



Chemorheological Monitoring of Cross-Linking in Slide-ring Gels Derived From α -cyclodextrin Polyrotaxanes

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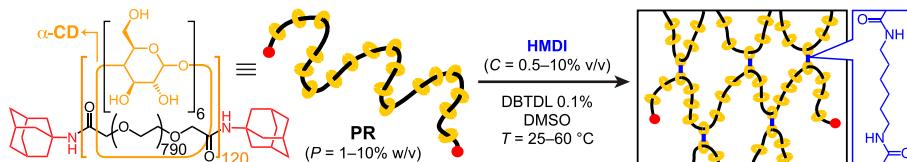
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Despite hundreds of studies involving slide-ring gels derived from cyclodextrin (CD)-based polyrotaxanes (PRs), their covalent cross-linking kinetics are not well characterized. We employ chemorheology as a tool to measure the gelation kinetics of a model slide-ring organogel derived from α -cyclodextrin/poly (ethylene glycol) PRs cross-linked with hexamethylenediisocyanate (HMDI) in DMSO. The viscoelastic properties of the gels were monitored *in situ* by small-amplitude oscillatory shear (SAOS) rheology, enabling us to estimate the activation barrier and rate law for cross-linking while mapping experimental parameters to kinetics and mechanical properties. Gelation time, gel point, and final gel elasticity depend on cross-linker concentration, but polyrotaxane concentration only affects gelation time and elasticity (not gel point), while temperature only affects gelation time and gel point (not final elasticity). These measurements facilitate the rational design of slide-ring networks by simple parameter selection (temperature, cross-linker concentration, PR concentration, reaction time).

Keywords: chemorheology, rheology, cyclodextrins, organogels, slide-ring gels, polyrotaxane, viscoelasticity

INTRODUCTION

Main-chain polyrotaxanes are mechanically bonded macromolecules with sliding bead-on-string structures which, when appropriately cross-linked, give rise to slide-ring networks Okumura and Ito (2001); Mayumi et al. (2015) having remarkable stress-dissipative properties. Mayumi and Ito (2010) The most highly researched slide-ring networks are derived from the poly (ethylene glycol) (PEG)/ α -cyclodextrin (α -CD) polyrotaxanes first introduced by Harada, Harada et al. (1992) due in large part to their favorable cost, biocompatibility, and accessibility. Araki and Ito (2007) These networks can exhibit high softness, Kato et al. (2013) extensibility, Bin Imran et al. (2014); Kato et al. (2015b); Jiang et al. (2018) and fracture toughness, Liu et al. (2017, 2019) leading to varied applications in technologies such as cell-growth substrates Hyodo et al. (2019); Rajendran et al. (2019), dental materials Matsunaga et al. (2020), piezoelectric sensors Seo et al. (2021), scratch-resistant coatings, Noda et al. (2014); Seo et al. (2019) and battery electrode binders. Choi et al. (2017); Cho et al. (2019); Yoo et al. (2019) Despite the growing reach of slide-ring gels, Hart et al. (2021) reports on their kinetics are limited mainly to gel degradation Kang et al. (2021) or physical gels formed by hydrogen-bond-driven α -CD micro-crystallization. Travelet et al. (2009, 2010a,b).



SCHEME 1 | Synthesis of slide-ring gels from α -CD/PEG polyrotaxane (PR) and cross-linker HMDI.

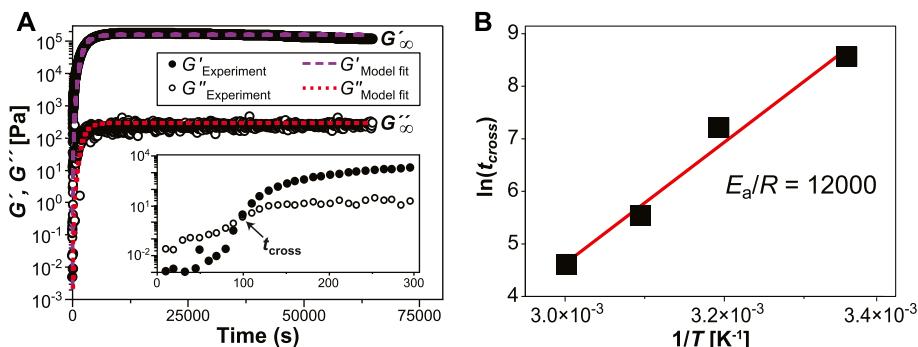


FIGURE 1 | (A) Chemorheological time sweep of sample $P_{10}C_5T_{60}$ over 68,400 s (18 h) show the plateau moduli (G', G'') when gelation is complete. Inset magnifies the gel point at crossover time (t_{cross}) in the first 300 s. (B) Activation energy of gelation. An Arrhenius plot of t_{cross} against $1/T$ gives an activation energy of 96 kJ/mol for the cross-linking reaction.

