ORGANIC LETTERS
2011
Vol. 13, No. 10
2706–2709

Mechanically Interlocked Mechanophores by Living-Radical Polymerization from Rotaxane Initiators

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Received March 26, 2011

ABSTRACT

Two [2]rotaxane initiators for single-electron-transfer living-radical-polymerization were synthesized and used for the controlled polymerization of methyl acrylate. The mechanically interlocked polymers exhibited distinct responses to mechanical activation by ultrasound. Monitoring the fate of the rotaxanes' charge transfer absorption bands provides evidence for preferential mechanical degradation of a midsection rotaxane unit as compared to a terminal rotaxane entity as a consequence of mechanical forces accumulating in the central region of the polymer chain.

Over the past couple of decades, interest in “smart” materials[1] containing mechanically interlocked components[2] has increased dramatically because of their ability to function as nanoswitches and nanomachines. Numerous examples of polymers based on rotaxanes and catenanes — the best known of the mechanically interlocked molecules (MIMs) — have been described[3] in the literature. In practice, MIMs can be incorporated either into a polymer's main chain or appended to side-chains, attached to a polymer's backbone. Based on the constitutions and sitings of these MIMs, four major architectures can be distinguished: they are main-chain [n]rotaxanes[4] and

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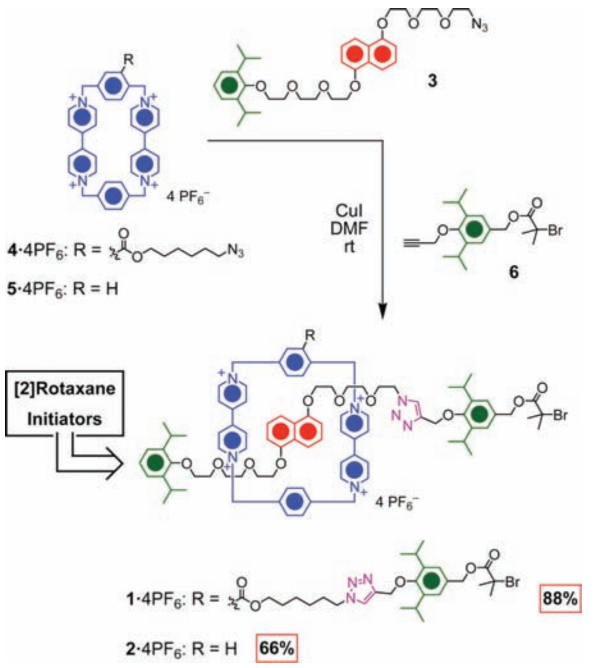
10.1021/ol200801b

[n]catenanes,[5] and poly-([2]rotaxanes)[6] and -([2]catenanes).[7] Their physical as well as their chemical properties are influenced largely by the constitutions and relative dispositions of their component MIMs. By contrast, examples of the incorporation of a *single* MIM component into a polymer chain are few and far between.[8] Such polymers are unique, however, since they offer the possibility to investigate the effect of the surrounding polymeric environment upon MIMs.

In this communication, we describe the synthesis of cyclobis(paraquat-*p*-phenylene)-derived[9] [2]rotaxane initiators and their use in the single-electron-transfer living-radical-polymerization[10] (SET-LRP) of methyl acrylate, leading to well-defined polymers with exactly one MIM per polymer chain. The transfer of mechanical force to these single rotaxanes during sonication experiments[11] was investigated in order to probe for the potential use of MIM-based structures as a new class of mechanophores.[11f]

Polymer cleavage by acoustic activation is a nonrandom process and is known[12] to occur preferentially in the midsection of a polymer chain. To investigate the influence of the rotaxane's position along the polymer chain, we synthesized (Scheme 1) two different mechanically interlocked initiators **1**·4PF_6 and **2**·4PF_6. SET-LRP using the bifunctional initiator $\mathbf{1}^{4+}$ is expected to give polymers with a single rotaxane in the middle of the polymer chain, whereas polymers with a single rotaxane end-group are accessible by employing the monofunctional initiator $\mathbf{2}^{4+}$.

