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Gels Based on Cyclic Polymers

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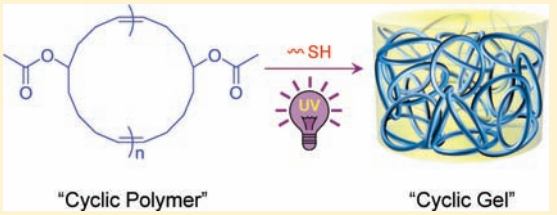
Supporting Information

ABSTRACT: Cyclic poly(5-hydroxy-1-cyclooctene) (PACOE) was synthesized by ring-expansion metathesis polymerization (REMP), and thiol−ene chemistry was used to cross-link the internal double bonds in the PACOE backbone. This created a novel network material (gels formed from cyclic polymers) with unique structural units, where the cyclic PACOE main chains, which serve as secondary topological cross-linkages, were connected by primary *inter*molecular chemical cross-linkages. The resulting properties were notably different from those of traditional chemically cross-linked linear PACOE gels, whose gel fraction (GF) and modulus (G) increased while the swelling ratio (Q) decreased with increasing initial polymer concentration in the gel precursor solution (C_0). For the gels formed from cyclic polymers, however, the GF, Q, and G all simultaneously increased as C_0 increased at the higher range. Furthermore, at the same preparation state (same C_0), the swelling ability and the maximum strain at break of the gels formed from cyclic polymers were always greater than those of the gels formed from linear polymers, and these differences became more pronounced as C_0 increased.



INTRODUCTION

The properties of substances are determined by their inherent chemical structures, and this holds true for one of the most widely used soft materials nowadays − swollen networks, or gels. In recent years, many excellent examples have shown how manipulating the cross-linking structure can significantly alter the final characteristics of the gel. One example is the topological (TP) gel, developed by Okumura et al. in 2001,[1] where polyrotaxane, consisting of α-cyclodextrin (α-CD) and poly(ethylene glycol) (PEG), was used as the structural units. By chemically cross-linking the α-CD component, the 'figure-of-eight' cross-linkages were constructed, which can slide along the PEG chains in the TP gel. This special structural topology provided the TP gel with good tensile strength and a large swelling capacity. In 2002, Haraguchi et al. developed nanocomposite (NC) gels,[2] in which poly(*N*-isopropylacrylamide) chains were cross-linked by inorganic clay slabs with a scale of several tens of nanometers. Compared to the corresponding gels made via traditional organic cross-linking agents, the moderate fluctuation in cross-link density as well as the cooperative force sustained by the clay particles connecting individual polymer chains endowed the NC gel with excellent optical transparency, rapid response times, large equilibrium swelling, and the ability to undergo superior elongation with near-complete recovery. The same concept was further developed for making physically cross-linked hydrogels by mixing the clay slabs with dendritic molecular binders.[3] From this method, highly transparent hydrogels with exceptional mechanical strength, as well as rapid and complete self-healing abilities, were obtained. A third example are the double network (DN) gels, recently developed by Gong et al.[4] A highly cross-linked, stiff poly(2-acrylamido-2-methylpropanesulfonic acid) network was interpenetrated by a loosely cross-linked poly(acrylamide) network, forming a hydrogel with high mechanical strength, which was ascribed to the structural inhomogeneity of the DN gel.[5] Finally, inspired by the concept of using a self-threading-based approach to form cross-linked polyrotaxane networks,[6,7] a series of novel mechanically cross-linked (MC) gels were developed by polymerizing the cyclic macromonomers.[8−11] In these gels, the mobility of their non-bonding cross-linkages provided them with superior swelling abilities.

It is well-known that structural defects in networks, such as loops and dangling chain ends, greatly deteriorate gel properties because they do not contribute to the elasticity of the cross-linked networks. In many widely used methods for network formation, such as the radical copolymerization of monomers with a small amount of cross-linker, or the direct cross-linking of linear polymer chains, there is no way to eliminate these inherent defects. However, if cyclic polymer chains are used as the basic structural units rather than their linear counterparts, then, in theory, perfect networks without any dangling chain ends can be formed when more than two cross-linkages per polymer chain are constructed. Even short of this ideal behavior, *intra*molecular cross-links, which typically yield loops with no elastic contribution, are more likely to contribute to the network due to the unique cyclic topology. This should result in gels with remarkably improved properties. Surprisingly, even after several decades of developments in gel materials, this concept remains largely unexplored, most likely due to the difficulties in obtaining functional cyclic polymers with high yields using conventional polymerization techniques.[12−16] However, in 2002, Grubbs et al.[17] introduced a powerful method, known as ring-expansion metathesis polymerization (REMP), which made it possible to

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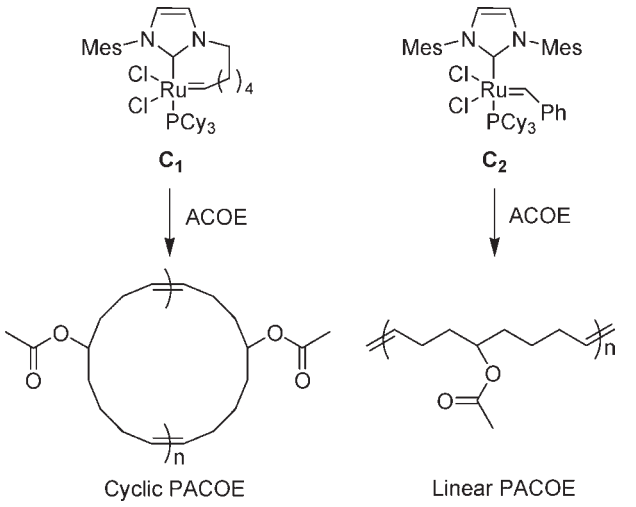
Scheme 1. Structures of the Cyclic REMP Catalyst C1 and Olefin Metathesis Catalyst C2, and the Resultant Cyclic PACOE and Linear PACOE



produce pure cyclic polyolefins in large quantities from high reaction concentrations. Through further work in this area, the mechanism of REMP has been elucidated and a series of cyclic Ru-alkylidene catalysts have been developed.[17−21] An additional virtue of REMP is that the resulting polymers contain a large quantity of double bonds in their main chain, providing a chemical handle for further modification, using methods like thiol−ene chemistry.[22−24] Compared to the traditional free radical polymerization of double bonds, oxygen inhibition can be reduced significantly in the presence of a small amount of thiol.[22,25] Furthermore, due to the controllable step-growth mechanism, thiol−ene chemistry can produce polymer networks with delayed gelation, low levels of shrinkage, high conversions, and uniform cross-linking densities, resulting in unique physical and mechanical properties.[22,23]