In the course of our own slide-ring experiments, Dikshit and Bruns (2021) we sought to characterize the kinetics of chemically cross-linked polyrotaxane gels in order to calibrate our reaction times. Here we chemically cross-link α -CD PRs and use SAOS rheological time sweeps to characterize the gelation process *in situ* by observing the temporal evolution of the viscoelastic moduli. We show how the kinetics and mechanics of a model slide-ring gel depend on temperature, cross-linker concentration, PR concentration, and reaction time. This information will facilitate the selection and fine-tuning of desired network structure and properties.

RESULTS AND DISCUSSION

We chose to measure the chemical gelation kinetics by chemorheology Halley and Mackay (1996) to serve our interests in gel mechanics. The PR physical gelation studies Travelet et al. (2009, 2010a,b) have validated a rheological approach to measuring gelation kinetics in PR systems. Among a variety of hydroxyl-reactive cross-linkers, Karino et al. (2006); Samitsu et al. (2006); Shinohara et al. (2006); Ito (2007) HMDI has been reacted with CD-based PRs to give slide-ring gels, Kato et al. (2013) adhesives, Dikshit and Bruns (2021) elastomers, Minato et al. (2017) nanocomposites, Iida et al. (2021) polymer electrodes, Lin et al. (2018) and piezoelectric sensors. Seo et al. (2021) In our model system, we employ HMDI in DMSO with 0.1% v/v dibutyltin dilaurate (DBTDL) to cross-link (Scheme 1) the α -CD rings of an adamantine-capped Araki

et al. (2005) polyrotaxane (PR) based on a PEG backbone of molecular weight (MW) 35,000 Da and an inclusion ratio (proportion of threaded diethylene glycol units in the chain) of ~30%, corresponding to ~120 α -CD rings per chain based on NMR signal integration. The number-average molecular weight of 152 kDa obtained using NMR analysis (Supplementary Figure S1) is comparable to that estimated by gel permeation chromatography (138 kDa, Supplementary Figure S2). Specimen labels of the form $P_pC_cT_t$ differentiate the samples based on PR concentration (P_p), HMDI concentration (C_c) and temperature (T_t). By monitoring the isothermal evolution of viscoelastic moduli in SAOS, we describe how these parameters impact gelation kinetics and mechanical properties. Other gelation parameters, such as sample volume (0.5 ml) and reaction time (18 h), were held constant across all experiments.

Figure 1A shows an example of the evolution of storage moduli (G') and loss moduli (G'') in specimen $P_{10}C_5T_{60}$ ([PR] = 10% w/v [HMDI] = 5% v/v, $T = 60^\circ\text{C}$) over 18 h. The inset magnifies the data at the gel point, where G' and G'' intersect at crossover time t_{cross} . We performed the analogous sweeps while varying PR concentration from 1 to 10% w/v (Supplementary Figure S3, [HMDI] = 5% v/v, $T = 60^\circ\text{C}$), HMDI concentration from 0.5 to 10% v/v (Supplementary Figure S4, [PR] = 10% w/v, $T = 25^\circ\text{C}$), and temperature from 25 to 60°C (Supplementary Figure S5, [PR] = 10% v/v, [HMDI] = 5% w/v). A thin layer of heavy mineral oil is maintained around the sample throughout the *in situ* gelation to prevent drying. Without the ring of mineral oil, an 18-h time sweep of sample $P_{10}C_0T_{25}$ (no cross-linker) exhibits an increase in viscoelastic moduli and gel point due to

TABLE 1 | Fitting parameters using modified Hill equation.

