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Ring-opening metathesis polymerization of a strained stilbene-based macrocyclic monomer†

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We report the synthesis of a new class of strained macrocycle that performs well in ring-opening metathesis polymerization (ROMP). The polymerization displays chain growth characteristics with evidence of secondary metathesis in the form of chain transfer. The unique structure enables access to stilbene-based polymers that are traditionally prepared *via* uncontrolled polymerizations.

Introduction

Ring-opening metathesis polymerization (ROMP) has become an indispensable synthetic tool in modern polymer chemistry and materials science.[1–6] The monomer landscape for ROMP is dominated largely by four motifs: norbornenes, cyclobutenes, cyclopropenes, and cyclooctenes (Fig. 1).[2,7–15] These motifs share relatively high ring strain that provides a driving force for polymerization. From these frameworks, functional groups are typically introduced *via* side chains, whereas increasing the diversity of the backbone composition within ROMP is generally achieved by the polymerization of macrocycles (ring size >14 atoms). Most macrocyclic monomers however, have little or no ring strain.[16] Therefore, a trade off exists between selection of monomers with high ring strain *versus* macrocyclic systems of greater diversity albeit without an enthalpic driving force.

The lack of an enthalpic driving force for ROMP of macrocycles suggests that an entropic driving force must be present for polymerization to occur, and as such, these polymerizations are categorized as entropy-driven ring-opening metathesis polymerizations (ED-ROMPs).[16–18] ED-ROMPs exist in a ring-chain equilibrium between macrocyclic oligomers and linear polymers, and the thermodynamic drive is provided by the increase in conformational entropy as the macrocyclic oligomers become linear polymer chains.[16] Macrocyclic platforms for ED-ROMP have been used to synthesize polymers with many unique features including liquid crystalline polymers, poly(catenates), poly(calixarenes), as well as sequence-controlled polymers (Fig. 1).[19–22] Disadvantages of using ED-ROMP include high molecular weight

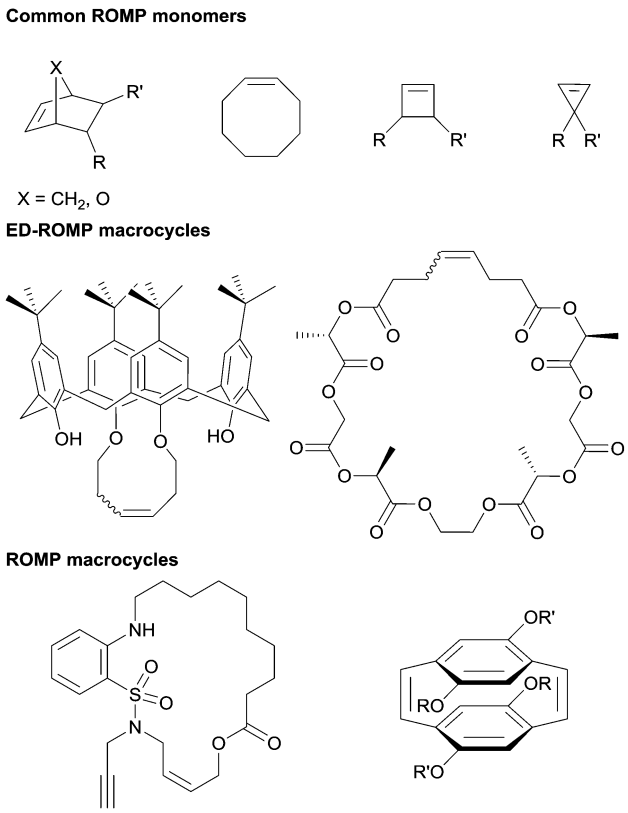

Fig. 1 Examples of both small molecule and macrocyclic monomers for ROMP and ED-ROMP.