Herein, by combining REMP and thiol−ene chemistry, novel gel materials formed from cyclic polymers were prepared by chemically cross-linking cyclic poly(5-acetoxy-1-cyclooctene) (PACOE), the basic structural unit. The unique formation process and resulting properties, which are distinctly different from traditional gels based on cross-linked linear PACOE, are described for the first time.

RESULTS AND DISCUSSION

Polymerization Chemistry. The cyclic REMP catalyst **C1**,[19,26] the standard olefin metathesis catalyst **C2**[26] (Scheme 1), and the 5-acetoxy-1-cyclooctene (ACOE) monomer[27] were synthesized according to previous publications and are detailed in the experimental section (Supporting Information). Polymerization of ACOE by **C1** and **C2** was performed in benzene at 40 °C for 12 h to produce cyclic and linear PACOE respectively, whose structures are shown in Scheme 1. Table 1 lists the detailed synthesis conditions for cyclic **PACOE-1** with **C1** and linear **PACOE-2** and **PACOE-3** with **C2** and their GPC characterization details, as shown in Figure S4 of the Supporting Information. The molecular weight of PACOE can be manipulated by simply changing the molar ratio between the ACOE monomer and catalyst. In the ^{1}H NMR of cyclic **PACOE-1** (part A of Figure S5 of the Supporting Information) and linear **PACOE-2** (part B of Figure S5 of the Supporting Information) following polymerization but before purification, the peaks at 5.73−5.60 ppm corresponding to the double bonds of ACOE disappeared completely in both cases, which means that the polymerization of ACOE by both **C1** and **C2** is highly efficient and proceeds to completion.

Table 1. Synthesis and Characteristics of Poly(5-acetoxy-1-cyclooctene) (PACOE)

run[a]	feed ratio[b]	M_n[c]	M_w/M_n[c]	$M_{n,\ MALLS}$[d]
cyclic **PACOE-1**	1000:1	178 900	1.77	595 700
linear **PACOE-2**	1000:1	127 200	1.68	273 200
linear **PACOE-3**	1500:1	248 300	1.70	571 000

[a] **C1** was used as the catalyst for cyclic **PACOE-1**; **C2** was used as the catalyst for linear **PACOE-2** and **PACOE-3**; $[ACOE]_0$ = 0.5 M in benzene; reaction temperature = 40 °C; reaction time = 12 h. [b] Initial molar ratio between ACOE monomer and catalysts. [c] Apparent molecular weight and its polydispersity index were calculated from GPC with a RI detector; THF was used as the eluent and polystyrene standards were used for the calibration. [d] Absolute molecular weight was characterized from GPC with a multiangle laser light scattering detector; THF was used as the eluent; dn/dc for PACOE in THF was measured as 0.086 mL/g.

To confirm the cyclic topology of **PACOE-1**, the apparent and absolute molecular weights of the PACOEs were measured by GPC using refractive index and multiangle laser light scattering detectors, respectively. The determined apparent molecular weight for a cyclic polymer should be lower than that of its linear counterpart having the same absolute molecular weight, due to the lower hydrodynamic volume of cyclic polymers.[13,15,17] In fact, it has been shown from GPC measurements that a cyclic polymer's apparent molecular weight is lower than that of its linear counterpart by a factor of approximately 0.7 in the high molecular weight range (>20 kDa).[17,28] From Table 1, the absolute molecular weights of cyclic **PACOE-1** (596 kDa) and linear **PACOE-3** (571 kDa) were similar, whereas the apparent molecular weight of cyclic **PACOE-1** (179 kDa) was much less than that of linear **PACOE-3** (245 kDa). Here, the experimentally determined factor is 0.72, demonstrating that **PACOE-1** has a smaller hydrodynamic volume, and strongly suggesting it has a cyclic topology.

Cross-linking Chemistry. Thiol−ene chemistry was utilized to initiate radical formation and the subsequent cross-linking of the internal double bonds in PACOE, leading to network formation. Because of the steric hindrance of internal alkenes and the slow chain-transfer hydrogen-abstraction process between alkyl thiols and internal alkenes,[22,29,30] when an alkyl thiol with lower activity is used as a transfer agent with PACOE, the carbon-centered radicals formed should theoretically have a longer lifetime, resulting in an increased probability of termination via coupling. As a result, thiol−ene chemistry is a powerful tool that allows us to either modify the PACOE chains or make cross-linked gels simply by manipulating the molar ratio between the alkyl monothiol and the PACOE double bonds. Here, 1-hexanethiol was selected to demonstrate this concept.

