Topological Effects in Isolated Poly[n]catenanes: Molecular Dynamics Simulations and Rouse Mode Analysis

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S *Supporting Information*

ABSTRACT: Poly[n]catenanes are mechanically interlocked polymers consisting of interlocking ring molecules. Over the years, researchers have speculated that the permanent topological interactions within the poly[n]catenane backbone could lead to unique dynamical behaviors. To investigate these unusual polymers, molecular dynamics simulations of isolated poly[n]catenanes have been conducted, along with a Rouse mode analysis. Owing to the mechanical bonds within the molecule, the dynamics of poly[n]catenanes at short length scales are significantly slowed and the distribution of relaxation times is broadened; these same behaviors have been observed in melts of linear polymers and are associated with entanglement. Despite these entanglement-like effects, at large length scales poly[n]catenanes do not relax much slower than isolated linear polymers and are less strongly impacted by increased segmental stiffness.
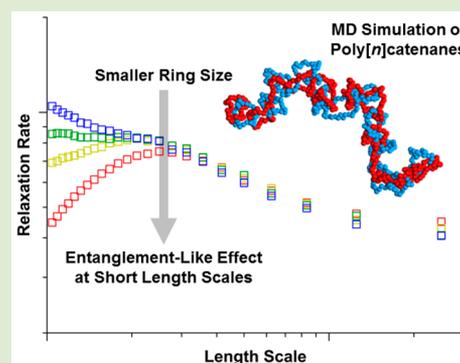
Many unique dynamical properties of polymeric materials depend on molecular architecture and topological interactions. For instance, high molecular weight (MW) melts of linear polymers behave quite differently than their low-MW counterparts due to entanglement effects.[1,2] Entangled ring polymers tell an entirely different story, exhibiting unusual rheology[3] and glass transitions[4] that continue to intrigue polymer scientists. In recent decades, researchers have synthesized polymer architectures that incorporate mechanical (or topological) bonds, such as polyrotaxanes[5,6] and polycatenanes.[7] These mechanically interlocking polymers (MIPs) possess distinct, well-defined topological interactions and, as a result, exhibit a variety of unique properties, which have been explored in experiments[6−9] and simulations.[10,11] For several decades, a highly sought-after MIP architecture has been the "poly[n]catenane" (Figure 1), a linear chain of *n* mechanically interlocking ring molecules (macrocycles); this architecture was recently synthesized in our laboratory for the first time.[12] These molecules are dominated by mechanical bonds, rather than traditional covalent linkages. Mechanical bonds have long been recognized as an important class of topological interactions[13] and have even been used to identify and characterize entanglements between linear polymers.[14] Therefore, one may expect poly[n]catenanes to exhibit topological effects not only between chains (as in linear polymers), but also between neighboring macrocycles, perhaps offering access to new dynamical and rheological regimes. With the goal of understanding these new architectures, molecular dynamics (MD) simulations were conducted on single,
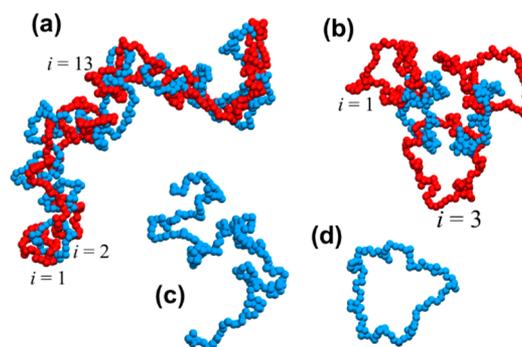
Figure 1. Some of the polymers studied.: (a) poly[n]catenane with number of rings *n* = 25, macrocycle size *m* = 30, total size *N* = 750; (b) poly[n]catenane, *n* = 5, *m* = 100, *N* = 500; (c) linear polymer, *N* = *m* = 225; (d) ring polymer, *N* = *m* = 100. Macrocycles are indexed by position along the chain (*i*).

isolated poly[n]catenane molecules, and the results were compared to those of traditional linear and cyclic polymers.