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dispersity ($Đ$) for the resulting polymers, often the $Đ$ for these polymerizations fall between 1.5–2.0, with notable exceptions.[16,18,23,24]

Approaches to address the challenges with ED-ROMP include designing macrocycles with high ring strain and engineering effectively irreversible reactions into the polymerization mechanism, the former being the more common of these approaches.[25] For instance, Miao *et al.* utilized [2.2]paracyclophan-1-ene, a highly strained macrocycle, to synthesize a homopolymer as well as block and random co-polymers with norbornene initiated by a Schrock-type catalyst.[26] Since this initial demonstration, several other cyclophanenes and cyclophanedienes have been used in ROMP to synthesize homo- and co-polymers.[27–29] In addition, a series of donor–acceptor block co-polymers have been synthesized *via* ROMP of macrocycles based on arylenevinylenes.[27,30,31] Inspired by this work, we set out to investigate methods to synthesize a new class of strained macrocycles capable of undergoing ROMP.

Results and discussion

We conceived of *cis*-stilbene-based macrocycle **1**, which we predicted would possess a high degree of ring strain and would enable predefined control of the structure of the resulting polymer backbone (Fig. 2).[32] By synthesizing a polymer through chain growth polymerization instead of intensive step growth condensation polymerization, we envisioned that we could readily obtain polymers with low $Đ$ and controlled molecular weight. Additionally, the polymer resulting from macrocycle **1** would be similar in structure to many high-performance polymers, such as poly(phenylene)s, poly(phenylenevinylene)s, and poly(aryletherketone)s, that with a few exceptions have traditionally been synthesized through uncontrolled polymerizations.[33–40] The potential to synthesize high-performance polymers through readily accessible chain growth polymerizations instead of step growth polymerizations could be an exciting advancement toward complex polymer structures that were previously unachievable.

Despite the broad utility of strained macrocycles for ROMP, there are few efficient synthetic routes to obtain macrocyclic monomers with enough ring strain to drive ring-opening polymerization. We therefore employed oxidative bisboronate homocoupling—a simple, scalable, and efficient strain-building reaction—for the preparation of macrocycle **1** (Fig. 3).[41] First, we constructed curved diol intermediate **2** by double lithiation of 4,4′-dibromostilbene and subsequent nucleophilic addition to 4-bromobenzaldehyde. Deprotonation of the free alcohols with sodium hydride and treatment with 1-bromohexane yielded **3**. Lithium-halogen exchange followed by treatment with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane yielded bisboronate **4**. Finally, **4** was subjected to mild Pd-catalysed oxidative homocoupling conditions to yield final macrocyclic monomer **1** on a multigram scale. The key cyclization reaction is 50% yielding with the remaining mass balance primarily attributed to oligomeric byproducts. In principle, other sized macrocycles could form as well, but we did not observe these products to any appreciable extent.

With monomer **1** in hand, we investigated the polymerization of **1** using the third generation Grubbs catalysts in tetrahydrofuran-d_8 ($[\mathbf{1}]_0$ = 1 M) with an initial monomer to initiator ratio of 100 : 1 (Table 1, entries 1 and 2). With each initiator, conversion

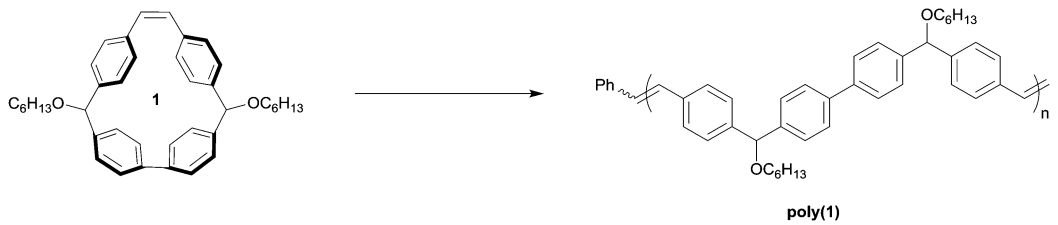


Fig. 2 Proposed polymerization of macrocycle (**1**).