When the molar ratio of PACOE double bonds to 1-hexanethiol was 1:20, no gels were obtained even after 4 h of UV irradiation, due to extensive addition of 1-hexanethiol across the double bonds. Part C of Figure S5 of the Supporting Information shows the ^{1}H NMR of modified linear **PACOE-2** after this

Table 2. Gel Fraction, Swelling Ratio in Different Organic Solvents, Shear Modulus of Gels Formed from Cyclic Polymers, and Gels Formed from Linear Polymers in Xylene

		Q (mL/g)[c]					
run[a]	GF (%)[b]	DCM	THF	benzene	anisole	xylene	G (Pa)[d]
			Cyclic **PACOE-1**				
1[e]	51.3	126.2	112.8	110.1	101.3	94.74	111
2[f]	47.5	124.1	104.5	103.8	100.6	87.39	72
3[g]	35.7	199.6	160.5	157.9	150.8	125.4	ND
			Linear **PACOE-2**				
4[e]	73.0	43.47	39.72	38.66	36.75	34.15	1899
5[f]	56.1	76.08	66.49	65.31	62.85	56.69	915
6[g]	43.6	184.4	150.1	137.4	140.7	118.6	ND
			Linear **PACOE-3**				
7[e]	74.3	40.95	38.56	37.14	34.62	31.16	3979
8[f]	59.8	71.92	61.29	62.96	58.25	51.46	1028
9[g]	42.9	174.3	146.4	137.9	132.9	116.8	ND

[a] For runs 1−3, gels were obtained from cyclic **PACOE-1**; for runs 4−6, gels were obtained from linear **PACOE-2**; for runs 7−9, gels were obtained from linear **PACOE-3**. [b] Gel fractions (GF) were calculated by the mass ratio between the dried gel and the addition of PACOE and 1-hexanethiol. [c] Swelling ratios (Q) were obtained by the ratio of organic solvent volume at equilibrium swelling to the mass of the dried gel. Volume/mass was used to calculate Q because each organic solvent has a different density. [d] Shear moduli (G) were obtained from fitting the Mooney−Rivlin model to the strain−stress compression data of gels swollen in xylene, where ND means 'not determined'. [e] The initial PACOE concentration was 84 mg/mL. [f] The initial PACOE concentration was 42 mg/mL. [g] The initial PACOE concentration was 21 mg/mL.

thiol−ene addition. Compared to part B of Figure S5 of the Supporting Information (the ^{1}H NMR of unmodified linear **PACOE-2**), the peak corresponding to double bonds in the PACOE main chains at 5.36 ppm essentially disappeared, giving a conversion of 96%. Signals at 2.48 and 0.99 ppm are observed, which correspond to the $-CH_2-S-$ and CH_3- of 1-hexanethiol from the newly formed thiol ether. In addition, the FTIR spectrum of linear **PACOE-2** functionalized by 1-hexanethiol (curve 2 of part A of Figure S6 of the Supporting Information) shows that the bands corresponding to the double bonds at 965 cm^{-1} decreased significantly when compared to the FTIR spectrum of pure linear **PACOE-2** (curve 1 of part A of Figure S6 of the Supporting Information). Thus, when reacted in the presence of excess 1-hexanethiol, the major reaction is thiol addition across the internal double bonds of PACOE.

Conversely, by reducing the molar ratio from 1:20 to 1:0.5, gels were formed in all cases after just 10 min of UV irradiation in air. To obtain the highest gel fraction (GF), a reaction time of 4 h was maintained. In part A of Figure S6 of the Supporting Information, curves 3−5 are the FTIR spectra of gels from **PACOE-1**, **2**, and **3** with the same initial mass concentration of PACOE (C_0) of 84 mg/mL. No obvious decrement of the double bond peak at 965 cm^{-1} was observed when compared to curve 1 (unmodified linear **PACOE-2**), however the area ratio between the double bond peak at 965 cm^{-1} and the ester group signal at 1731 cm^{-1} (shadowed peaks 1 and 2 of part B of Figure S6 of the Supporting Information) can be used to quantify the double bond conversion in the gels. The ratios for curves 1, 3, 4, and 5 were calculated to be 0.37, 0.34, 0.34, and 0.32 respectively, indicating that only a small fraction of double bonds was consumed to form lightly cross-linked networks. Importantly, there was little difference in the results of the thiol−ene cross-linking chemistry between cyclic and linear PACOE. The FTIR curves and the quantitative area ratios for gels obtained from cyclic and linear PACOE at different initial concentrations (C_0 equal to 84 mg/mL, 42 and 21 mg/mL) are shown in Figure S7 of the Supporting Information. The conversion of the double bonds in the thiol−ene cross-linking reaction was found to be independent of C_0.

Network Characterization. Table 2 shows the GF, swelling ratio (Q) in different organic solvents, and shear modulus (G) of gels obtained from cyclic and linear PACOE at different C_0. The GF was determined by the mass ratio between the dried gel and the addition of PACOE and 1-hexanethiol used to make the gel. Q was calculated from the ratio of organic solvent volume at equilibrium swelling to the mass of the dried gel. Because of the different solubility parameters of PACOE in the various organic solvents, Q decreased from DCM to xylene sequentially. G was obtained from the fit of the Mooney−Rivlin model to the strain−stress data from the compression of equilibrium-swollen gels in xylene.

From Table 1 and Figure S4 of the Supporting Information, it can be seen that the absolute molecular weights of linear **PACOE-2** and linear **PACOE-3** were different, whereas the absolute molecular weights of **PACOE-1** and **PACOE-3** were similar. This was done to demonstrate that the differences in the gel formation process and resulting properties were caused only by the variation in the topology of the polymer chains (cyclic vs linear) and were not due to differences in molecular weight. As shown in Table 2, although the absolute molecular weight of linear **PACOE-3** was approximately two times larger than that of linear **PACOE-2**, at the same C_0, similar values for the GF, Q (in different solvents), and G were obtained, indicating that the gel formation and properties were independent of the PACOE molecular weight within this range. Given that the molecular weights of linear PACOE did not impact gel formation or gel properties, the absolute molecular weight of cyclic **PACOE-1** was chosen to be similar to that of the higher molecular weight linear **PACOE-3** (Table 1).

Some of the differences in behavior between the gels formed from cyclic polymers and gels formed from linear polymers are illustrated in Figure 1. Part A of Figure 1 compares the GF and Q (swollen to equilibrium in DCM) as a function of C_0 for gels from cyclic **PACOE-1** and linear **PACOE-3** (data in Table 2). The same relationships for gels from linear **PACOE-2** are illustrated in Figure S8 of the Supporting Information. From part A of Figure 1, Figure S8 of the Supporting Information, and Table 2, it can be seen that the linear PACOE gels followed the expected trends for conventional chemically cross-linked gels, as both the GF and G increased with increasing C_0, whereas Q decreased. The behavior of the cyclic PACOE gels, however, deviated from these trends. When C_0 increased from 21 to 42 mg/mL, the GF increased and Q decreased, as expected, but when C_0 was increased further to 84 mg/mL, the GF increased only slightly (from 47.5 to 51.3), but so did Q (from 124.1 to 126.2 in DCM). Surprisingly, even though Q increased, G was also found to increase, going from 72 to 111 Pa. Typically, for conventional networks, Q and G are inversely proportional ($Q \approx G^{-3.0}$ in theta solvents);[31] however, for these novel cyclic networks, neither Q nor G decreased at the higher C_0.

To further compare the differences in GF and Q between networks made from cyclic and linear polymers, the ratios of GF

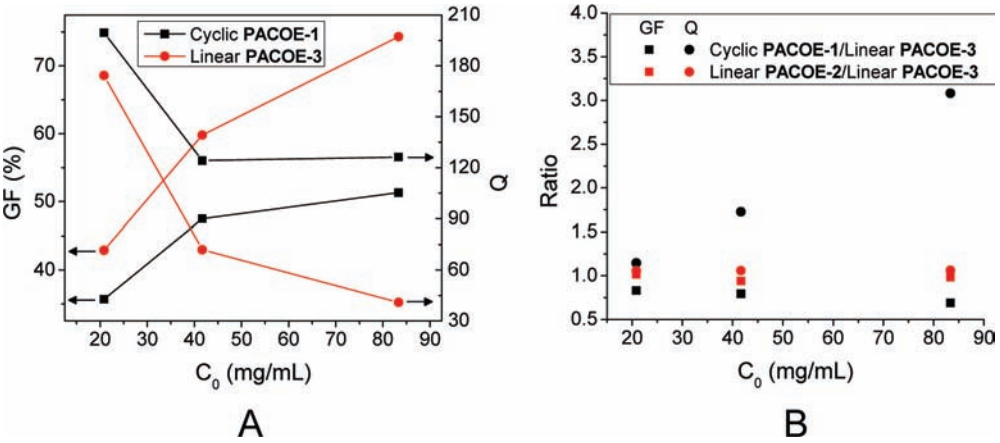


Figure 1. (A) Gel fraction (GF) and swelling ratio (Q) in DCM of gels from cyclic **PACOE-1** and linear **PACOE-3** as a function of the initial PACOE concentration (C_0). (B) The ratios of GF (squares) and the ratios of Q (circles) in DCM at the same C_0 as a function of C_0. The ratios of GF are between gels from cyclic **PACOE-1** and linear **PACOE-3**, and between gels from linear **PACOE-2** and linear **PACOE-3**. The ratios of Q are between gels from cyclic **PACOE-1** and linear **PACOE-3**, and between gels from linear **PACOE-2** and linear **PACOE-3**.

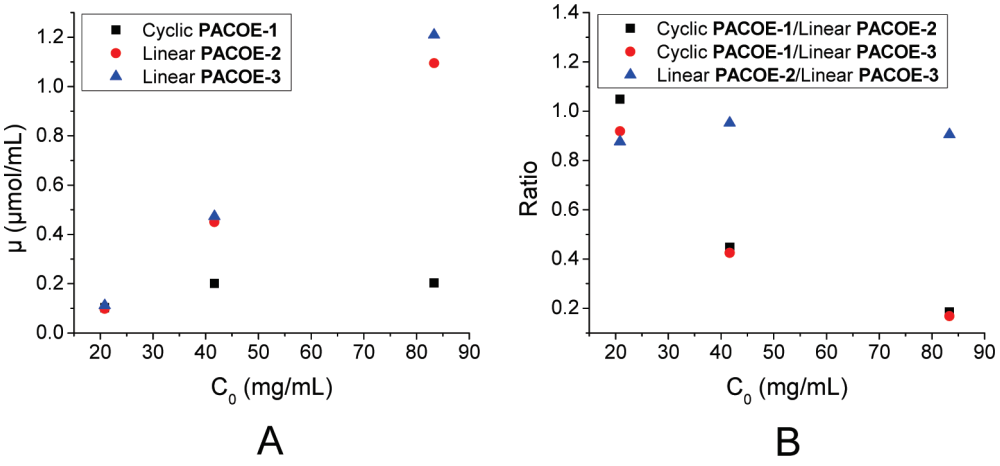


Figure 2. (A) Approximate statistical cross-link density (μ) of gels from cyclic **PACOE-1**, linear **PACOE-2**, and linear **PACOE-3** as a function of the initial PACOE concentration (C_0). (B) The ratios of μ at the same C_0 between gels from cyclic **PACOE-1** and linear **PACOE-2**, between gels from cyclic **PACOE-1** and linear **PACOE-3**, and between gels from linear **PACOE-2** and linear **PACOE-3** as a function of C_0.

and the ratios of Q in DCM between gels from cyclic **PACOE-1** and linear **PACOE-3** at the same C_0 were plotted as a function of C_0 and are shown in part B of Figure 1. The same ratios between gels from linear **PACOE-2** and linear **PACOE-3** are also presented for comparison. Regardless of C_0, the ratios between gels from linear **PACOE-2** and **PACOE-3** were around one, which again demonstrates that similar network structures were obtained from linear PACOE of different molecular weights. At the lower C_0 of 21 mg/mL, the ratios for the gels from cyclic **PACOE-1** and linear **PACOE-3** all had similar values of approximately one, which suggests that PACOE gels cross-linked at this concentration, both cyclic and linear, behave in a similar manner. With increasing C_0, the ratio of the GF between gels from cyclic **PACOE-1** and linear **PACOE-3** decreased slightly, from 0.83 at 21 mg/mL to 0.79 at 42 mg/mL, and again to 0.69 at 84 mg/mL. However, the corresponding ratio of Q between gels from cyclic **PACOE-1** and linear **PACOE-3** increased remarkably. When the gels were cross-linked at a C_0 of 21 mg/mL, the Q of gels from cyclic **PACOE-1** was 1.14 times larger than that of gels from linear **PACOE-3**. When C_0 was increased to 84 mg/mL, the Q of gels from cyclic **PACOE-1** increased to 3.08 times larger than that of gels from linear **PACOE-3**.