Isolated poly[n]catenanes have previously been studied by Pakula and Jeszka using an athermal cooperative-motion algorithm on a lattice.[15] The authors calculated various static and dynamic properties and found that poly[n]catenanes generally relax more slowly than linear and cyclic polymers. Building on that initial work, here we study poly[n]catenane

dynamics in greater detail, employing a continuum MD approach. We quantify dynamics at various length scales using a Rouse mode analysis,[16] which is sensitive to topological interactions in polymeric systems.[17−24] The Rouse theory is the simplest model of polymer dynamics and forms the basis for many more sophisticated treatments, making it a natural starting point. To simulate polymers in good solvent conditions, the model of Kremer and Grest[25] is adopted for all molecules, including linear and cyclic polymers, as well as macrocycles within poly[n]catenanes. This model precludes chain crossings, enforcing topological restrictions, which makes it suitable for MIPs.[10,14,26−29] The impact of segment stiffness is studied by introducing an angle-bending potential between neighboring (covalent) bond vectors to model flexible, semiflexible, and stiff segments; unless otherwise stated, all segments are completely flexible. See Supporting Information for additional details. We note that an isolated poly[n]catenane was recently simulated using this same model,[28] but only as a test system for a new relaxation mode analysis method; the behavior of the molecule itself was not discussed in detail.

In this Letter, n denotes the number of macrocycles within a poly[n]catenane, m denotes the number of beads in a covalently continuous molecule (i.e., a free polymer or a macrocycle within a poly[n]catenane), and N is the total number of beads in a polymer. For linear and cyclic polymers, $m = N$; for poly[n]catenanes, $N = m \times n$. Poly[n]catenanes were simulated with $n = 25$ macrocycles (comparable to the largest molecules synthesized[12]) with the number of beads-per-ring $m = 10, 15, 20,$ or 30; a [5]catenane[30] with $m = 100$ was also considered. These poly[n]catenanes have total number of beads, $N = 250, 375, 500, 750,$ and 500, respectively. Macrocycles are labeled by an index i, with $i = 1$ referring to an arbitrarily chosen chain end. For comparison, ring polymers with $N = m = 30$ and 100, and linear polymers with $N = m = 75, 100, 150,$ and 225 were also simulated. Figure 1 depicts some of these molecules. Static properties of the polymers are detailed in the Supporting Information. In general, the structure of poly[n]catenanes is qualitatively similar to that of linear polymers at large length scales.

In recent years, several computational studies[17−21,24] have examined the dynamics of polymer melts and blends using a Rouse mode analysis.[16] In the Rouse model, a traditional, covalent polymer is represented by N beads connected to their neighbors by harmonic springs. The bead coordinates can be transformed into a series of normal modes, X_p, with mode number $0 \leq p \leq N − 1$, where the pth mode represents motions of subchains of N/p beads. The quantity N/p therefore defines a length scale along the polymer backbone, with low mode numbers corresponding to large length scales and vice versa. The normalized autocorrelation functions (ACFs) of X_p can be described by a stretched exponential, $\exp[−(t/\tau_p)^{\beta_p}]$. The exponent β_p characterizes the distribution of relaxation times, with $\beta_p = 1$ indicating simple exponential decay and smaller values corresponding to broader distributions. Values $\beta_p > 1$ may be attributed to inertial effects. Note that $\beta_p \neq 1$ does *not* necessarily imply coupling between modes. Integrating the ACFs yields effective relaxation times for each mode, which are used to calculate the effective relaxation rate, W_p^{eff}, for each mode (see Supporting Information). For ideal chains, both W_p^{eff} and β_p should be independent of mode number, that is, they should not vary with the length scale, N/p. However, recent computational studies using both coarse-grained and all-atom models have

shown that W_p^{eff} and β_p *do* in fact depend on mode number and are correlated with entanglement.[17−19] For instance, Kalathi et al.[17,18] showed that both W_p^{eff} and β_p decrease dramatically as N/p approaches N_e, the entanglement length. Hsu and Kremer[19] confirmed these results, demonstrating that the effective relaxation time exhibits two scaling regimes, revealing the crossover from Rouse to reptation dynamics. Throughout this Letter, we will refer to such concomitant reductions in W_p^{eff} and β_p as the "entanglement-like effect" (not to be conflated with other signatures of entangled dynamics). In contrast, when chain crossings are allowed (eliminating entanglement), β_p is relatively constant, while W_p^{eff} increases modestly at higher modes, the latter being attributed to local correlations between monomers.[17] Similar results have been observed in all-atom simulations of unentangled melts of linear poly(ethylene-*alt*-propylene)[20] and cyclic polyethylene.[21] Rouse modes are also sensitive to topological interactions in blends of cyclic and linear polymers: Tsalikis et al.[22,23] showed that slow relaxation modes emerge when linear chains thread ring polymers and Papadopoulos et al. found that this threading is accompanied by a decrease in W_p^{eff} of the rings at low mode number.[24] In light of these findings, a Rouse mode analysis provides a useful starting point to study the dynamics of poly[n]catenanes, since these molecules contain permanent topological interactions in the mechanical bonds. Note that there are no other relevant topological interactions since the poly[n]catenanes studied here are too short to self-entangle.