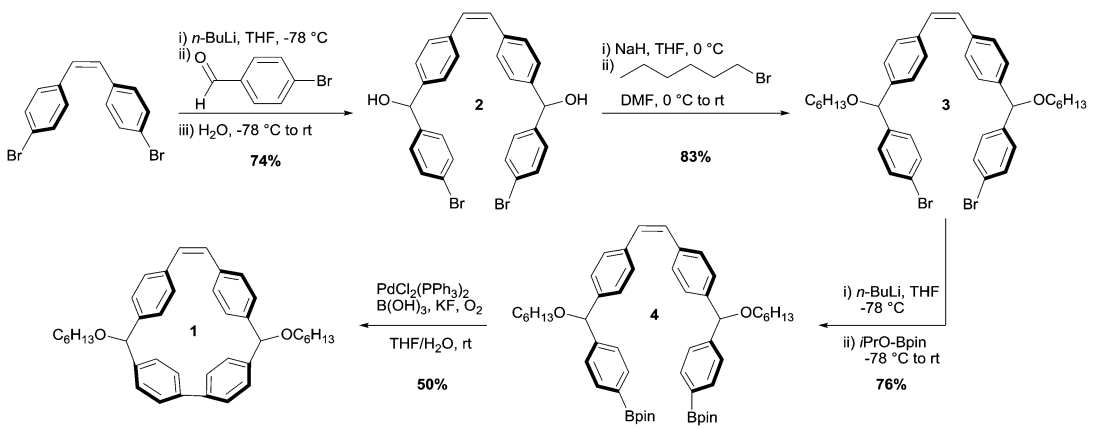
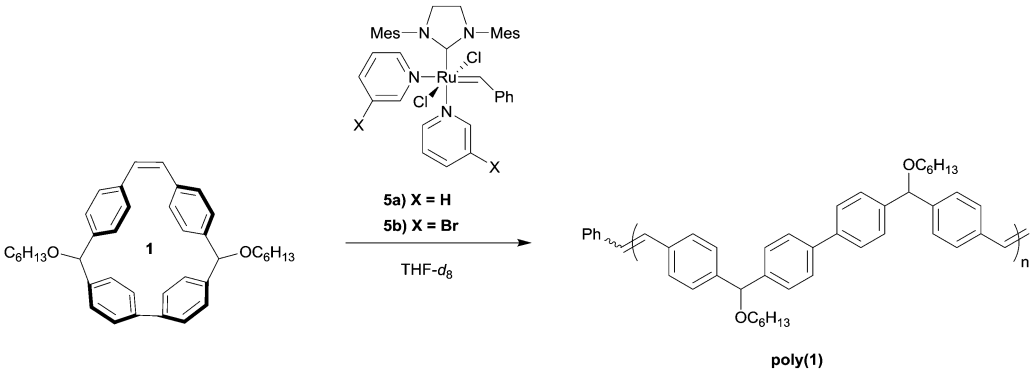


Fig. 3 Synthetic scheme for **1**.

Table 1 Summary of ROMP experiments performed



Entry	[1] : [5]	Conc. (M)	Temp. (°C)	Conv. (%)	$M_{n,\ theo}$ (kg mol^{-1})	M_n (kg mol^{-1})	M_w (kg mol^{-1})	$Đ$	k^d (s^{-1})
1[a]	100 : 1	1	60	>99	55.9	62.1	107.0	1.7	—
2[b]	100 : 1	1	60	99	55.9	55.4	102.2	1.7	—
3[a]	75 : 1	0.1	40	>99	42.4	53.4	79.7	1.5	—
4[a,c]	35 : 1	1	20	45	8.6	8.0	8.7	1.1	$9.97 \times 10^{-6} \pm 0.02$
5[a,c]	35 : 1	1	30	>99	20.1	18.3	27.8	1.5	$5.1 \times 10^{-5} \pm 0.4$
6[a,c]	35 : 1	1	40	>99	18.4	23.9	36.0	1.5	$2.2 \times 10^{-4} \pm 0.3$

[a] Initiator **5b**. [b] Initiator **5a**. [c] Average of 3 experiments. [d] Error represents the standard deviation.