From Q, approximate values of the statistical cross-link density, μ, of the networks were calculated using the Flory−Rehner theory with the modifications developed by Peppas and Merrill for networks cross-linked in solution.[32−34] The related equations and results are included in the Supporting Information as equations S1−3 and Table S1. Part A of Figure 2 shows how μ varies as a function of C_0 for the gels formed from linear polymers and gels formed from cyclic polymers. For the gels formed by cross-linking linear **PACOE-2** and **PACOE-3**, μ increased with the increment of C_0, as expected.[35−39] The gels made by cross-linking cyclic **PACOE-1**, however, exhibited a different trend. When C_0 was increased from 21 to 42 mg/mL, μ increased slightly, and then remained essentially constant when C_0 was increased further to 84 mg/mL. The ratios of μ among the three different gels are shown in part B of Figure 2 as a function of C_0. The ratio of μ between the gels from linear **PACOE-2** and **PACOE-3** was found to be one, regardless of C_0. Conversely, the ratio of μ between the gels formed from cyclic polymers and gels formed from linear polymers decreased continuously with the

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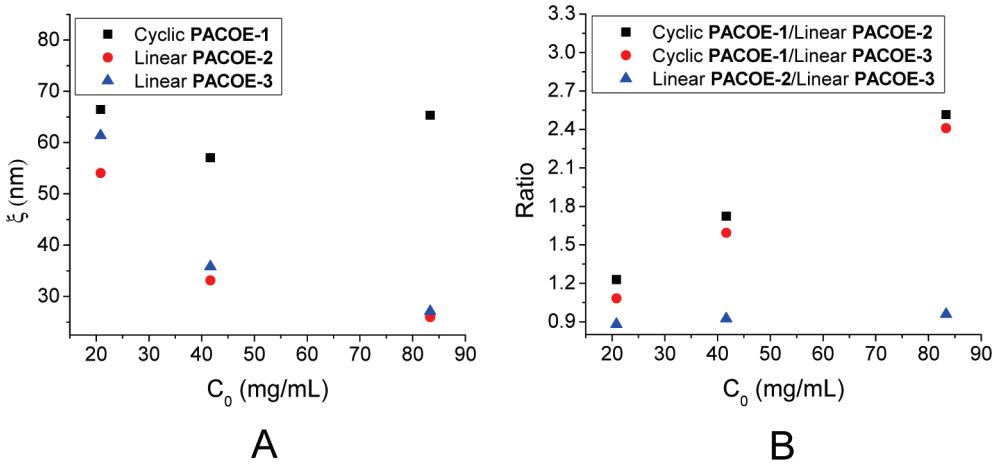

Figure 3. (A) The approximate statistical mesh size (ξ) of gels from cyclic **PACOE-1**, linear **PACOE-2**, and linear **PACOE-3** as a function of the initial PACOE concentration (C_0). (B) The ratios of ξ at the same C_0 between gels from cyclic **PACOE-1** and linear **PACOE-2**, between gels from cyclic **PACOE-1** and linear **PACOE-3**, and between gels from linear **PACOE-2** and linear **PACOE-3** as a function of C_0.

increase of C_0, suggesting that the structural differences between them became more significant as C_0 increased.

Continuing the previous calculations based on the Flory–Rehner theory, approximate values for the statistical mesh size (ξ) of the networks were determined.[39] The related equations and calculated results are given in the Supporting Information as equations S4–6 and Table S2. The relationships between the ξ and C_0 for the gels formed from linear polymers and gels formed from cyclic polymers are illustrated in part A of Figure 3. As C_0 increased, the ξ decreased for the gels formed by cross-linking linear **PACOE-2** and **PACOE-3**, as would be expected from the regular increase in μ. For the gels made by cross-linking cyclic **PACOE-1**, the ξ decreased slightly when C_0 was increased from 21 to 42 mg/mL; however, when C_0 was increased further to 84 mg/mL, an unexpected increase in the ξ was observed. As shown in part B of Figure 3, the ratio of ξ between gels from linear **PACOE-2** and **PACOE-3** was always approximately 1, regardless of C_0. The ratio of ξ between the gels formed from cyclic polymers and gels formed from linear polymers, however, became larger and larger with increasing C_0.

These results highlight two main points. First, compared to conventional networks formed by cross-linking linear polymer chains such as **PACOE-2** and **PACOE-3**, the gels formed from cyclic **PACOE-1** had a lower GF, μ, and G, a larger ξ, and a higher Q at the same C_0. These differences became more pronounced with increasing C_0. Second, for the gels formed from linear polymers, the increment of C_0 resulted in the expected increase in GF, μ, and G, as well as the corresponding decrease in ξ and Q, which is consistent with previous literature on networks formed by cross-linking linear polymer chains.[35−39] Whereas the gels formed from cyclic polymers demonstrated similar behavior at the lower range of C_0, at the higher range of C_0, the increase of C_0 led to the abnormal increase of the GF, Q, G, and ξ simultaneously. These can be explained by considering the unique molecular topology of cyclic polymers, its impact on network formation and the resulting architecture.

Because of the large quantity of internal double bonds in the PACOE backbone, there is a competition between *intra*molecular and *inter*molecular free radical coupling of the carbon centered radicals formed by thiol–ene chemistry. This competition is influenced not only by the initial polymer concentration (C_0), but also by the conformation (behavior) of cyclic and linear polymer chains in solution. The mean square radius of gyration ($\langle R_g^2 \rangle$) of linear polymers is known to be two times larger than that of cyclic polymers,[17] which means that cyclic polymers are more compact and are more likely to have a higher number of *intra*molecular than *inter*molecular cross-linking sites at a given C_0 compared to linear polymers. This results in gels from linear **PACOE-2** and **PACOE-3** having a higher GF, μ, and G, and a smaller ξ and Q than the corresponding gels from cyclic **PACOE-1** at each C_0, as shown in Table 2 and Figures 1–3.