Two different sets of Rouse modes are calculated here to account for the unique structure of poly[n]catenanes. The first set describes the individual macrocycles within the poly[n]-catenanes, and the coordinates of beads within a single macrocycle are used as monomer positions for the calculation, as in an ordinary analysis. In this scenario, the length scale of relaxation is *absolute* in that it corresponds to a particular number of beads (m/p). The second set of modes describes entire poly[n]catenane molecules by using the macrocycle centers-of-mass as monomer positions. Here, the relaxation length scale is *relative*, since it corresponds to a particular number of macrocycles (n/p), which may comprise different numbers of beads depending on m. The relaxation spectra W_p^{eff} (in inverse time units) are analyzed as a function of the relaxation length scale (m/p or n/p). Both sets of modes are orthogonal to within good approximation (see Supporting Information), ensuring that we obtain meaningful dynamical information at well-defined length scales.

The first set of Rouse modes described above has been calculated for macrocycles of size $m = 30$ and $m = 100$ within poly[n]catenanes of $n = 25$ and $n = 5$ total rings, respectively. The macrocycles at the chain end ($i = 1$) and chain center ($i \approx n/2$) are considered separately since they have different numbers of threadings, which greatly affects the dynamics.[22−24] Figure 2 compares the results to linear and noncatenated ring polymers with identical m. At high mode number, W_p^{eff} is independent of polymer topology as all spectra converge. However, at low mode number, W_p^{eff} decreases substantially as topological restrictions are added: linear chains relax fastest, followed by ring polymers, poly[n]catenane chain ends, and poly[n]catenane chain centers. This result agrees well with recent work on blends of cyclic and linear polymers.[24] Interestingly, the largest decrease in W_p^{eff} occurs at the longest modes, regardless of the macrocycle size, m. This indicates that the mechanical bond slows dynamics at a length scale relative to the macrocycle itself, rather than at some absolute length
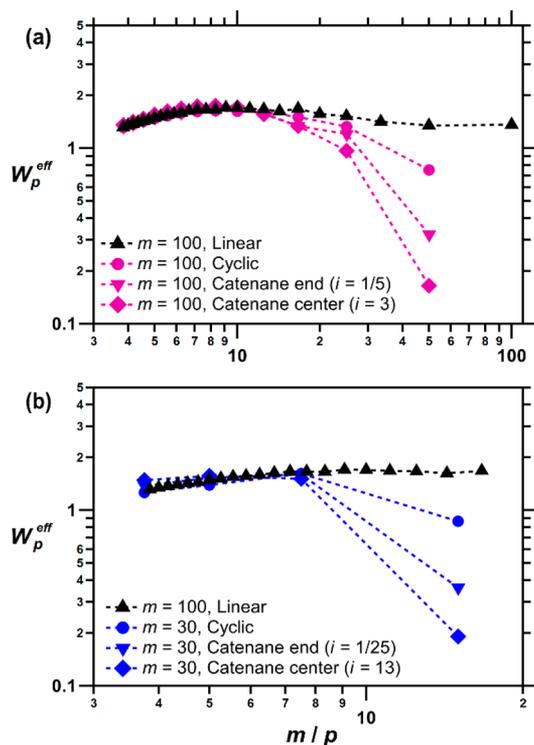
Figure 2. Mode-dependent relaxation rates for poly[n]catenane macrocycles at the chain center (diamonds) and chain ends (downward triangles), compared to ring and linear polymers: (a) m = 100; (b) m = 30.