reached >99% within 12 h at 60 °C, as determined by ^{1}H NMR spectroscopy. From these experiments, we found that the molecular weight distribution of **poly(1)** was monomodal with a M_w = 107 kDa and $Đ$ of 1.7, based upon SEC analysis using multi-angle laser light scattering and refractive index detection. The structure of **poly(1)** was confirmed by ^{1}H NMR spectroscopy and matrix-assisted laser desorption ionization time of flight mass spectrometry (MALDI-TOF/MS). In the case of **poly(1)** only a single vinylic signal at δ = 7.24 ppm was observed, while no other vinylic signals were present above the detection limit for ^{1}H NMR spectroscopy. This observation is consistent with the backbone of **poly(1)** being primarily *trans*-stilbene isomers (Fig. S11, ESI†).[42–44] MALDI-TOF/MS then was used to better understand the structural speciation within samples of **poly(1)**. The repeat unit for **poly(1)** has an experimental mass of 558.9 amu, which is consistent with the predicted molecular weight of **1** (Fig. 4). Notably, we did not see evidence of cyclic polymer structures from any of the analyses.

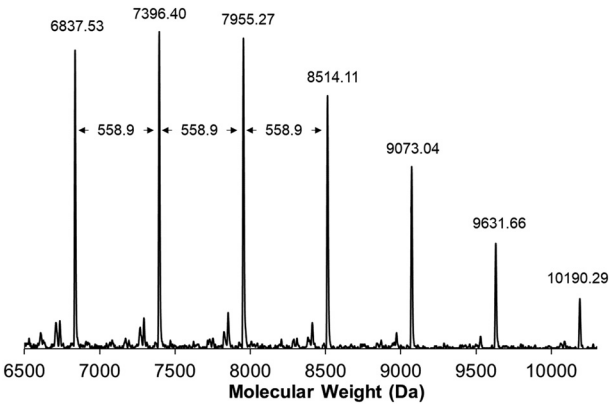


Fig. 4 MALDI-TOF/MS spectrum for **poly(1)**. The molecular weight between repeat units was measured to be 558.9 amu, consistent with the molecular weight of the monomer.

We also evaluated the thermal properties of **poly(1)** using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The decomposition temperature (T_d) for **poly(1)** was found to be 281 °C under N_2, determined by the onset of weight loss using TGA (Fig. S13, ESI†). A close comparison to **poly(1)** would be poly(phenylenevinylene)s, which have T_d > 300 °C.[43] A glass transition temperature (T_g) for **poly(1)** was found to be 94 °C determined by DSC, and no other thermal transitions were observed (Fig. S14, ESI†).

Given the ring strain and addition of an enthalpic driving force for the ROMP of **1**, we expected the polymerization to demonstrate chain growth characteristics, and a high degree of molecular weight control. To better understand the polymerization mechanism of **poly(1)**, monomer conversion was monitored by ^{1}H NMR spectroscopy using the benzylic ether hydrogen of the monomer and polymer at δ = 5.39 and 5.48 ppm, respectively (Fig. S15, ESI†). The polymerization displayed first order kinetics with respect to consumption of **1** (Fig. S16, ESI†) and a linear correlation between M_n and conversion (Fig. 5). Collectively, these results are consistent with a chain growth polymerization mechanism that does not exhibit slow initiation or early irreversible termination. Rate constants (k) for propagation where measured at 20, 30, and 40 °C (Table 1 entries 4–6), in all experiments the polymerization was stopped after 16 hours. An activation energy was determined to be 28.2 kcal mol^{-1} (Fig. S17, ESI†). We next turned our attention toward understanding the underlying reason for the high $Đ$.