Examining the effect of concentration shows that at lower C_0, *intra*molecular cross-linking reactions dominate over *inter*molecular ones. For conventional linear chains (part A of Figure 4), this produces loop defects that essentially waste the cross-linking points and result in a lower μ, as the loops do not contribute to the elasticity of the network. As a result of cross-linking at low C_0, gels formed from linear polymers are formed with a large ξ, which is reflected by a smaller GF and G, and a larger Q. For cyclic polymer chains (part B of Figure 4), however, *intra*molecular cross-links make the effective ring size smaller, but, because of the ring topology, some of these *intra*molecular cross-links still contribute to the network elasticity. This is evidenced by the similar values of μ for the gels formed from cyclic polymers and gels formed from linear polymers at the C_0 of 21 mg/mL but a slightly lower GF and slightly larger ξ and Q for the gels formed from cyclic polymers, as shown in Table 2 and Figures 1–3.

Upon increasing C_0, the overlap of polymer chains in solution leads to more *inter*molecular cross-linking reactions within the network. Further, it is known for linear chains that this increase in *inter*molecular cross-links results in a higher μ, a tighter network structure, and thus a smaller ξ,[35−39] which can be observed by a larger GF and G, and a smaller Q. This behavior is seen in the gels made from linear PACOE, where the increase in C_0 leads to an increase in the GF, μ, and G, and a decrease in ξ and Q, as expected (Table 2 and Figures 1–3). However, for cyclic polymer chains, the decrease in *intra*molecular cross-links reduces the number of these effectively smaller rings so that, as more *inter*molecular cross-links are formed, the effective cyclic polymer ring size expands and begins to approach the cyclic polymer's molecular weight. Thus, whereas the classical mesh size is reduced at higher C_0 as expected, the larger ring size of the

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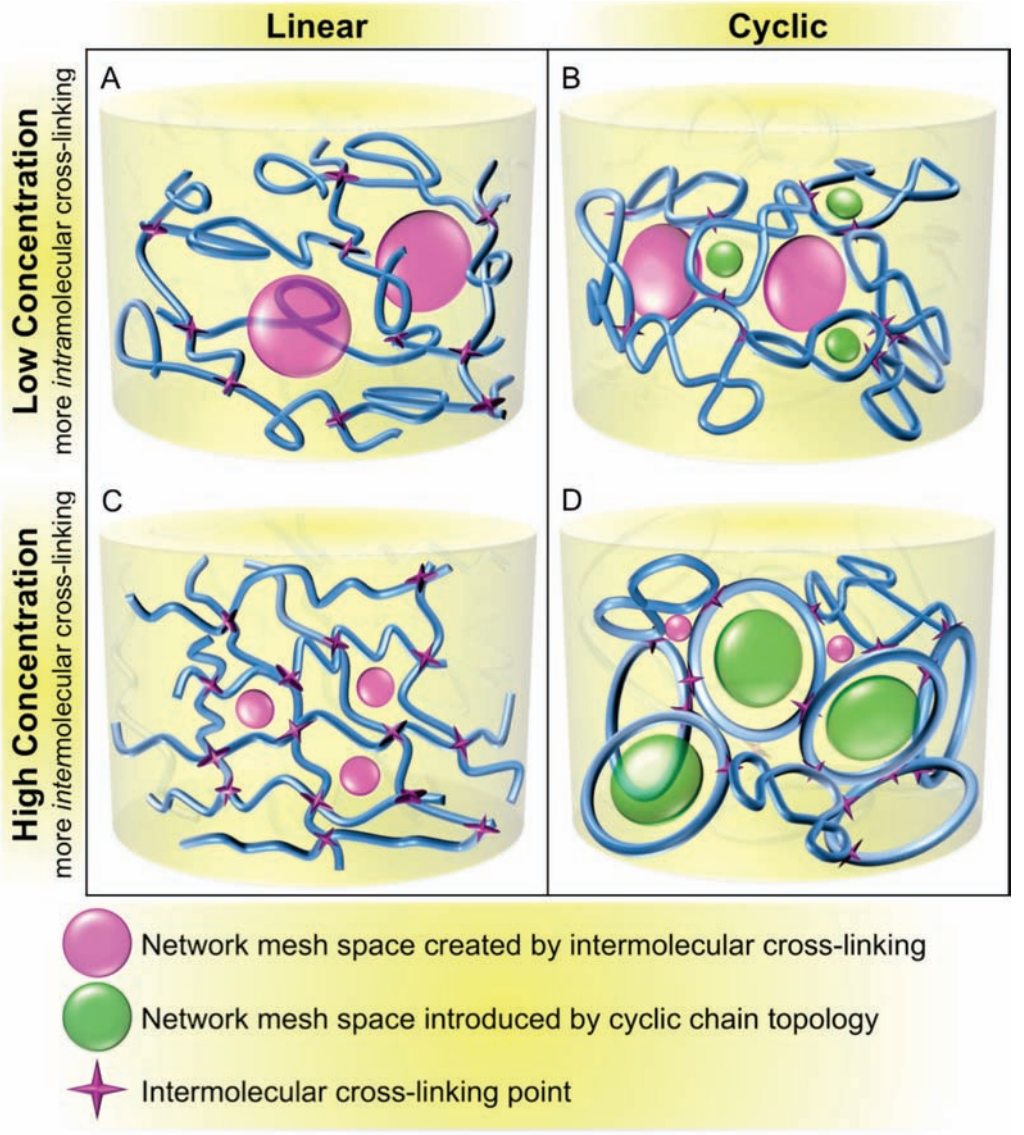

Figure 4. Ideal network structural units are shown to highlight the most important features in each system. The top two systems correspond to low C_0 for linear PACOE (A) and cyclic PACOE (B), whereas the bottom two panels correspond to high C_0 for linear PACOE (C) and cyclic PACOE (D).

cyclic polymer chains creates a compensatory mesh spacing, so that, statistically, more space is available in the network of the gels formed from cyclic polymers at this concentration (part D of Figure 4). This leads to the nontraditional trends of μ and ξ as a function of C_0 (Figures 2 and 3), which result in the simultaneous increase of all three parameters, GF, G, and Q (Table 2 and Figure 1).