Scheme 1. Synthesis of Initiators **1**·4PF_6 and **2**·4PF_6



The rotaxane initiators **1**·4PF_6 and **2**·4PF_6 were synthesized by a templated "threading-followed-by-stoppering" approach[13] taking advantage of the high functional group tolerance and remarkable efficiency of the Cu-catalyzed azide–alkyne cycloaddition (CuAAC) "click" chemistry.[14] This synthetic strategy involves (Scheme 1) the initial formation of a pseudorotaxane between the electron-rich 1,5-dioxynaphthalene (DNP) unit in the half-dumbbell **3** and the electron-poor tetracationic cyclophane present in either **4**·4PF_6 or **5**·4PF_6, followed by reaction with the propargyl ether **6** to (i) prevent dissociation of the pseudorotaxane by stoppering with a bulky aryl group to give either **1**·4PF_6 or **2**·4PF_6 and (ii) introduce the desired number of α-bromoisobutyrate initiation sites.

Subsequent polymerization of methyl acrylate using initiators **1**·4PF_6 and **2**·4PF_6 proceeded smoothly to yield (Scheme 2) well-defined polymers **7**·4PF_6 and **8**·4PF_6, respectively. Following the same protocol, polymer **9** was synthesized as a control compound from dumbbell

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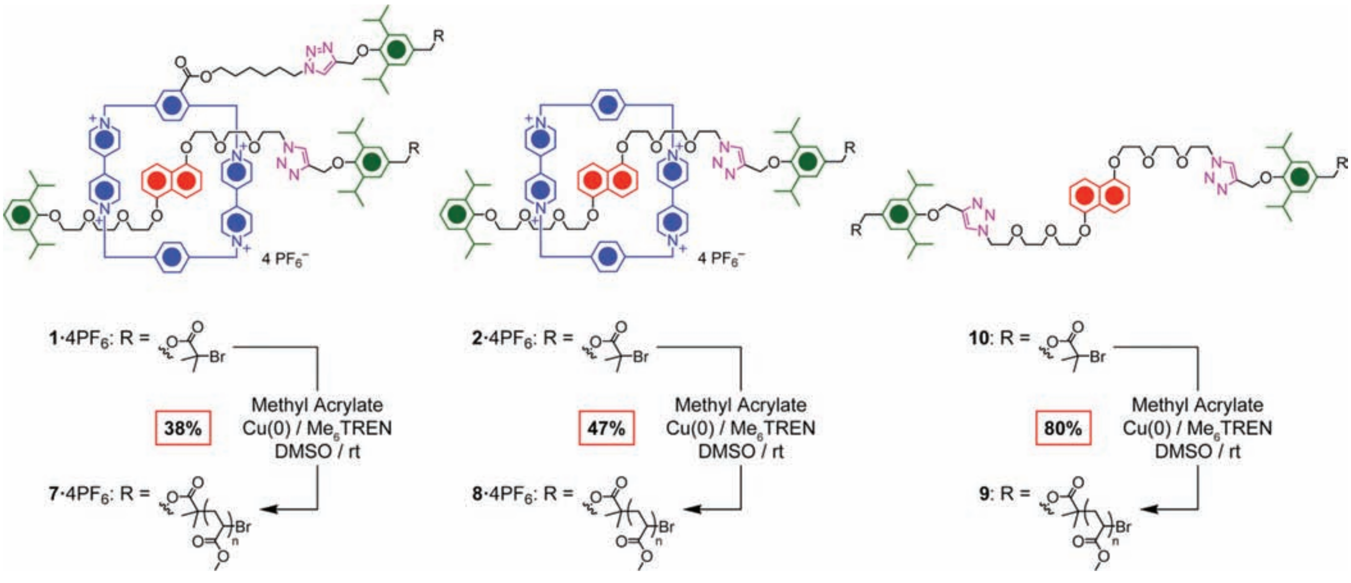
Scheme 2. Synthesis of Mechanically Interlocked Polymers **7**·4PF$_6$ and **8**·4PF$_6$ and the Control Polymer **9**