Specimen Name	θ [s]	G'_∞ [kPa]	α	P [Pa.s ⁻¹]
$P_1C_5T_{60}$	6.49×10^4	10.6	2.47	1.14
$P_2C_5T_{60}$	4.17×10^4	15.2	1.86	0.169
$P_5C_5T_{60}$	1.94×10^4	71.5	1.24	0.101
$P_{10}C_{0.5}T_{25}$	6.02×10^4	1.30	9.13	0.049
$P_{10}C_1T_{25}$	5.67×10^4	4.74	5.42	0.113
$P_{10}C_1T_{50}$	2.79×10^3	4.63	3.05	1.26
$P_{10}C_1T_{60}$	1.43×10^3	4.92	3.25	2.79
$P_{10}C_5T_{25}$	5.18×10^4	130	2.83	1.78
$P_{10}C_{10}T_{25}$	1.72×10^4	562	2.72	22.2
$P_{10}C_5T_{40}$	2.90×10^4	100	2.19	1.88
$P_{10}C_5T_{50}$	1.06×10^4	105	1.60	3.97
$P_{10}C_5T_{60}$	2.88×10^3	159	3.18	44.1

physical gelation associated with sample drying; in the presence of mineral oil the same solution does not dry and the moduli remain unchanged over the 18-h interval (**Supplementary Figure S6**). Isothermal time sweeps have been used to capture time-resolved viscoelasticity data in other cross-linking reactions, Chambon and Winter (1987); Adrus and Ulbricht (2013); Vo et al. (2020) where the evolution of G' and G'' can be linked to specific processes in the sample. G' and G'' are equal at the gel point, above which the material attains enough elastically effective cross-links to exhibit solid-like behavior. Vlassopoulos et al. (1998) The Arrhenius plot (**Figure 1B**) of $\ln(t_{cross})$ vs inverse temperature ($1/T$) was used to estimate Yang et al. (2015) a gelation activation energy of 96 kJ/mol. Since this activation energy exceeds that of small-molecule isocyanate-hydroxyl coupling, Cheikh et al. (2019) we infer that autore retardation due to cross-linker immobilization on the PR and nearest neighbor effects Alfrey and Lloyd (1963) are involved. This finding also supports the presumed mechanism of gelation driven by urethane formation between HMDI and α -CD, since the physical gelation process driven by hydrogen bonding in α -CD PRs has negative activation energy. Travelet et al. (2009) Further information can be extracted Sun Han Chang et al. (2019) from the time sweeps by fitting the data to the modified Hill Eq (1):

$$G'(t) = G'_\infty \frac{t^\alpha}{t^\alpha + \theta^\alpha} \quad (1)$$

where θ is gelation halftime, G'_∞ is the plateau modulus and α is an exponential fitting parameter. Adibnia and Hill (2016)

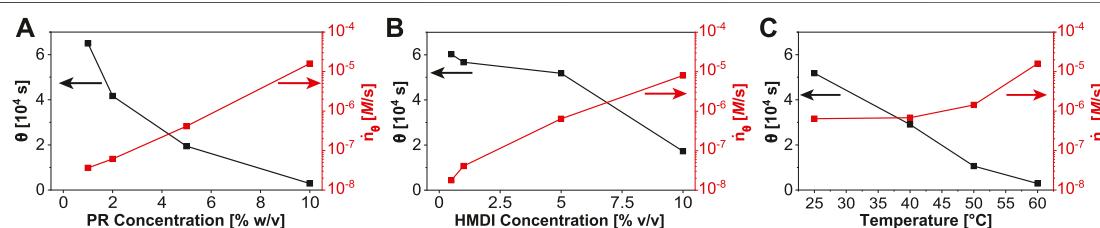
The modified Hill equation is a kinetic equation adapted to understand systems that evolve with time, often used to evaluate dose response curves in pharmacology Giraldo et al. (2002) and in supramolecular chemistry. Gorteau et al. (2005); Benedini et al. (2021) The fitting parameters obtained from the modified Hill equation shed light on how cross-links form over time in the gel. Junior et al. (2019); Kodavaty et al. (2020) G'_∞ captures the stiffness of the final gel. θ reflects the speed of the reaction after t_{cross} . These terms can be used to calculate (**Table 1**) the rate of production of elastically effective cross-links (\dot{n}_θ) at gelation halftime according to **Eq (2)**.