Chain transfer has been observed during ROMP, typically facilitating an equilibration of chain lengths *via* intermolecular cross metathesis reactions. We investigated the occurrence of chain transfer by combining two different molecular weight

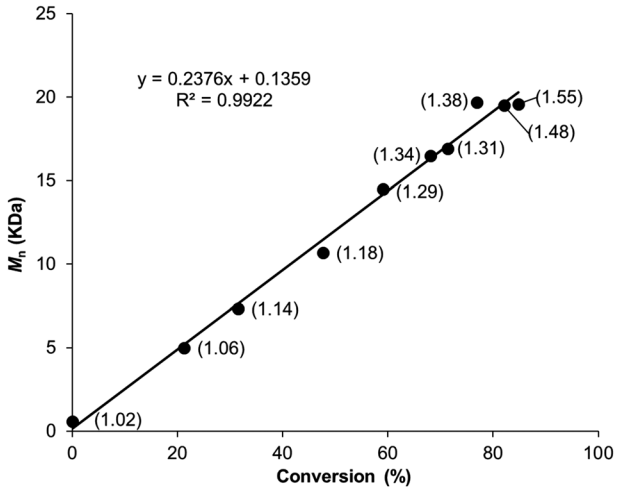


Fig. 5 M_n *vs.* conversion plot for the polymerization of **1** follows a linear progression consistent with a chain growth mechanism, $Đ$ for each time point in parenthesis.

polymers (M_n = 71.5 kDa and 15.2 kDa) in the presence of **5b** in THF. After 4 hours, the resulting polymer had an intermediate molecular weight (M_n = 24 kDa) that was consistent with the weighted average of the feed polymers (Fig. 6a) and a higher $Đ$ of 2.0. Chain transfer with *trans*-stilbene was also found to be efficient under our polymerization conditions. Specifically, 1 equivalent of *trans*-stilbene (relative to repeat unit) was combined with a sample of **poly(1)** (M_n = 41.5 kDa, $Đ$ = 1.6) and **5b** in THF. After 3.5 hours, the molecular weight of **poly(1)** decreased (M_n = 16.9 kDa) (Fig. 6b). These results are consistent with chain transfer occurring during the polymerization of **1**. It should be noted in the latter experiment no change in $Đ$ was observed contrary to what is expected, this result could be due to a change in column resolution between the molecular weights.

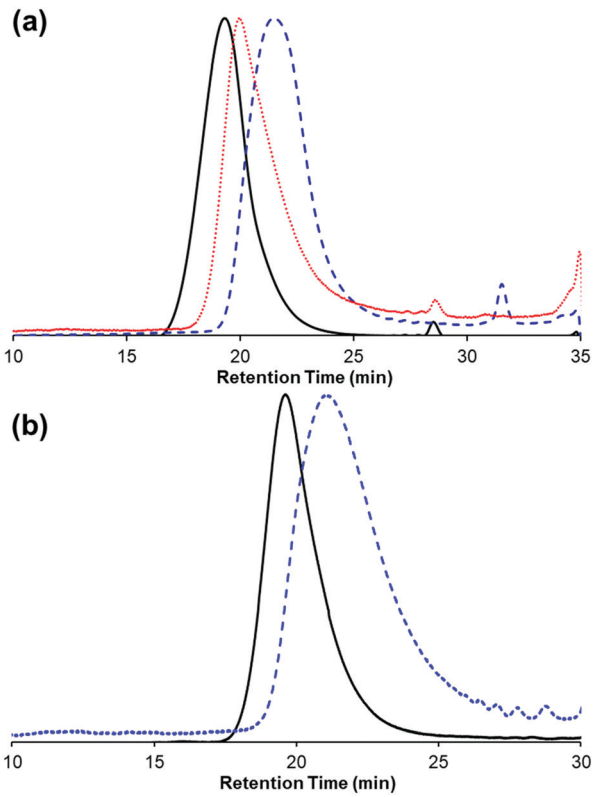


Fig. 6 (a) GPC traces for polymer–polymer chain transfer experiment for the two starting polymers (black solid, M_n = 71 kDa; blue dash, M_n = 15.2 kDa) and the final polymer (red dot, M_n = 24 kDa). (b) GPC traces for polymer–stilbene chain transfer experiment for the starting polymer (black solid, M_n: 41.5 kDa) and the final polymer (blue dash, M_n: 16.9 kDa).

Taken together, our results suggested to us that, likely due to the ring strain of **1**, the polymerization proceeds through a chain growth mechanism and is not an entropy-driven polymerization. During the course of the polymerization of **1** the $Đ$ of **poly(1)** increased from 1.0 to 1.5 further corroborating the presence of chain transfer during the polymerization (Fig. 5).