Figure 3. (a) Raw relaxation spectra for poly[n]catenanes with various ring sizes. (b) Scaled spectra for poly[n]catenanes. For high modes, dynamics slow as ring size decreases.

scale (i.e., some specific number of beads). β_p also decreases with increased threading for the longest modes (Table S1); such concomitant reductions in W_p^{eff} and β_p are reminiscent of the entanglement-like effect in linear polymer melts,[17−19] suggesting that this effect may be related to topological interactions quite generally, rather than just the specific case of linear polymers.

To describe entire poly[n]catenane molecules, the second set of Rouse modes described above was calculated, using the macrocycle centers-of-mass as monomer positions in the standard transformation. A representative subset of Rouse mode ACFs with stretched exponential fits is shown in Figure S1. We begin by considering the effect of macrocycle size, m; as the ring size is decreased, the density of mechanical bonds increases, so the effects of topological interactions should be magnified. Figure 3a compares W_p^{eff} for poly[n]catenanes with n = 25 and m = 10, 15, 20, and 30 as a function of n/p. W_p^{eff} for all modes increases with decreasing ring size, which is expected since smaller ring sizes lead to smaller polymers. To compare the spectra on more equal footing, we introduce a theoretically informed scaling procedure that accounts for: (1) effective drag on the macrocycles, (2) effective segment length, and (3) excluded volume effects; see Supporting Information for details. Using this procedure, the various spectra collapse onto a master curve at long length scales, as shown in Figure 3b. However, on the length scale of about three macrocycles ($n/p \sim 3$), smaller ring sizes lead to *slower* dynamics, with the effect growing as n/p approaches unity. Importantly, these trends cannot be explained by local stiffness effects or nonasymptotic scaling behavior (see Supporting Information). As discussed later, β_p also decreases markedly in this regime, consistent with the entanglement-like effect observed above in
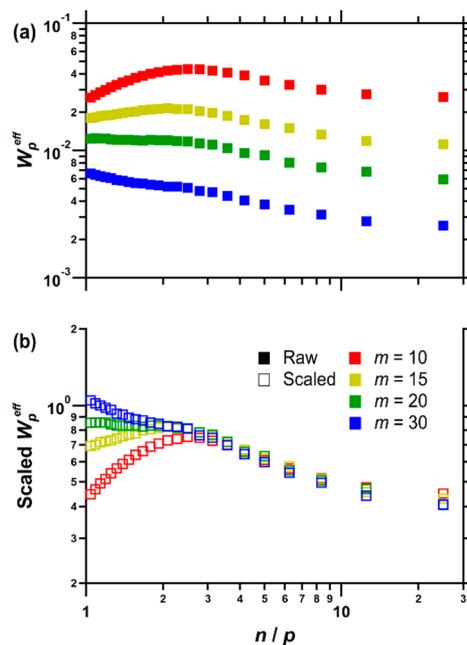
individual macrocycles. However, the entanglement-like effect occurs at *short* length scales in poly[n]catenanes, while ordinary linear polymers are only subject to entanglements at relatively *long* length scales. Interestingly, some systems exhibit an overlap between the two sets of Rouse modes. For instance, the shortest modes in poly[n]catenanes with m = 30 relax considerably faster than the longest modes of the constituent macrocycles, suggesting that poly[n]catenane melts and glasses may exhibit interesting dynamical responses in these regimes.

Next, poly[n]catenanes dynamics are compared to those of linear polymers. An analysis based on molecular weight results in linear chains with much greater contour length than their poly[n]catenane counterparts, setting up a somewhat unbalanced comparison. To identify more appropriate linear analogues, effective monomers were defined for linear polymers as the centers-of-mass of segments of m_{eff} beads, such that the mean bond length between effective monomers matches the mean intermacrocycle distance of the targeted poly[n]catenane. Accordingly, the linear polymer analogue for a poly[n]catenane with n macrocycles will have n effective monomers, and total number of beads $N = n \times m_{\text{eff}}$, where m_{eff} depends on the particular macrocycle size m. Using this method, the poly[n]catenanes and linear analogues will have roughly the same contour length, so that differences in relaxation spectra are primarily related to the underlying molecular topology. For poly[n]catenanes with n = 25 and m = 10, 20, and 30, linear analogues have m_{eff} = 3, 6, and 9, and N = 75, 150, and 225, respectively. Although mean effective bond lengths differ by at most 2% between architectures, poly[n]-catenanes are somewhat stiffer than linear chains (see Table S2), leading to slower dynamics, as discussed in the Supporting Information. Indeed, at low mode number, W_p^{eff} for poly[n]-catenane with m = 30 is roughly 50−80% of W_p^{eff} for the linear analogue (m_{eff} = 9), as shown in Figure 4a (after accounting for mass differences between macrocycles and effective mono-mers). At higher modes, linear polymers show an increase in
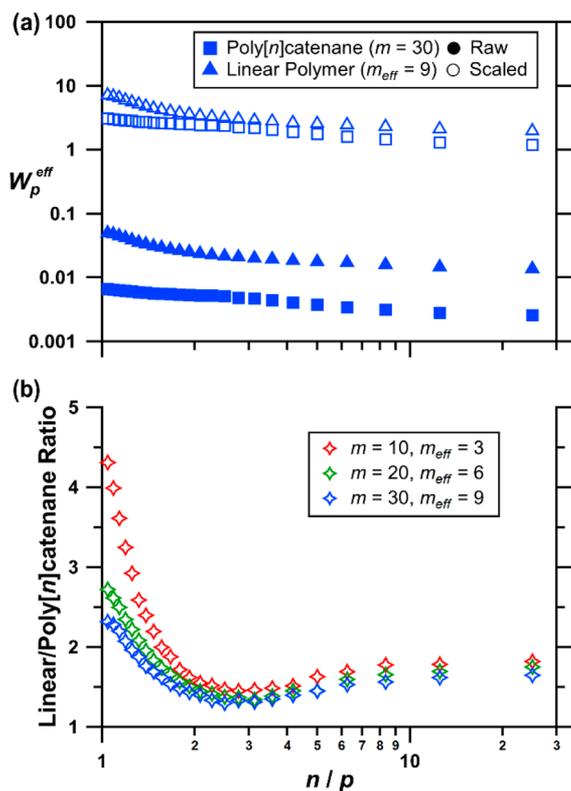
Figure 4. (a) Raw and scaled relaxation spectra for poly[n]catenane (n = 25 and m = 30) compared to linear analogue (N = 225, n = 25, m_{eff} = 9). (b) Ratio of relaxation rates for poly[n]catenanes and linear analogues.

W_p^{eff}, attributed to local correlations,[17] while catenanes exhibit the entanglement-like effect instead, which slows dynamics and widens the gap between the architectures. This behavior is observed for all ring sizes: Figure 4b shows the ratio of linear/catenane W_p^{eff} as a function of n/p for various poly[n]catenane/linear analogue pairs. At low mode number, the ratio is relatively constant at a factor of 1−2. However, it increases sharply starting at n/p ∼ 3, where the entanglement-like effect emerges in poly[n]catenanes and dominates the behavior.

In linear polymer melts, the stretching exponents $β_p$ decrease to ∼0.5 at length scales comparable to the entanglement length, N_e, indicating that topological interactions are correlated with a broadening of relaxation times.[17−19] A similar trend is observed in poly[n]catenanes, but at relatively short length scales: $β_p$ exhibits a shoulder at n/p ∼ 3 and then decreases dramatically as n/p approaches unity, as shown in Figure 5. Interestingly, this decrease occurs at the relative length scale of n/p ∼ 3 for all m. These results are in direct contrast to those for linear polymers, which show an *increase* in $β_p$ at small length scales which are attributed to inertial affects. As expected, this upturn always occurs at the same *absolute* length scale of ∼10 beads, no matter the value of m_{eff} (Figure S2). These observations are consistent with the above results for individual macrocycles: the effect of the mechanical bond is manifested at a length scale *relative* to the macrocycles (no matter their size), rather than at some *absolute* number of beads. This suggests that the entanglement-like effect is a general feature of the mechanical bond that distinguishes it from traditional covalent linkages.