$$\dot{n}_\theta = \frac{\alpha G'_\infty}{4\theta RT} \quad (2)$$

The fitted data show that gelation can be accelerated by increasing PR concentration (**Figure 2A**), HMDI concentration (**Figure 2B**), or temperature (**Figure 2C**). The rate \dot{n}_θ increases by almost three orders of magnitude as the concentration of either PR or HMDI increases from 1 to 10%. We do not exceed 10% v/v for HMDI concentration because the pulley effect is suppressed Fleury et al. (2007) with increasing cross-link density, while 10% w/v is approaching the solubility limit of PR in DMSO. We could not obtain gels reliably below 1% PR or 0.5% HMDI concentrations. The rate \dot{n}_θ is insensitive to temperature over the range of 25–50°C, but increases by an order of magnitude between 50 and 60°C. The rate of crosslink production shows a second-order dependence with respect to the cross-linker concentration (**Supplementary Figure S7**), while it is 2.5 order with respect to PR concentration (**Supplementary Figure S8**). Using the empirical data (**Table 1**; **Figure 2**), the rate law for the production of elastically effective cross-links is determined to be:

$$\dot{n}_\theta = (1.9 \times 10^4 M^{-3.5} s^{-1}) [HMDI]^2 [PR]^{2.5}$$

The plateau modulus, G'_∞ , reflects the final count of cross-links when gelation is complete. As shown in **Figure 3**, G'_∞ is sensitive to PR concentration (**Figure 3A**) and highly sensitive to HMDI concentration (**Figure 3B**), but insensitive to temperature (**Figure 3C**). The plateau modulus increases by almost three orders of magnitude as [HMDI] increases from 0.5 to 10% v/v, while it increases approximately one order of magnitude as [PR]

**FIGURE 2** | Tracking gelation as a function of reaction conditions. Gelation halftime (θ) and rate of production of elastically effective crosslinks (\dot{n}_θ) against **(A)** polyrotaxane concentration (60°C , 5% HMDI) **(B)** cross-linker concentration (25°C , 10% PR) and **(C)** temperature (5% HMDI, 10% PR).

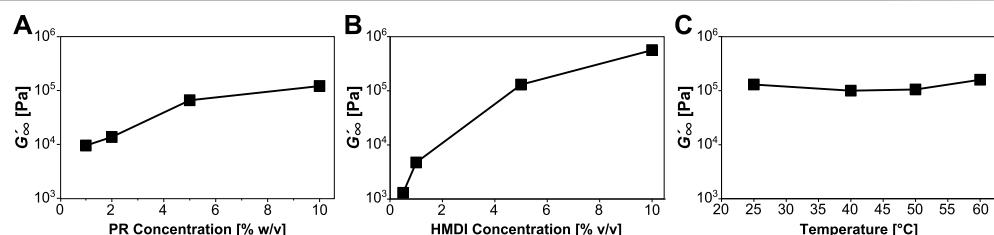


FIGURE 3 | Post-gelation mechanics of slide-ring gels. Plateau modulus (G'_{∞}), which serves as a proxy for mechanical properties after completion of gelation, is plotted against **(A)** PR concentration **(B)** cross-linker concentration and **(C)** temperature. Concentration of HMDI, which dictates the formation of elastically effective crosslinks, has a significantly higher impact on G'_{∞} than temperature and PR concentration.

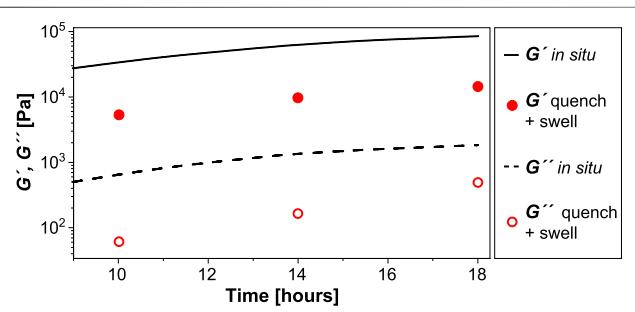


FIGURE 4 | Controlling gelation and polyrotaxane mechanics. Storage and loss moduli values (circular symbols) of gels terminated at 10 h, 14 h, and 18 h are compared with the time sweep data of $P_{10}C_5T_{25}$. The swelling ratios (by weight) of the organogel are mentioned at the specific time points in the gelation process.

increases from 1 to 10% w/v. The insensitivity of G'_{∞} to temperature, also observed in the case of sample $P_{10}C_1T_x$ ($x = 25, 50$, or 60°C , **Supplementary Figure S9**), suggests that the final network structure is similar when [PR] and [HMDI] are held constant, given sufficient reaction time. This observation further implies that the solution-state structure of PR does not vary between 25 and 60°C , and that the cross-linker is consumed completely in all the experiments. We confirmed that HMDI is consumed completely over the 18-h interval by monitoring the gelation of $P_{10}C_5T_{25}$ by *in situ* FTIR spectroscopy. The absorption band at $2,260\text{ cm}^{-1}$ attributable to the isocyanate group disappears completely as it is replaced by signals corresponding to the NH and C=O groups of the urethane cross-links (**Supplementary Figure S10**).