Conclusions

In summary, we have reported the synthesis and subsequent polymerization of a new class of strained macrocycle. The polymerization of **1** demonstrated first order kinetics and a linear correlation between M_n and conversion, consistent with chain growth polymerization. The resulting linear polymer obtained through this method had a T_g of 94 °C and a T_d of 281 °C. Further work is being done to use variations of **1** to make more complex polymeric materials that cannot be achieved using traditional small molecule-based poly(olefins). In this way, we hope to be able to control and modify the thermal and physical properties of these modular polymers. Ultimately, ROMP of highly strained macrocyclic monomers provides an exciting avenue to create and develop new polymeric materials from efficient synthetic methods.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Notes and references

1 O. Nuyken and S. D. Pask, *Polymers*, 2013, **5**, 361–403.
2 C. W. Bielawski and R. H. Grubbs, *Prog. Polym. Sci.*, 2007, **32**, 1–29.

3 H. Unsal, S. Onbulak, F. Calik, M. Er-Rafik, M. Schmutz, A. Sanyal and J. Rzayev, *Macromolecules*, 2017, **50**, 1342–1352.
4 J. A. Johnson, Y. Y. Lu, A. O. Burts, Y. Xia, A. C. Durrell, D. A. Tirrell and R. H. Grubbs, *Macromolecules*, 2010, **43**, 10326–10335.
5 Y. Hu, X. Li, A. W. Lang, Y. Zhang and S. R. Nutt, *Polym. Degrad. Stab.*, 2016, **124**, 35–42.
6 Y. Wang, L. Zhang, J. Sun, J. B. Bao, Z. Wang and L. Ni, *Ind. Eng. Chem. Res.*, 2017, **56**, 4750–4757.
7 H. Martinez, N. Ren, M. E. Matta and M. A. Hillmyer, *Polym. Chem.*, 2014, **5**, 3507–3532.
8 Z. Chen, J. A. M. Mercer, X. Zhu, J. A. H. Romaniuk, R. Pfattner, L. Cegelski, T. J. Martinez, N. Z. Burns and Y. Xia, *Science*, 2017, **357**, 475–479.
9 B. R. Elling, J. K. Su and Y. Xia, *Chem. Commun.*, 2016, **52**, 9097–9100.
10 W. H. Binder, S. Kurzhals, B. Pulamagatta, U. Decker, G. M. Pawar, D. Wang, C. Kühnel and M. R. Buchmeiser, *Macromolecules*, 2008, **41**, 8405–8412.
11 R. Singh, C. Czekelius and R. R. Schrock, *Macromolecules*, 2006, **39**, 1316–1317.
12 Z. Wu and R. H. Grubbs, *Macromolecules*, 1994, **27**, 6700–6703.
13 N. T. Lin, Y. Z. Ke, K. Satyanarayana, S. L. Huang, Y. K. Lan, H. C. Yang and T. Y. Luh, *Macromolecules*, 2013, **46**, 7173–7179.
14 F. Leroux, S. Pascual, V. Montembault and L. Fontaine, *Macromolecules*, 2015, **48**, 3843–3852.
15 J. Yang, M. Horst, J. A. H. Romaniuk, Z. Jin, L. Cegelski and Y. Xia, *J. Am. Chem. Soc.*, 2019, **141**, 6479–6483.
16 P. Hodge, *Chem. Rev.*, 2014, **114**, 2278–2312.
17 C. Y. Tastard, P. Hodge, A. Ben-Haida and M. Dobinson, *React. Funct. Polym.*, 2006, **66**, 93–107.
18 Z. Xue and M. F. Mayer, *Soft Matter*, 2009, **5**, 4600–4611.