Finally, the effect of segmental stiffness is examined by strengthening the angle-bending potential between neighbor-
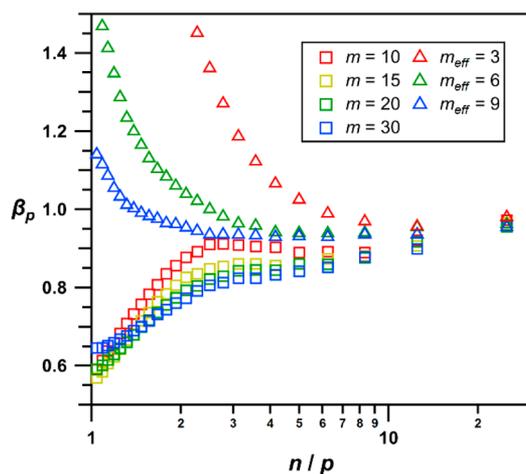
Figure 5. Stretching exponents $β_p$ vs n/p for poly[n]catenanes (squares) and linear polymers (triangles).

ing covalent bonds. As stiffness is increased, the (unscaled) W_p^{eff} for linear chains is greatly reduced at low modes, but remains mostly unperturbed at higher modes (Figure 6a). This
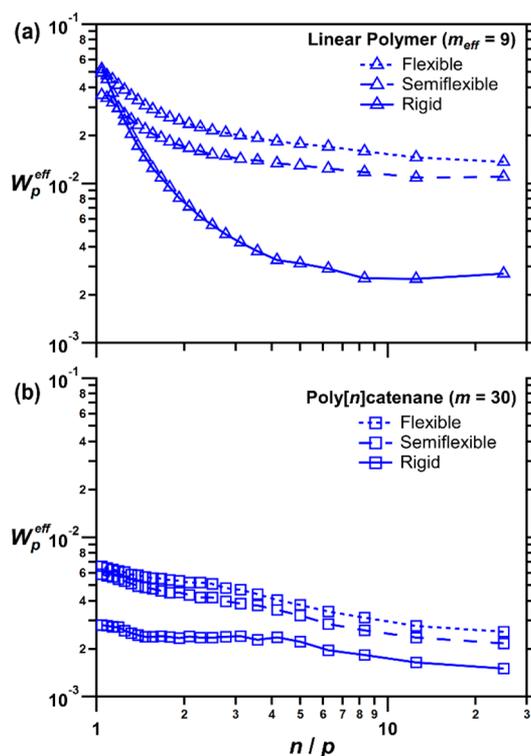
Figure 6. (a) Unscaled relaxation spectra for linear polymers with varying segment stiffness (m_{eff} = 9). (b) Unscaled relaxation spectra for poly[n]catenanes with varying segment stiffness (m = 30).

is not surprising, since the additional stiffness increases the size of the polymers while also increasing the spring constant between effective monomers, leading to faster dynamics at high modes. In contrast, W_p^{eff} for poly[n]catenanes is only moderately reduced at low modes, but *more* so at high modes (Figure 6b). This may be understood in qualitative terms: just as a steel chain is highly flexible in spite of its rigid links, stiff molecular segments will not greatly affect the large-scale mobility in poly[n]catenanes. However, at short length

scales, the topological interactions may be exacerbated by the stiffness, leading to slower dynamics at higher modes.

At present, there are limited data on poly[n]catenane dynamics,[12] so comparison with experiment is not possible. However, since the modes studied here are orthogonal to a good approximation, they can be used to compute various experimental quantities, such as shear relaxation modulus and dynamic structure factor.[1] The former could be measured by rheological experiments on poly[n]catenane solutions; since the largest effects are found at short length scales, high frequencies and/or low temperatures may be required. Meanwhile, dynamic structure factor can be measured by neutron scattering experiments. In particular, dynamics of individual rings could be probed by introducing labeled macrocycles during poly[n]catenane synthesis. As in the rheological measurements, the large wave-vector regime is likely to be of greatest interest.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacro-lett.8b00393.

> Additional figures/tables and details of the molecular model, simulation protocols, static properties of the polymers, and Rouse mode analysis (PDF).

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Notes
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(13) See, for instance, section 5.4 of ref 1, which discusses a [2] catenane (a.k.a. a Hopf link) in the context of the entanglement effect. Also, p 384 of ref 2 illustrates the slip-link model of entanglement using a doubly threaded poly[3]rotaxane.

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(30) A note on terminology: [*n*]catenane refers to a catenane molecule with *n* interlocking rings where *n* is a specific integer. "Poly[*n*]catenane" usually refers to a sample of [*n*]catenanes, where *n* is generally large and has a dispersity Đ ≥ 1. Since this Letter focuses on isolated molecules, the two terms have the same physical meaning, that is, a poly[*n*]catenane with *n* = 5 is equivalent to a [5]catenane. When referring to the interlocking components of poly[*n*]catenanes, the terms "ring" and "macrocycle" are used interchangeably.