initiator **10**.[15] The catalytically active Cu(0) species for SET-LRP was generated in situ from Cu-wire and tris-(2-(dimethylamino)ethyl)amine[10e] (Me$_6$TREN). Gel permeation chromatography (GPC) of polymers **7**·4PF$_6$, **8**·4PF$_6$ and **9** in THF confirmed (Figure 1) good control of their molecular weight distributions during SET-LRP. The narrow molecular weight distribution (Table 1) of the control polymer **9** and a good match between the targeted and obtained degree of polymerization (925 vs 1050) constitute evidence for the living character of the polymerization. Incorporation of the rotaxane initiators in polymers **7**·4PF$_6$ and **8**·4PF$_6$ was confirmed by UV/vis spectroscopy in THF. A characteristic charge-transfer (CT) absorption associated with the interaction between the DNP unit and the bipyridinium units on the cyclophane was observed centered on 530 nm. Whereas the fluorescence from the DNP units is efficiently quenched by the CT interactions present in **7**·4PF$_6$ and **8**·4PF$_6$, the emission intensity of polymer **9** is at least 2 orders of magnitude higher.[16] Sonication (~6 W, 1 h, 0 °C) of polymers **7**$^{4+}$, **8**$^{4+}$ and **9** in THF induced partial degradation of the polymer backbones. GPC analyses of the sonicated samples confirmed (Table 1) decreases in molecular weights for all polymers. Profound differences, however, in the optical properties of polymers **7**$^{4+}$, **8**$^{4+}$, and **9** were observed. The absorption intensity of polymer **7**$^{4+}$ at 529 nm decreased (Figure 2a) by a factor of 0.32 (67% decrease), indicating a substantial reduction in the CT interactions. By contrast, a smaller decrease (Figure 2b) by a factor 0.83 (15% decrease) was observed for polymer **8**$^{4+}$ containing a terminal rotaxane. The absorption spectrum (Figure 2c) of control polymer **9** remained essentially unchanged. The larger decrease in the CT absorption band

Table 1. Comparison of polydispersity indices and molecular weights for polymers **7**·4PF$_6$, **8**·4PF$_6$ and **9** before and after sonication (~6 W, 1 h, 0 °C) in THF

	7·4PF$_6$		**8**·4PF$_6$		**9**	
	before:	after:	before:	after:	before:	after:
PDI[a]	1.8	1.8	1.8	1.7	1.1	1.1
M_n (kDa)[a]	85	47	180	100	90	62
M_w (kDa)[a]	150	85	330	170	94	66

[a] GPC in THF using a refractive index detector.

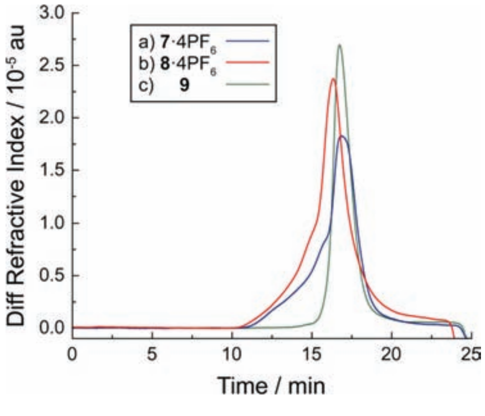


Figure 1. GPC traces of polymers (a) **7**·4PF$_6$, (b) **8**·4PF$_6$ and (c) **9** in THF. The tailing observed at higher molecular weights for **7**·4PF$_6$, and **8**·4PF$_6$ can be attributed to partial aggregation – leading (Table 1) to broader molecular weight distributions – of the polycationic rotaxane units in THF.

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(15) Dumbbell initiator **10** was synthesized in good yield by reacting the known DNP diazide derivative with propargyl ether **6**. See ref 12b.

(16) See Supporting Information.