Schematically, Figure 4 represents the four extreme cases just discussed. At low C_0, *intra*molecular cross-links dominate within the network, leading to a large mesh size, which is shown in pink (parts A and B of Figure 4). In the gels formed from cyclic polymers, this classic mesh size is expected to be larger than the cyclic polymer ring diameter, as the *intra*molecular (*intra*-ring) cross-links effectively reduce the cyclic ring size (shown in green in part B of Figure 4). As a result, at low C_0, the differences in the behavior of the networks from linear and cyclic PACOE are not as obvious. However, at higher C_0, *inter*molecular cross-links become more dominant due to the increased overlap of polymer chains in solution, and the network mesh size is reduced, especially for the linear networks, as shown in pink (part C of Figure 4). Whereas this classical mesh size is also reduced in the cyclic polymer system because there are more *inter*molecular cross-links than *intra*molecular bonds, the full size of the cyclic polymers is now available to the network, as shown in green (part D of Figure 4). Therefore, it is the presence of these additional secondary cyclic topological cross-linkages within the cyclic networks that results in the unique behavior of the gels formed from cyclic polymers, and allows for the simultaneous increase in GF, G, and Q.

Scaling Behavior. For lightly cross-linked networks made by cross-linking long flexible linear polymer chains, Obukhov et al. described the relationship between swelling ability and preparation conditions with the scaling equation: $Q' \approx \Phi_0^{\,y}$, where $y = -0.75$ for gels swollen by theta solvents and $y = -1$ for gels swollen by good solvents.[31] The equilibrium volumetric swelling ratio, Q', is defined as the ratio of volumes of the gel in the fully swollen and dry states, and Φ_0 is the polymer volume fraction in the preparation state. For estimation purposes, suppose the

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density of PACOE is 1 g/cm^3, then $Q' = 1 + Q$ and $\Phi_0 = C_0GF$.[31] Figure 5 shows the dependence of Q' on Φ_0 for gels from cyclic **PACOE-1** and linear **PACOE-2** and **PACOE-3** in DCM, which

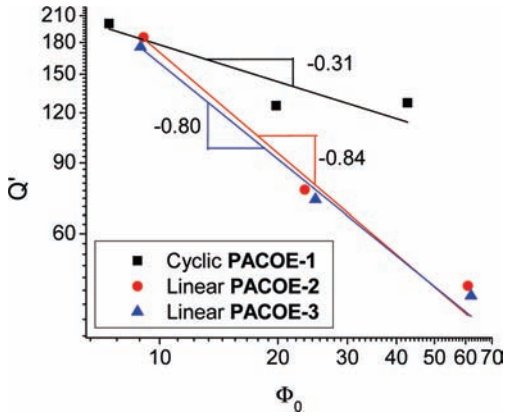

Figure 5. Volumetric equilibrium swelling ratio (Q') in DCM as a function of initial cross-linked polymer volume fraction (Φ_0) for gels from cyclic **PACOE-1** and linear **PACOE-2** and **PACOE-3**, where $Q' = 1 + Q$ and $\Phi_0 = C_0GF$.

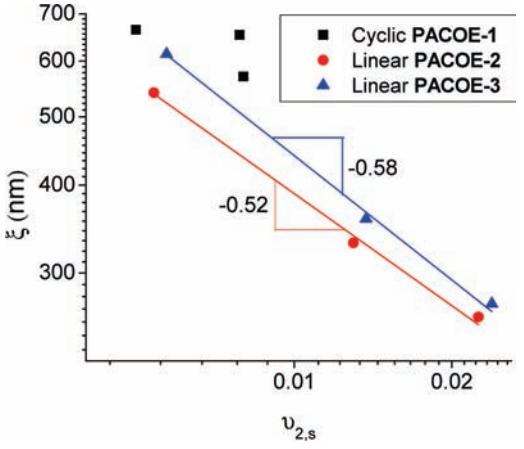

Figure 6. Approximate statistical network mesh size (ξ) as a function of equilibrium polymer volume fraction ($\upsilon_{2,s}$) for gels from cyclic **PACOE-1** and linear **PACOE-2** and **PACOE-3** swollen to equilibrium in DCM.

results in the largest Q and is therefore the best solvent of the five studied here. A fit to the swelling data for gels from linear **PACOE-2** and **PACOE-3** yields exponents of −0.84 and −0.80 respectively, which are in reasonable agreement with the scaling theory and fall within the predicted range of −0.75 to −1. The swelling data for gels from cyclic **PACOE-1**, however, is not consistent with the scaling theory. The data is not well described by the predicted relationship (standard deviation R^2 = 0.687, Figure S9 of the Supporting Information), and the exponent of −0.31 deviates greatly from the theoretical range for good and theta solvents. Similar scaling results for gels from cyclic **PACOE-1** swollen by different organic solvents are shown in Figure S9 of the Supporting Information, where the exponents range from −0.19 to −0.31 with poor fitting statistics. Figures S10 and S11 of the Supporting Information show the scaling results for gels from linear **PACOE-2** and **PACOE-3** in different organic solvents. The exponents range from −0.70 to −0.83 for the different molecular weight and solvent combinations, which is in good agreement with the theoretical range.