We leveraged our time-resolved viscoelasticity data to demonstrate a novel way to tune slide-ring gel softness based on reaction time. We hypothesized that quenching the cross-linking reaction prior to completion would result in softer final gels with moduli that are predictably lower, proportional to the *in situ* viscoelastic moduli at quench time. Samples of $P_{10}C_5T_{25}$ in glass scintillation vials were quenched at time points of 10, 14, and 18 h by the addition of excess methanol, followed by vacuum drying overnight at 70°C . The quenched gels were swollen in DMSO for 24 h before carrying out frequency sweeps (0.1–100 rad/s, strain 1%, **Supplementary Figure S11**). The red data points representing these gels, softened

due to swelling, Subramani et al. (2020) are superimposed on the *in situ* sweep of $P_{10}C_5T_{25}$ in **Figure 4**, showing uniformly lower values. The storage moduli of the swollen quenched gels increase from 5.3 kPa (10 h) to 14.4 kPa (18 h), while the corresponding loss moduli increase from 61 to 491 Pa, respectively. The ratio of $G'_{18h};G'_{10h}$ is 2.7 *in situ* and 2.5 after quenching and swelling. Likewise, $G'_{14h};G'_{10h}$ is 1.8 *in situ* and 1.9 after quenching and swelling. The nearly matching ratios confirm that the chemorheological sweeps can be used to predict and select desired modulus values (below the maximum) by quenching at an appropriate time in the evolution of the cross-linking reaction. The swelling ratio of the quenched gel decreases from 16 at 10 h to eight at 18 h (**Supplementary Table S1**), confirming the higher cross-link density of the latter sample. This quenching procedure provides an additional handle to fine-tune gel stiffness beyond HMDI concentration, which is a more coarse-tuning factor. Since it is performed at room temperature, it also reduces equipment and labor requirements.

CONCLUSION

In summary, chemorheological characterization of polyrotaxane gelation kinetics provides insight on the evolution of gel elasticity and its dependence on polymer and cross-linker concentration, as well as temperature. Our kinetics data confirm that the mechanism of polyrotaxane gelation is driven by the formation of chemical cross-links and may also help researchers calibrate their gelation conditions to achieve desired gel structure and properties. The reaction is, unsurprisingly, most sensitive to cross-linker concentration [HMDI], which influences the gelation time, gel point, and final elasticity. PR concentration impacts the reaction rate more strongly, but the final gel elasticity is less affected, while the gel point is almost unchanged at all PR concentrations. The reaction temperature does not affect the final gel mechanics, but the total reaction time is reduced from 18 h at room temperature to less than 1 h at 60°C , information which is of practical consequence for preparing these gels. We also showed that the gelation may be arrested mid-reaction by quenching, and the elasticity of the resulting swollen gels are proportional to those made *in situ*. In addition to the experimental parameters probed here, other work has shown

that factors such as PR molecular weight, Ohmori et al. (2016) inclusion ratio, Kato et al. (2015b); Jiang et al. (2018) ring size, Kato et al. (2015a) functional groups, Bin Imran et al. (2014); Liu et al. (2021) and type of cross linker Kato et al. (2019); Liu et al. (2021) also play major roles in the mechanical properties of slide-ring gels. Our chemorheological data add to this body of knowledge and enable judicious selection of reactant concentrations, temperature, and reaction time to control the viscoelastic properties of slide-ring gels over a wide range of modulus values between 1 kPa and 1 MPa.

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/**Supplementary Material**. Further inquiries can be directed to the corresponding author.

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AUTHOR CONTRIBUTIONS

KD and CB planned experiments, performed analysis, and wrote the manuscript. KD performed all experiments.

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SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/fchem.2022.923775/full#supplementary-material>

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