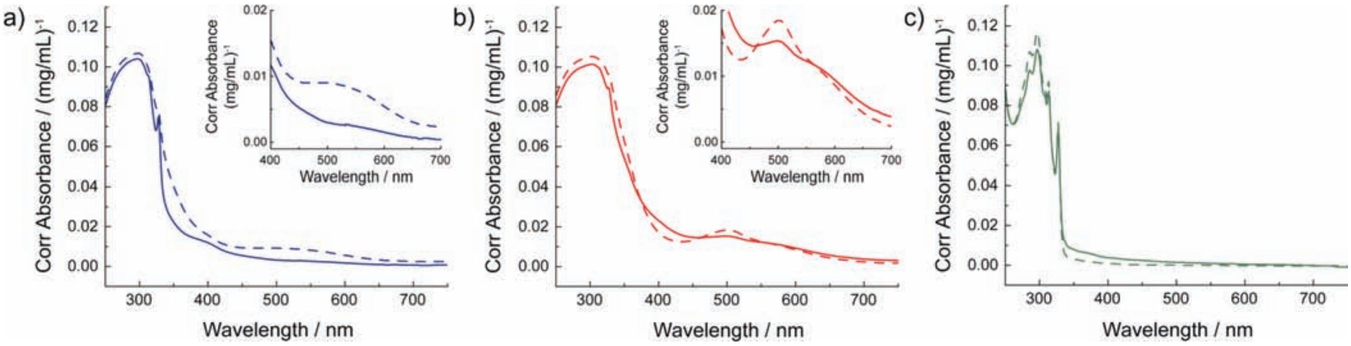

Figure 2. UV/vis spectra of (a) **7**·4PF$_6$, (b) **8**·4PF$_6$ and (c) **9** before (dotted lines) and after (solid lines) sonication (THF, ~6 W, 1 h, 0 °C). The spectra were recorded in THF and are corrected for the concentration of the polymer (insets: zoom in region from 400–700 nm).

intensity for polymer **7**$^{4+}$ compared with that of polymer **8**$^{4+}$ can be ascribed to the higher efficiency of mechanical activation in the midsection of the polymer chain, resulting in increased mechanical degradation and hence breaking of the centrally located rotaxane unit.[12] The rotaxane end-group of **8**$^{4+}$ is less prone to degradation since mechanical forces are less efficiently transferred to the mechanically interlocked unit.

Interestingly, the substantial decrease in CT absorption by **7**$^{4+}$ is not reflected in a corresponding increase of emission intensity arising from a potentially liberated DNP unit. It is not unlikely that alternative deactivation pathways for the emission lead to this observation since GPC provides clear evidence (Table 1) for a decrease in the molecular weight during sonication and absorption spectra (Figure 2) support a substantial interruption of the CT interactions originally present in **7**$^{4+}$. Furthermore, the emission intensity of control polymer **9** decreased by only 19% after sonication, presumably because of the partial destruction of the central DNP unit under these conditions.[15] Assuming a similar extent of sonication-induced degradation of liberated DNP moieties during sonication of polymer **7**$^{4+}$ — and to a smaller extent in the case of polymer **8**$^{4+}$ — a much higher emission intensity would be expected in the absence of alternative deactivation pathways. We conclude, therefore, that the mechanically interlocked midsection of polymer **7**$^{4+}$ is efficiently destroyed during application of mechanical stress, leading to a loss of CT interactions with a concomitant destruction of the DNP unit. Consequently, a less efficient degradation of the rotaxane end-group in **8**·4PF$_6$ is expected to cause an even smaller increase in fluorescence intensity. Nonetheless, destruction of polymer chains is also observed for **8**$^{4+}$ and **9**.

In summary, we designed, synthesized and characterized poly(methyl acrylate) polymers grown from mechanically interlocked initiators under SET-LRP conditions with good control over molecular weights and polydispersities. The potential of mechanically interlocked moieties as mechanophores has been investigated and efficient transfer of mechanical forces to a rotaxane incorporated into the midsection of a polymer chain has been demonstrated.

Acknowledgment. This research was supported by the Non-Equilibrium Energy Research Center (NERC), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0000989 and also by the Air Force Office of Scientific Research (AFOSR) under their Multidisciplinary University Research Initiative (MURI) award number FA9550-07-1-0534. R.S.S. is indebted to the Alexander von Humboldt-Foundation for a postdoctoral fellowship. We thank Matthew Duch and the research group of Professor Mark Hersam at Northwestern University for access to sonication equipment.

Supporting Information Available. Experimental details, spectroscopic characterization data for all new compounds, and GPC analysis results. This material is available free of charge via the Internet at http://pubs.acs.org.