figure. The cross-over time of $G'$ and $G''$ plus the interval time (5 min) is defined as the apparent critical gelation time ($t_{gel}$). (b) Dynamic storage $G'$ (solid symbol) and loss $G''$ (open symbol) modulus against frequency ($\omega$) for samples with different HAc volume fractions tested after fully gelated. (c) Equilibrium modulus ($G_e$) as a function of HAc volume fraction. Gelator concentration is fixed on 10.4 wt%.

2. The viscosity of the samples with concentration below $c_g$

The steady state flow was performed on the samples with concentration below $c_g$ (1.8, 2.2, 2.4, 2.6, 2.8, and 3 wt%) which had reacted 48 hours. Shear rate dependence of apparent viscosity is shown in Figure S2. The independence of apparent viscosity on the shear rate indicates that the sample with concentration below $c_g$ is a pseudo-Newtonian fluid.

![Figure S2](image)

**Figure S2.** Shear rate dependence of apparent viscosity for the samples with concentration below $c_g$. The independence of apparent viscosity on the shear rate indicates that the sample with concentration below $c_g$ is a pseudo-Newtonian fluid.

3. Determination of the equilibrium constant $K_{eq}$ using NMR analysis
$^1$H-NMR measurements were carried out on a Bruker AV 400 spectrometer at 25 °C; δ in ppm downfield from Me$_4$Si as internal standard. A$_2$ and B$_3$ were dissolved in 2ml DMF-d$_7$ separately (both at 0.04M of the functional group in DMF-d$_7$). The $^1$H-NMR spectra of B$_3$ solution were shown in Figure S3. The signal of methyl hydrogen of DMF-d$_7$ (since small quantities of H atoms of DMF can not be deuterated) was chosen as reference to determine the relative concentration of B$_3$. The integral intensity of B$_3$ is 0.79.

**Figure S3.** $^1$H NMR spectrum of B$_3$ in DMF-d$_7$

2 ml A$_2$ solution and 2 ml B$_3$ solution were mixed together (so equimolar functional groups) and 13.0 v% HAc catalyst, relative to the volume of mixed solution, was added. Therefore, the initial concentration of aldehyde group (B$_3$) in the mixed solution was diluted to 0.02 M, and the integral intensity of B$_3$ is 0.79/2 = 0.395. The mixed solution was kept at room temperature for 24 hours to make sure that the reaction arrives to the equilibrium state. The $^1$H-NMR spectra of the mixed solution were shown in Figure S4. A new signal of H1" at 8.6 ppm was assigned to the hydrogen connected to the carbon of the acylhydrazone bond. The integral intensity of H1 and H1" is 0.03 and 0.36, respectively. The sum of two integral intensities is 0.39 which is close to 0.395, indicating that the element is conservation. Conclusively, at the equilibrium state the concentration of the aldehyde group (B$_3$) and the concentration of the acylhydrazone bond (A-B) are 0.0015M and 0.018M, respectively. The
concentrations of groups of reactors and products are shown in Table S1. Since A₂ and B₃ were mixed with equimolar functional groups, A₂ and B₃ have same initial and equilibrium concentrations. In fact, A₂ concentration at equilibrium state can not be measured directly, since the acylhydrazine (A₂) is easy to be bonded by the HAc.

Figure S4. ¹H NMR spectrum of A₂+B₃ with 13v% HAc in DMF-d₇ after 24h reaction.

The condensation reaction of acylhydrazine and aldehyde groups to yield acylhydrazone bonds proceeds by a stepwise mechanism involving the formation of an intermediate hemiaminal.¹ At the low pH condition, hemiaminal formation is the rate-determining step.² In addition, the water molecules generated by the dehydration of the hemiaminal were immediately absorbed by the HAc, so the signal of water hydrogen is not appeared in Figure S4. Therefore, the equilibrium constant $K_{eq}$ can be calculated by using equation as

$$K_{eq} = \frac{[A-B]}{[A_2][B_3]}.$$  

The $K_{eq}$ is about 8000 M⁻¹ by using NMR analysis.

Table S1. Concentration of groups of reactors and products

<table>
<thead>
<tr>
<th></th>
<th>[A₂]/M</th>
<th>[B₃]/M</th>
<th>[A-B]/M</th>
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<td>0.0015</td>
<td>0.018</td>
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<tr>
<td>-----------------</td>
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<tr>
<td>Equilibrium state</td>
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</tbody>
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[A_2]: molar concentration of acylhydrazine groups in A_2; [B_3]: molar concentration of aldehyde group in B_3; [A-B]: molar concentration of characteristic functional group in product.

Reference: