Mechanochemistry

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The Mechanical Strength of a Mechanical Bond: Sonochemical Polymer Mechanochemistry of Poly(catenane) Copolymers

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Dedicated to Professor Edel Wasserman

Abstract: *Topological molecular connections and structures, including physical entanglements in polymer networks, knots along polymer chains, and rotaxanes in sliding ring gels, have important consequences for the physical properties of polymeric materials. Often these topologies contribute through their ability to bear mechanical stress, but experimental measures of their relative mechanical strength are rare. Here, we use sonochemical polymer mechanochemistry to assess the relative mechanical strength of a multicatenane copolymer relative to copolymers of cyclic and linear analogs. The relative mechanical strengths are obtained by comparing the limiting molecular weights (M_{lim}) and contour lengths (L_{lim}) of the polymers under pulsed ultrasound of their dilute solutions. The values of M_{lim} and L_{lim}, and thus the inferred mechanical strengths of the polymers, are effectively identical. The mechanical bonds of the catenanes are therefore as strong, or stronger, mechanically as the covalent bonds along the polymer backbone.*

As put forth by Kauzmann and Eyring,[1] mechanical forces in polymer networks can lead to the scission of covalent bonds and ultimately to the fracture and failure of materials such as thermosetting polymers and covalent polymer gels.[2] The forces associated with chain fracture are implicated as determinants of material fracture toughness, for example as proposed by Lake and Thomas.[3] In recent years, understanding the coupling of mechanical force and bond scission has created new mechanical responses in materials, including damage sensing[4,5] and self-strengthening.[6,7] With the exception of Stoddart et al.'s report of rotaxane switching,[8] the role of topology in mechanochemical transduction, including the effects of knots[9,10] and mechanically interlocked connections such as rotaxanes[11–13] and catenanes,[14–23] is less understood. An understanding of the mechanics of these interactions is of increasing importance due to the growing use of mechanical bonding in polymers. For example, the slide ring gels developed by Ito[24,25] efficiently redistribute applied tension to the mechanical bonds that serve to cross-link the polymer chains. Mechanically interlocked structures such as those found in catenanes might further serve as limiting models for the behavior of strong entanglements[26–28] that are difficult to study directly. Despite the effort devoted to the synthesis of catenane polymers[21,22,29–33] and studies of the mobility of catenanes in polymers,[34,35] however, to the best of our knowledge no direct measures of the strength of a catenane mechanical bond have been reported. Here, we use polymer sonomechanochemistry to assess the mechanical strength of the mechanical bond in the context of a specific catenane motif. We find that the mechanically bonded polymer chain is as strong as a conventional, purely covalent linear analog.

Our approach is shown in Figure 1. We recently reported that the sonication of polymer solutions could be used as a quantitative probe of the strength of polymer chains by embedding multiple putative "weak bond" mechanophores along the polymer backbone.[36] The relative strengths of the analyte moieties can be assessed by comparing the effective limiting molecular weight (M_{lim}) or limiting length (L_{lim}) of the polymers at long sonication times (here, 4 h).[36] We apply this technique to copolymers of Leigh's benzamide [2]catenanes (Scheme 1),[37] and we compare the results to those obtained from copolymers with linear and cyclic analogs of the catenanes.

Following our previously reported protocol, monomers with the various topological analogs were synthesized by ring-closing metathesis (RCM)[38] of the corresponding bisalkenes, which were synthesized by procedures previously published elsewhere (Scheme 1; additional synthetic details are provided in the Supporting Information).[37] Entropy-driven ring-opening metathesis copolymerization (ED-ROMP)[39–41] of each macrocycle with (*Z*)-9,9-dichloro-bicyclo[6.1.0]non-4-ene (DCBCN) yielded a *gem*-dichlorocyclopropanated-poly-

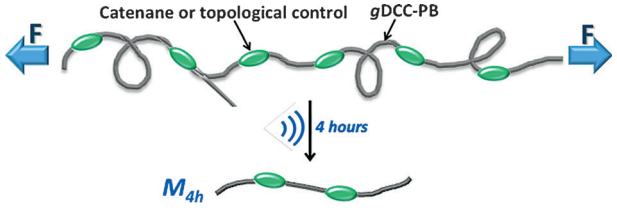

Figure 1. Schematic of strategy for characterizing the mechanical strength of mechanical bonds. Polymers embedded with catenanes, or the relevant topological controls (green ellipses), are subjected for 4 h to the elongational flow fields generated by pulsed ultrasound. The polymer chain is cleaved mechanically until it becomes so short (average contour length L_{lim}) that subsequent scission is negligible on the timescale of hours. The relative values of L_{lim} provide a gauge of the mechanical strengths of the catenated polymer relative to controls.

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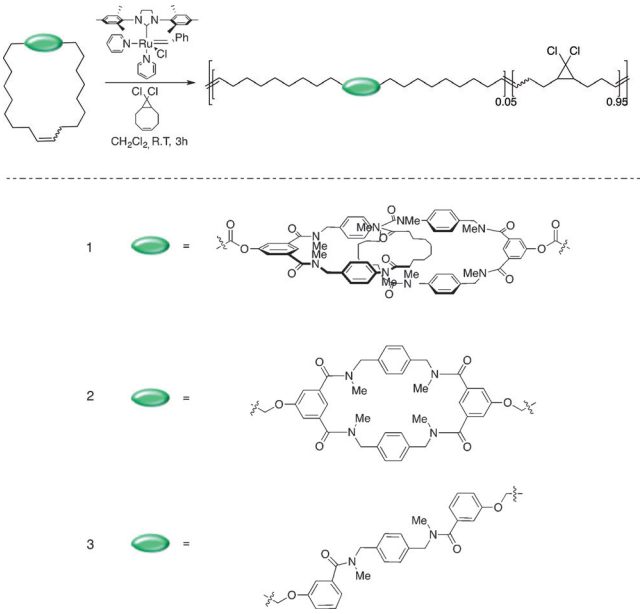

Scheme 1. General synthetic strategy and naming convention for random copolymers containing controlled content of topological molecules embedded in gDCC polymer chain.

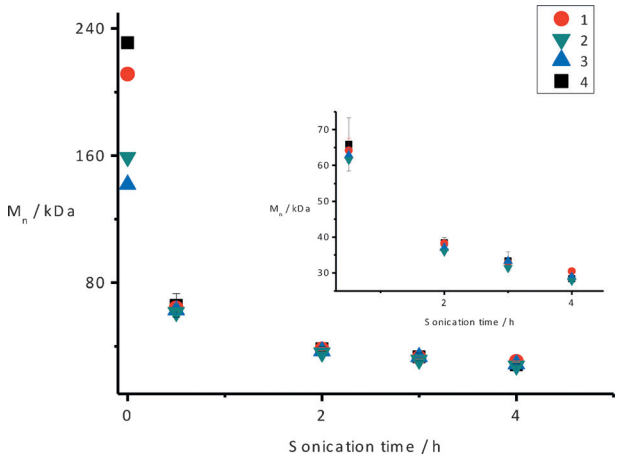

Figure 2. Decrease of molecular weight at time intervals during sonication. After 4 h, the molecular weight of each polymer approaches between 28–30 kDa as M_{lim}.

Table 1: Initial M_n, final M_{lim}, and calculated L_{lim} of each polymer studied. Uncertainties reflect 5% intrinsic uncertainty in measurements; actual experimental variance ranged from 0–5%.

Polymer	M_n [kDa]	Conc. [mg mL^{-1}]	M_{lim} [kDa]	L_{lim} [Å]
1	211	1.6	30.4 ± 0.6	1430 ± 70
1	165	1.6	29.8 ± 0.6	1400 ± 70
1	165	0.8	29.8 ± 0.6	1400 ± 70
1	88	1.6	29.4 ± 0.6	1380 ± 70
2	159	1.6	27.8 ± 0.6	1430 ± 70
3	142	1.6	28.8 ± 0.6	1560 ± 80
4	231	1.6	28.3 ± 0.6	1470 ± 70

butadiene (*g*DCC-PB) copolymer with 5 mol% of either the catenane or a corresponding topological control. Following prior procedures,[36] the use of DCBCN in preference to cyclooctadiene reduced backbiting to form cyclododecatriene byproducts,[42] and polymerizations were run for more than 3 h to ensure cross-metathesis and thus the formation of nearly random copolymers.

Three polymers were prepared (Scheme 1): poly(catenane) **1**, and the macrocyclic and linear control polymers **2** and **3**, respectively. In addition, a third non-catenated control polymer, alternating dichlorocyclopropanated poly(butadiene) **4**, was prepared by ROMP of DCBCN without a co-monomer. The polymer solutions (1.6 mg mL^{-1}; THF stabilized with 0.2 mg mL^{-1} BHT) were subjected to pulsed ultrasound at 6–9 °C in an ice-water bath under a nitrogen atmosphere. Sonication experiments were performed for 4 h to obtain M_{lim}. Aliquots (0.4 mL) were extracted at various time intervals and the number-averaged polymer molecular weight (M_n) was determined by gel permeation chromatography with multi-angle light scattering (GPC-MALS).

The change in M_n with increasing sonication time is shown in Figure 2. Over 4 h of sonication, each polymer approached an M_{lim} in the range of 28–30 kDa (Table 1). Several recent studies have shown that contour length, rather than molecular weight, is the more appropriate characteristic for polymer sonochemistry.[43,44] Thus, M_n was converted to average contour length (L_c) by taking into account the length of each repeat unit and its content in the polymer. Monomer length was determined by extrapolating CoGEF (constrained geometry simulates external force) calculations[45] to zero force, as has been done previously in our lab (see the Supporting Information).[36]

After 4 h of sonication, each of the polymers approaches an L_{lim} of 1500 ± 70 Å (Table 1). The ± 5% deviation is within the experimental uncertainty of the measurements, and so we are unable to distinguish a difference in strength between poly(catenane) **1** and any of the controls **2–4.** The extent of sonochemical scission depends on polymer concentration relative to overlap concentration,[46,47] which we noted might be different for the series of polymers under investigation here. We therefore confirmed that M_{lim} (and L_{lim}) are not affected by concentration in the range examined here. Sonication of **1** at 0.8 mg mL^{-1} and 1.6 mg mL^{-1} gave effectively identical values of M_{lim} = 29.8 kDa (Table 1). Similarly, the use of M_{lim} and L_{lim} assumes that neither value is sensitive to the initial molecular weight of the polymer, but instead reflects a pseudo-steady state interplay of sonication conditions and bond strength. Subjecting **1** of three different initial molecular weights (211 kDa, 165 kDa, and 88 kDa) to the same sonication conditions employed in the original studies gave M_{lim} and L_{lim} that vary within the same range of ± 5% as the variation among polymers **1–4** (Figure 2, Table 1). We conclude that the similar M_{lim} and L_{lim} across the series is an accurate reflection of the relative mechanical integrity of the polymers. Because the limiting force for chain scission on the representative time scale of the sonication conditions employed is proportional to $(L_{lim})^2$,[36] the effective mechanical strength of the catenane polymers under these conditions deviates by no more than 10% from that of similar linear polymers.

The catenated repeat unit in **1** is therefore introduced without sacrificing the mechanical stability of the polymer. Given the attachment points, overextension of **1** should effectively "bend" alkane chains against each other, similar to the interactions found in trapped physical entanglements in overstressed polymer networks (Figure 3).[28] Another com-

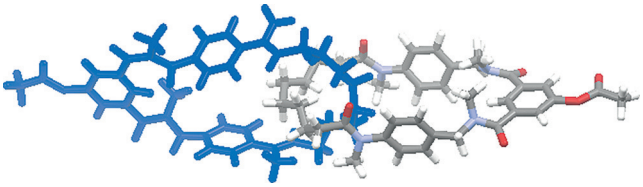

Figure 3. Molecular mechanics simulation of stretching a [2]catenane shows that the physically contacted regions of the two halves (color coded to aid the eye) comprise the alkyl regions of each macrocycle.

parable interaction is found in Ito's rotaxanated slide ring gels, in which rotaxanes act like a series of pulleys to redistribute stress that ends up concentrated in junctions of a poly(ethylene glycol) chain that is looped through a cyclodextrin.[24] The results here are, of course, specific to the catenane and polymer combination in question, but they suggest that these and similar topologies likely come without a substantial sacrifice in the intrinsic mechanical stability of the connection, relative to covalent cross-links. We note that a previous analysis suggests that the mechanical integrity of the polymer backbone used here is typical of a hydrocarbon.[36] Thus, these results suggest that the unique mechanical properties expected of poly(catenane)s[26,27,37] might be achieved without a significant, concomitant reduction in high stress yield at the single molecule level. Finally, the fact that notional "bond bending" comes without a substantial cost in mechanical strength is consistent with the prevailing view that the loss of mechanical integrity in molecular trefoil knots is a result of constriction at the entrance/exit to the knot,[9,10] rather than the bending-like components found elsewhere in the structure.

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