Further, for the networks prepared by cross-linking linear polymer chains in solution, a scaling theory was established to describe the behavior of equilibrium swollen gels with the equation: $\xi \approx \upsilon_{2,s}^{\ y}$, where $\upsilon_{2,s}$ is the equilibrium polymer volume fraction.[39] In this scaling equation: $y = -0.75$ when $\upsilon_{2,s}$ is less than 0.01; $y = -0.5$ when $\upsilon_{2,s}$ is between 0.01 and 0.1; and $y = -1$ when $\upsilon_{2,s}$ is greater than 0.1. Figure 6 shows the scaling relationship between ξ and $\upsilon_{2,s}$. For the gels formed from linear polymers, the power law fitting curve accurately described the dependence of ξ on $\upsilon_{2,s}$, and exponents of −0.52 and −0.58 were obtained for the gels from linear **PACOE-2** and **PACOE-3**, respectively. This is in reasonable agreement with the predicted scaling theory. For the gels from cyclic **PACOE-1**, however, the corresponding relationship between ξ and $\upsilon_{2,s}$ does not follow the scaling theory.

As a result, whereas the gels formed from linear polymers follow the theoretical scaling predictions, the strong deviation of the gels formed from cyclic polymers indicates that the properties depend not only on the chemical cross-linking and polymer content, but are also affected by the unique topological cross-linking architecture.

Mechanical Properties. Finally, uniaxial compression testing was used to characterize the mechanical properties of gels made from cyclic and linear PACOE. Figure 7 shows representative

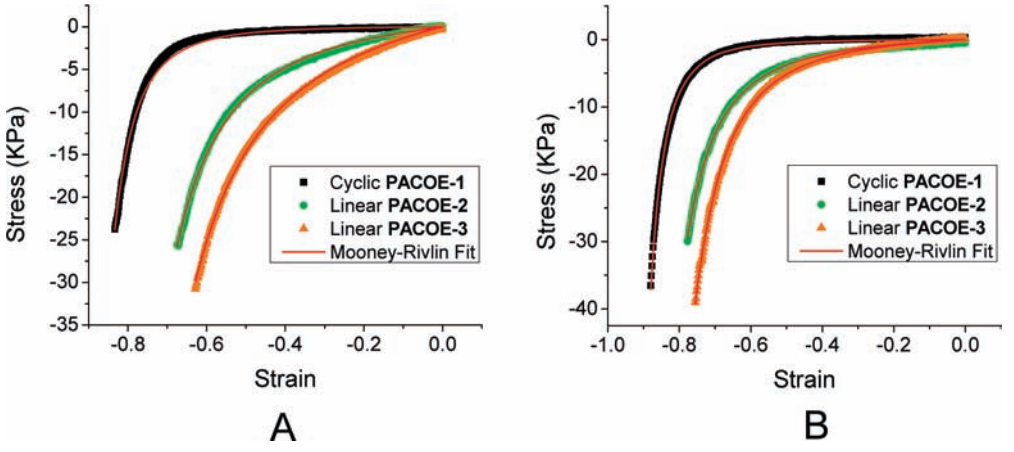

Figure 7. Representative stress−strain curves for cyclic and linear PACOE gels swollen to equilibrium in xylene and the corresponding fitting curves for the Mooney−Rivlin model, (A) the initial PACOE concentration was 84 mg/mL and (B) the initial PACOE concentration was 42 mg/mL.

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stress−strain curves of gels swollen to equilibrium in xylene, as well as the corresponding fitting curves for the Mooney−Rivlin model (further details shown in Figure S12 of the Supporting Information). The gels synthesized at the lowest initial concentration (C_0 = 21 mg/mL) were too soft to be characterized accurately with this technique. The stress−strain behavior of gels made from both cyclic and linear PACOE was well described by the Mooney−Rivlin model, which has two fitting parameters. As shown in Figure S13 of the Supporting Information, the one-parameter neo-Hookean model was not sufficient to describe the stress−strain behavior of the PACOE gels. The values of G calculated from the Mooney−Rivlin model (Table 2) for gels from cyclic **PACOE-1** were always less than those for gels from linear PACOE at the same initial concentration due to the difference in Q. As shown in Figure 7, the maximum strains at break for the gels from cyclic **PACOE-1** were above 80% for both concentrations, which is greater than the corresponding values for gels from linear **PACOE-2** and **PACOE-3**, especially at the higher C_0. The gels made from cyclic PACOE were able to withstand greater strains in compression without fracturing than the gels made from linear PACOE.

CONCLUSIONS

Unique gels were prepared by combining REMP and thiol−ene chemistry. The use of cyclic polymers as the primary constituents in network formation resulted in an important secondary topological cross-link that allowed the GF, G, and Q to increase simultaneously at higher initial concentrations. This behavior is quantitatively different than that of networks made from traditional linear polymers, in which the GF and G have an inversely proportional relationship to Q. These differences can be attributed to several essential factors. Linear and cyclic polymer chains have inherently different conformations in solution. This, combined with the C_0, impacts the competition between *intra*molecular and *inter*molecular cross-linking reactions. The more compact cyclic polymers presumably have more *intra*molecular than *inter*molecular cross-links compared to linear polymers at the same concentration. At the same time, however, the *intra*-rings that result from *intra*molecular cross-links within the cyclic polymers are more likely to contribute to the network elasticity because of the unique topology of the cyclic polymer chains. In addition, this contribution is enhanced with increasing C_0, as the effective *intra*-ring size expands (up to the cyclic polymer's molecular weight) due to the increased probability of *inter*-molecular cross-links. This is the first detailed report on chemically cross-linked networks in which the primary chains are cyclic polymers. The interesting observations in this article suggest these are fundamentally new systems and represent well-defined architectures for future theoretical studies.

EXPERIMENTAL SECTION

All experimental procedures, including catalysts, monomer, and polymer synthesis, as well as the gel preparation and characterization are included in the Supporting Information.

ASSOCIATED CONTENT

Supporting Information. Experimental section, figures of ^{1}H−NMR spectra, and tables of calculation parameters and results. This material is available free of charge via the Internet at http://pubs.acs.org.

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