19 J. H. Swisher, J. A. Nowalk and T. Y. Meyer, *Polym. Chem.*, 2019, **10**, 244–252.
20 J. Berrocal, L. M. Pitet, M. M. L. Nieuwenhuizen, L. Mandolini, E. W. Meijer and S. Di Stefano, *Macromolecules*, 2015, **48**, 1358–1363.
21 L.-L. Deng, L.-X. Guo, B.-P. Lin, X.-Q. Zhang, Y. Sun and H. Yang, *Polym. Chem.*, 2016, **7**, 5265–5272.
22 Y. Yang and T. M. Swager, *Macromolecules*, 2007, **40**, 7437–7440.
23 A. L. Short, C. Fang, J. A. Nowalk, R. M. Weiss, P. Liu and T. Y. Meyer, *ACS Macro Lett.*, 2018, **7**, 858–862.
24 R. M. Weiss, A. L. Short and T. Y. Meyer, *ACS Macro Lett.*, 2015, **4**, 1039–1043.
25 W. R. Gutekunst and C. J. Hawker, *J. Am. Chem. Soc.*, 2015, **137**, 8038–8041.
26 Y.-J. Miao and G. C. Bazan, *Macromolecules*, 1994, **27**, 1063–1064.
27 E. Elacqua and M. Gregor, *Angew. Chem., Int. Ed.*, 2019, **58**, 9527–9532.
28 C.-Y. Yu, J. W. Kingsley, D. G. Lidzey and M. L. Turner, *Macromol. Rapid Commun.*, 2009, **30**, 1889–1892.
29 A. M. Spring, C.-Y. Yu, M. Horie and M. L. Turner, *Chem. Commun.*, 2009, 2676–2678.
30 V. Komanduri, D. J. Tate, R. Marcial-Hernandez, D. R. Kumar and M. L. Turner, *Macromolecules*, 2019, **52**, 7137–7144.
31 S.-W. Chang and M. Horie, *Chem. Commun.*, 2015, **51**, 9113–9116.
32 Ring strain calculated to be 28.9 kcal mol^{-1}. See ESI† for strain energy analysis.
33 A. K. Schönbein, M. Wagner, P. W. M. Blom and J. J. Michels, *Macromolecules*, 2017, **50**, 4952–4961.
34 J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns and A. B. Holmes, *Nature*, 1990, **347**, 539–541.
35 D. G. H. Ballard, A. Courtis, I. M. Shirley and S. C. Taylor, *Macromolecules*, 1988, **21**, 294–304.
36 A. Abdulkarim, K. P. Strunk, R. Bäuerle, S. Beck, H. Makowska, T. Marszalek, A. Pucci, C. Melzer, D. Jänsch, J. Freudenberg, U. H. F. Bunz and K. Müllen, *Macromolecules*, 2019, **52**, 4458–4463.
37 T. E. E. Attwood, P. C. Dawson, J. L. Freeman, L. R. J. Hoy, J. B. Rose and P. A. Staniland, *Polymer*, 1981, **22**, 1096–1103.
38 F. Papadimitrakopoulos, K. Konstadinidis, T. M. Miller, R. Opila, E. A. Chandross and M. E. Galvin, *Chem. Mater.*, 1994, **6**, 1563–1568.
39 F. Louwet, D. Vanderzande, J. Gelan and J. Mullens, *Macromolecules*, 1995, **28**, 1330–1331.
40 T. Junkers, J. Vandenbergh, P. Adriaensens, L. Lutsen and D. Vanderzande, *Polym. Chem.*, 2012, **3**, 275–285.
41 E. R. Darzi, B. M. White, L. K. Loventhal, L. N. Zakharov and R. Jasti, *J. Am. Chem. Soc.*, 2017, **139**, 3106–3114.
42 Y. Xu, W. L. Xu, M. D. Smith and L. S. Shimizu, *RSC Adv.*, 2014, **4**, 1675–1682.
43 D. Maker, C. Maier, K. Brodner, U. Bunz, D. Mäker, C. Maier, K. Brödner and U. Bunz, *ACS Macro Lett.*, 2014, **3**, 415–418.
44 R. Adhikary, C. A. Barnes, R. L. Trampel, S. J. Wallace, T. W. Kee and J. W. Petrich, *J. Phys. Chem. B*, 2011, **115**, 10707–10714.

